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Fourth External Review Draft of Air Quality Criteria for Particulate Matter (June, 2003):

Volume I

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Fourth External Review Draft

Air Quality Criteria for Particulate Matter

Volume I

National Center for Environmental Assessment-RTP Office
Office of Research and Development
U.S. Environmental Protection Agency
Research Triangle Park, NC

DISCLAIMER

This document is an external review draft for review purposes only and does not constitute U.S. Environmental Protection Agency policy. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

PREFACE

National Ambient Air Quality Standards (NAAQS) are promulgated by the United States Environmental Protection Agency (EPA) to meet requirements set forth in Sections 108 and 109 of the U.S. Clean Air Act (CAA). Sections 108 and 109 require the EPA Administrator (1) to list widespread air pollutants that reasonably may be expected to endanger public health or welfare; (2) to issue air quality criteria for them that assess the latest available scientific information on nature and effects of ambient exposure to them; (3) to set "primary" NAAQS to protect human health with adequate margin of safety and to set "secondary" NAAQS to protect against welfare effects (e.g., effects on vegetation, ecosystems, visibility, climate, manmade materials, etc.); and (5) to periodically (every 5 years) review and revise, as appropriate, the criteria and NAAQS for a given listed pollutant or class of pollutants.

The original NAAQS for particulate matter (PM), issued in 1971 as "total suspended particulate" (TSP) standards, were revised in 1987 to focus on protecting against human health effects associated with exposure to ambient PM less than 10 microns ($\leq$10 µm) that are capable of being deposited in thoracic (tracheobronchial and alveolar) portions of the lower respiratory tract. Later periodic reevaluation of newly available scientific information, as presented in the last previous version of this "Air Quality Criteria for Particulate Matter" document published in 1996, provided key scientific bases for PM NAAQS decisions published in July 1997. More specifically, the PM_{10} NAAQS set in 1987 (150 µg/m^3, 24-h; 50 µg/m^3, annual average) were retained in modified form and new standards (65 µg/m^3, 24-h; 15 µg/m^3, annual average) for particles $\leq$ 2.5 µm ($PM_{2.5}$) were promulgated in July 1997.

This Fourth External Review Draft of revised Air Quality Criteria for Particulate Matter assesses new scientific information that has become available mainly between early 1996 through April 2002. The present draft is being released for public comment and review by the Clean Air Scientific Advisory Committee (CASAC) to obtain comments on the organization and structure of the document, the issues addressed, the approaches employed in assessing and interpreting the newly available information on PM exposures and effects, and the key findings and conclusions arrived at as a consequence of this assessment. Public comments and CASAC review recommendations will be taken into account in making any appropriate further revisions to this document for incorporation into a final draft. Evaluations contained in the present document will be drawn on to provide inputs to associated PM Staff Paper analyses prepared by EPA's Office of Air Quality Planning and Standards (OAQPS) to pose alternatives for consideration by the EPA Administrator with regard to proposal and, ultimately, promulgation of decisions on potential retention or revision of the current PM NAAQS.

Preparation of this document was coordinated by staff of EPA's National Center for Environmental Assessment in Research Triangle Park (NCEA-RTP). NCEA-RTP scientific staff, together with experts from other EPA/ORD laboratories and academia, contributed to writing of document chapters; and earlier drafts of this document were reviewed by experts from federal and state government agencies, academia, industry, and non-governmental organizations (NGOs) for use by EPA in support of decision making on potential public health and environmental risks of ambient PM. The document describes the nature, sources, distribution, measurement, and concentrations of PM in outdoor (ambient) and indoor environments. It also evaluates the latest data on human exposures to ambient PM and consequent health effects in exposed human populations (to support decision making regarding primary, health-related PM NAAQS). The document also evaluates ambient PM environmental effects on vegetation and ecosystems, visibility, and man-made materials, as well as atmospheric PM effects on climate change processes associated with alterations in atmospheric transmission of solar radiation or its reflectance from the Earth's surface or atmosphere (to support decision making on secondary PM NAAQS).

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Abbreviations and Acronyms

AAS	atomic absorption spectrophotometry
AC	air conditioning
ACGIH	American Conference of Governmental Industrial Hygienists
ACS	American Cancer Society
ADS	annular denuder system
AES	atomic emission spectroscopy
AIRS	Aerometric Information Retrieval System
ANC	acid neutralizing capacity
AQCD	Air Quality Criteria Document
AQI	Air Quality Index
ARIES	Aerosol Research and Inhalation Epidemiology Study
ASOS	Automated Surface Observing System
ATOFMS	time-of-flight mass spectrometer
AWOS	Automated Weather Observing System
BaP	benzo(a)pyrene
BASE	Building Assessment and Survey Evaluation
BC	black carbon
BNF	bacterial nitrogen fertilization
BOSS	Brigham Young University Organic Sampling System
BYU	Bringham Young University
CAA	Clean Air Act
CAAM	continuous ambient mass monitor
CAMNET	Coordinated Air Monitoring Network
CARB	California Air Resources Board
CASAC	Clean Air Scientific Advisory Committee
CASTNet	Clean Air Status and Trends Network

C_B	base cations
CC	carbonate carbon
CCPM	continuous coarse particle monitor
CCSEM	computer-controlled scanning electron microscopy
CEN	European Standardization Committee
CFCs	chlorofluorocarbons
CFR	Code of Federal Regulations
CHAD	Consolidated Human Activity Database
CIF	charcoal-impregnated cellulose fiber
CIIT	Chemical Industry Institute of Technology
CMAQ	Community Multi-Scale Air Quality
CMB	chemical mass balance
CMSA	Consolidated Metropolitan Statistical Area
CO CD	Air Quality Criteria Document for Carbon Monoxide
COD	coefficient of divergence
COPD	chronic obstructive pulmonary disease
CPC	condensation particle counter
CRP	Coordinated Research Program
CSIRO	Commonwealth Scientific and Industrial Research Organisation
CSMCS	Carbonaceous Species Methods Comparison Study
CSS	coastal sage scrub
CTM	chemistry-transport model
CV	coefficient of variation
CVM	contigent valuation method
D_a	aerodynamic diameter
DAQ	Department of Air Quality
DCFH	dichlorofluorescin
DMPS	differential mobility particle sizer

DMS	dimethyl sulfide
D_p	particle diameter
dv	deciview index
EAD	electrical aerosol detector
EC	elemental carbon
ECAO	Environmental Criteria and Assessment Office
EDXRF	energy dispersive X-ray fluorescence
EEA	Essential Ecological Attributes
ENSO	El Nino-Southern Oscillation
EPA	Environmental Protection Agency
ESP	electrostatic precipitator
ETS	environmental tobacco smoke
EXPOLIS	Air Pollution Exposure Distribution within Adult Urban Populations in Europe
FID	flame ionization detection
FRM	Federal Reference Method
GAM	general additive models
GC	gas chromatography
GCMs	General Circulation Models
GCVTC	Grand Canyon Visibility Transport Commission
GC/MSD	gas chromatography/mass-selective detection
GHG	greenhouse gases
GSD	geometric standard deviation
HBEF	Hubbard Brook Experiment Forest
HDS	honeycomb denuder/filter pack sampler
HEADS	Harvard-EPA Annular Denuder Sampler
HEI	Health Effects Institute
HI	Harvard Impactors
hivol	High volume sampler

HTGC-MS	high temperature gas chromotography-mass spectrometry
HVAC	heating, ventilation, or air conditioning
IC	ion chromatography
ICP	inductively coupled plasma
IFS	Integrated Forest Study
IMPROVE	Interagency Monitoring of Protected Visual Environments
INAA	instrumental neutron activation analysis
IOVPS	integrated organic vapor/particle sampler
IPCC	Intergovernmental Panel on Climate Change
IPM	inhalable particulate matter
IPN	Inhalable Particulate Network
ISO	International Standards Organization
K	Koschmieder constant
LAI	leaf area indices
LOD	level of detection
LWC	liquid water content
LWCA	liquid water content analyzer
MAA	mineral acid anion
MAACS	Metropolitan Acid Aerosol Characterization Study
MADPro	Mountain Acid Deposition Program
MAQSIP	Multiscale Air Quality Simulation Platform
mCa	membrane-associated calcium
MDL	minimum detection level
MOUDI	micro-orifice uniform deposit impactor
MS	mass spectroscopy
MSA	methane sulfonic acid
MSA	metropolitan statistical area
mv	motor vehicle

NAAQS	National Ambient Air Quality Standards
NAMS	National Ambient Monitoring Stations
NAPAP	National Acid Precipitation Assessment Program
NARSTO	North American Research Strategy for Tropospheric Ozone
NAST	National Assessment Synthesis Team
NCEA	National Center for Environmental Assessment
NDDN	National Dry Deposition Network
NERL	National Exposure Research Laboratory
NESCAUM	Northeast States for Coordinated Air Use Management
NFRAQS	North Frontal Range Air Quality Study
NGOs	non-governmental organizations
NHAPS	National Human Activity Pattern Survey
NIOSH	National Institute for Occupational Safety and Health
NIR	near infared radiation
NIST	National Institute of Standards and Technology
NOPL	naso-oro-pharyngo-laryngeal
NO_x	nitrogen oxides
NPP	net primary production
Nr	reactive nitrogen
NRC	National Research Council
NuCM	nutrient cycling model
OAQPS	Office of Air Quality Planning and Standards
OAR	Office of Air and Radiation
OC	organic carbon
ORD	Office of Research and Development
PAH	polynuclear aromatic hydrocarbon
PAN	peroxyacetyl nitrate
PAR	photosynthetically active radiation

PBL	planetary boundary layer
PBP	primary biological particles
PBY	Presbyterian Home
PC	particle concentrator
PC	pyrolitic carbon
PC-BOSS	Particulate Concentrator-Brigham Young University Organic Sampling System
PCA	principal component analysis
PCBs	polychloronated biphenyls
PCDD	polychlorinated dibenzo-*p*-dioxins
PCDF	polychlorinated dibenzofurans
PCM	particle composition monitor
PEM	personal exposure monitor
PESA	proton elastic scattering analysis
PIXE	proton induced X-ray emission
PM	particulate matter
PM_{10-25}	coarse particulate matter
$PM_{2.5}$	fine particulate matter
PMF	positive matrix factorization
POP	persistent organic pollutant
PRB	policy-relevant background
PTEAMS	Particle Total Exposure Assessment Methodology
PTEP	PM_{10} Technical Enhancement Program
PUF	polyurethane foam
PWC	precipitation-weighted concentrations
RAMS	Regional Air Monitoring Study
RAMS	Real-Time Air Monitoring System
RAS	roll-around system
RCS	Random Component Superposition

RFO	residual fuels oils
RH	relative humidity
RIVM	Directorate-General for Environmental Protection
RPM	Regional Particulate Model
RPM	respirable particulate matter
RRMS	relatively remote monitoring sites
RTP	Research Triangle Park
RUE	radiation use efficiency
SA	Sierra Anderson
SAB	Science Advisory Board
SCAQS	Southern California Air Quality Study
SCOS	Southern California Ozone Study
sd	standard deviation
sec	secondary
SEM	scanning electron microscopy
SES	sample equilibration system
SEV	Sensor Equivalent Visibility
SIP	State Implementation Plans
SLAMS	State and Local Air Monitoring Stations
SMPS	scanning mobility particle sizer
SMSAs	Standard Metropolitan Statistical Areas
SOC	semivolatile organic compounds
SoCAB	South Coast Air Basin
SOPM	secondary organic particulate matter
SP	Staff Paper
SRM	standard reference method
STN	Speciation Trends Network
SUVB	solar ultraviolet B radiation

SVOC	semivolatile organic compounds
SVM	semivolatile material
TAR	Third Assessment Report
TDMA	Tandem Differential Mobility Analyzer
TEO	trace element oxides
TEOM	tapered element oscillating microbalance
THEES	Total Human Environmental Exposure Study
TNF	tumor necrosis factor
TOFMS	aerosol time-of-flight mass spectroscopy
TOR	thermal/optical reflectance
TOT	thermal/optical transmission
TPM	thoracic particulate matter
TRXRF	total reflection X-ray fluorescence
TSP	total suspended particulates
TVOC	total volatile organic compounds
UAM-V	Urban Airshed Model Version V
UCM	unresolved complex mixture
UNEP	United Nations Environment Programme
URG	University Research Glassware
USGCRP	U.S. Global Change Research Program
VAPS	Versatile Air Pollution Samplers
VMD	volume mean diameter
VOC	volatile organic compounds
WMO	World Meteorological Organization
VR	visual range
WINS	Well Impactor Ninety-Six
WMO	World Meteorological Organization
WRAC	Wide Range Aerosol Classifier

WTA	willingness to accept
WTP	willingness to pay
XAD	polystyrene-divinyl benzene
XRF	X-ray fluorescence

EXECUTIVE SUMMARY

E.1 INTRODUCTION

The purpose of this document, Air Quality Criteria for Particulate Matter (PM AQCD), is to present air quality criteria for particulate matter (PM) in accordance with Clean Air Act (CAA) Sections 108 and 109, which govern establishment, review, and revision of U.S. National Ambient Air Quality Standards (NAAQS) as follows:

- Section 108 directs the U.S. Environmental Protection Agency (EPA) Administrator to list pollutants that may reasonably be anticipated to endanger public health or welfare and to issue air quality criteria for them. The air quality criteria are to reflect the latest scientific information useful in indicating the kind and extent of all identifiable effects on public health and welfare expected from the presence of the pollutant in ambient air.
- Section 109 directs the EPA Administrator to set and periodically revise, as appropriate, (a) primary NAAQS, which in the judgement of the Administrator, are requisite to protect public health, with an adequate margin of safety, and (b) secondary NAAQS which, in the judgement of the Administrator, are requisite to protect the public welfare from any known or anticipated adverse effects (e.g., impacts on vegetation, crops, ecosystems, visibility, climate, man-made materials, etc.).
- Section 109 of the CAA also requires periodic review and, if appropriate, revision of existing criteria and standards. Also, an independent committee of non-EPA experts, the Clean Air Scientific Advisory Committee (CASAC), is to provide the EPA Administrator advice and recommendations regarding the scientific soundness and appropriateness of criteria and NAAQS.

To meet these CAA mandates, this document assesses the latest scientific information useful in deriving criteria as scientific bases for decisions on possible revision of current PM NAAQS. A separate EPA PM Staff Paper will draw upon assessments in this document, together with technical analyses and other information, to identify alternatives for consideration by the EPA Administrator with regard to possible retention or revision of the PM NAAQS.

The present document is organized into a set of 10 chapters, as follows:

- This Executive Summary summarizes key points from the ensuing chapters.
- Chapter 1 provides a general introduction, including information on legislative requirements and history of the PM NAAQS and an overview of approaches used to prepare this document.
- Chapters 2, 3 and 5 provide background information on PM atmospheric science, air quality, and human exposure aspects to help place the succeeding discussions of PM health and environmental effects into perspective.
- Chapter 4 deals with environmental effects of PM on vegetation and ecosystems, visibility, man-made materials, and climate.
- Human health issues related to PM are addressed in Chapter 6 (Dosimetry); Chapter 7 (Toxicology); and Chapter 8 (Community Epidemiology).
- Chapter 9 provides an integrative synthesis of key points from the preceding chapters.

E.2 AIR QUALITY AND EXPOSURE ASPECTS

The document's discussion of air quality and exposure aspects considers chemistry and physics of atmospheric PM; analytical techniques for measuring PM mass, size, and chemical composition; sources of ambient PM in the United States; temporal/spatial variability and trends in ambient U.S. PM levels; and ambient concentration-human exposure relationships. Overall, the atmospheric science and air quality information provides further evidence substantiating the 1996 PM AQCD conclusion that distinctions between fine and coarse mode particles (in terms of emission sources, formation mechanisms, atmospheric transformation, transport distances, air quality patterns, and exposure relationships) warrant fine and coarse PM being viewed as separate subclasses of ambient PM. Key findings are summarized in the next several sections.

E.2.1 Chemistry and Physics of Atmospheric Particles

- Airborne PM is not a single pollutant, but rather is a mixture of many subclasses of pollutants with each subclass containing many different chemical species. Particles suspended in the atmosphere originate from a variety of sources and possess a range of morphological, chemical, physical, and thermodynamic properties. A complete description of atmospheric particles would include an accounting of the chemical composition, morphology, and size of each particle, and the relative abundance of each particle type as a function of particle size. Recent developments in single particle analysis techniques are bringing such a description closer to reality.

- Particle size distributions show that atmospheric particles exist in two classes: fine particles and coarse particles. Fine and coarse particles are defined primarily in terms of their formation mechanisms and size; they also differ in sources, chemical composition, and removal processes (see Table 2-1). Subsequent chapters show that fine and coarse particles also differ in aspects of concentration, exposure, dosimetry, toxicology, and epidemiology. These differences support the setting of separate standards for fine and coarse particles.

- Fine and coarse particles overlap in the size range between 1 and 3 µm aerodynamic diameter where ambient PM concentrations are at a minimum. Coarse particles are generally larger than this minimum and are generally formed by mechanical processes. Energy considerations limit the break-up of large mineral particles and small particle aggregates generally to a minimum size of about 1 µm in diameter. Coarse particles and coarse-mode particles are equivalent terms.

- Fine PM is derived primarily from combustion material that has volatilized and then condensed to form primary PM or from precursor gases reacting in the atmosphere to form secondary PM. New fine particles are formed by the nucleation of gas phase species; they grow by coagulation (existing particles combining) or condensation (gases condensing on existing particles). Fine particles are subdivided into accumulation, Aitkin, and nucleation modes. In earlier texts, nuclei mode referred to the size range now split into the Aitkin and nucleation modes (see Figures 2-4 and 2-5). Particles in the size range below 0.1 µm diameter are called ultrafine or nanoparticles and include the Aitkin and nucleation modes.

- $PM_{2.5}$ is an indicator for fine particles. $PM_{10-2.5}$ is an indicator for thoracic coarse particles (coarse particles capable of reaching the thoracic portion of the respiratory system – trachea, bronchi, and alveolar regions). $PM_{2.5}$ has been selected as the indicator for fine particles to include all accumulation-mode particles during high relative humidity, while recognition that it also includes some coarse-mode particles between 1 and 2.5 µm. $PM_{2.5}$ specifies a sample collected through a size-selective inlet with a specified penetration curve at 50% cut point at 2.5 µm aerodynamic diameter.

- Aerosol scientists use three different approaches or conventions in the classification of particles by size: (1) modes, based on the observed size distributions and formation mechanisms; (2) cut point, usually based on the 50% cut point of the specific sampling device, including legally specified, regulatory sizes for air quality standards; and (3) dosimetry or occupational health sizes, based on the entrance into various compartments of the respiratory system.

E.2.2 Sources of Airborne Particles in the United States

- Because of the complexity of the composition of ambient $PM_{2.5}$ and $PM_{10-2.5}$, sources are best discussed in terms of individual constituents of both primary and secondary $PM_{2.5}$ and $PM_{10-2.5}$. Each of these constituents can have anthropogenic and natural sources as shown in Table 3-8. Major components of fine particles are sulfates, strong acid, ammonium nitrate, organic compounds, trace elements (including metals), elemental carbon, and water.

- Primary particles are emitted directly from sources. Secondary particles are formed from atmospheric reactions of sulfur dioxide (SO_2), nitrogen oxides (NO_x), and certain organic compounds. NO reacts with ozone (O_3) to form NO_2. SO_2 and NO_2 react with hydroxy radical (OH) during the daytime to form sulfuric and nitric acid. During the nighttime, NO_2 reacts with ozone and forms nitric acid through a sequence of reactions involving the nitrate radical (NO_3). These acids may react further with ammonia to form ammonium sulfates and nitrates. Some types of higher molecular weight organic compounds react with OH radicals, and olefinic compounds also react with ozone to form oxygenated organic compounds, which nucleate or can condense onto existing particles. SO_2 also dissolves in cloud and fog droplets, where it may react with dissolved O_3, H_2O_2, or, if catalyzed by certain metals, with O_2, yielding sulfuric acid or sulfates, that lead to PM when the droplet evaporates.

- Organic compounds constitute from 10 to 70% of dry $PM_{2.5}$ mass. Whereas the chemistry of particulate nitrate and sulfate formation has been relatively well studied, the chemistry of secondary organic particulate matter formation is especially complex. Although additional sources of secondary organic PM might still be identified, there appears to be a general consensus that biogenic compounds (monoterpenes, sesquiterpenes) and aromatic compounds (e.g., toluene and ethylbenzene) are the most significant precursors. Atmospheric transformations of the compounds, which are formed in the particle phase during the aging of particles, are still not adequately understood.

- The results of receptor modeling studies throughout the United States indicate that the combustion of fossil and biomass fuels is the major source of measured ambient $PM_{2.5}$. Fugitive dust, found mainly in the $PM_{10-2.5}$ range size, represents the largest source of measured ambient PM_{10} in many locations in the western United States. The application of any of the source apportionment techniques is still limited by the availability of source profile data. Whereas the Chemical Mass Balance approach relies directly on source profile data, solutions from the Positive Matrix Factorization technique yield profiles for the factors that contribute to PM.

- The use of organic compounds in source apportionment studies could potentially result in the attribution of PM to many more source categories than is possible using only trace elements. However, in the relatively few studies of the composition of the organic fraction of ambient particles that have been performed, typically only about 10 to 20 % of organic compounds have been quantified. The separation of contributions from diesel- and gasoline-fueled vehicles using organic marker compounds is still somewhat problematic. Additional efforts to develop protocols for extraction and analysis of organic markers are needed.

E.2.3 Atmospheric Transport and Fate of Airborne Particles

- Primary and secondary fine particles have long lifetimes in the atmosphere (days to weeks) and travel long distances (hundreds to thousands of kilometers). They tend to be uniformly distributed over urban areas and larger regions, especially in the eastern United States. As a result, they are not easily traced back to their individual sources.

- Coarse particles normally have shorter lifetimes (minutes to hours) and generally only travel short distances (<10's of km). Therefore, coarse particles tend to be unevenly distributed across urban areas and tend to have more localized effects than fine particles. However, dust storms occasionally cause long range transport of small coarse-mode particles.

E.2.4 Airborne Particle Measurement Methods

- Measurements of ambient PM mass and chemical composition are needed to determine attainment of standards; to guide progress towards attainment of a standard (including determination of source categories and validation of air quality models); and to determine health, ecological, and radiative effects. A comprehensive approach requires a combination of analytical techniques to assess (1) mass, (2) crustal and trace elements, (3) water-soluble ionic species including strong acidity, (4) elemental carbon, and (5) organic compounds.

- There are no calibration standards for suspended particle mass; therefore, the accuracy of particle mass measurements cannot be definitively determined. The precision of particle mass measurements can be determined by comparing results from collocated samplers. Intercomparisons, using different techniques and samplers of different designs, coupled with mass balance studies (relating the sum of components to the measured mass), provide a method for gaining confidence in the reliability of PM measurements.

- Mass concentration measurements with a precision of 10% or better have been obtained with collocated samplers of identical design. Field studies of EPA PM_{10} and $PM_{2.5}$ reference methods and reviews of field data from collocated PM_{10} and $PM_{2.5}$ samplers show high precision (better than ± 10%). The use of more careful techniques, including double weighing of filters, can provide higher precision and may be needed for precise determination of $PM_{10-2.5}$ by difference.

- 10 Analytical techniques exist for measurement of the mass and chemical composition of PM retained on a filter (nonvolatile mass) in terms of elements (except carbon) and certain key ions (sulfate, nitrate, hydrogen, and ammonium). Acceptable measurements can be made of the total carbon retained on a filter. However, the split into organic carbon and elemental carbon depends on the operational details of the analytical methods and varies somewhat among methods. Determination of the various organic compounds in the organic carbon fraction remains a challenge.

- 11 Important components of atmospheric PM (particle-bound water, ammonium nitrate, and many organic compounds) are termed semivolatile because significant amounts of both the gaseous and condensed phases may exist in the atmosphere in equilibrium. Particle-bound water is not considered a pollutant. Most of the particle-bound water is removed by heating the particles or by equilibration of the collected particles at a low relative humidity (40%) for 24 hours. However, these processes also cause the loss of other semivolatile components. Semivolatile components also evaporate from the filter during sampling due to the pressure drop across the filter or due to a reduction in the atmospheric concentration during the sampling time.

- 12 Continuous methods must dry the PM to remove particle-bound water. If heating is used to dry the particles, more of the semivolatile components may be removed than are lost in filter sampling. Collection and retention of ammonium nitrate and semivolatile organic compounds represents a major challenge in the effort to move to continuous measurement of PM mass. The use of diffusion dryers, which dehumidify the air stream without heating, represents a promising approach. Uncertainty in the efficiency of retention of ammonium nitrate and organic compounds on filters also affects source category attribution and epidemiologic studies.

- Semivolatile organic compounds and semivolatile ammonium compounds (such as NH_4NO_3) may be lost by volatilization during sampling. Such losses may be very important in woodsmoke impacted areas for organic compounds or in agricultural and other areas where low sulfate and high ammonia lead to high NH_4NO_3 concentrations. New techniques are now in use for measurement of nitrates and new research techniques are being tested for measurement of mass of semivolatile organic compounds in PM and of the total (semivolatile plus non-volatile) PM mass. The Federal Reference Methods (FRM) for PM_{10} and $PM_{2.5}$ give precise (± 10%) measurements of "equilibrated mass." However, the loss of semivolatile PM (ammonium nitrate and organic compounds) and the possible retention of some particle-bound water in current PM mass measurements contribute to uncertainty in the measurement of the mass of PM as it exists suspended in the atmosphere.

- Techniques are available to separate fine particles from coarse particles and collect the fine particles on a filter. No such technique exists for coarse particles. As yet, no consensus exists on the best technique for collecting a coarse particle sample for determination of mass and composition. Candidates include multistage impaction, virtual impaction, and difference (subtracting $PM_{2.5}$ mass or composition from PM_{10} mass or composition). Advances in the theory and practice of virtual impaction suggest that it should be possible to design virtual impactors with much less than the 10% of fine PM collected in the coarse PM sample, as is now the case for the dichotomous samplers used in air quality studies and with penetration curves as sharp as those used in the current FRM for $PM_{2.5}$.

E.2.5 Ambient PM Concentrations in the U.S.

- The recently deployed $PM_{2.5}$ FRM network has provided data for a large number of sites across the United States. The data are stored in the Aerometric Information Retrieval System (AIRS). Data have also been collected at remote sites as part of the IMPROVE and NESCAUM networks. Annual mean U.S. $PM_{2.5}$ concentrations from 1999 to 2000 range from about 5 $\mu g/m^3$ to about 30 $\mu g/m^3$. In the eastern United States, the data from 1999 to 2001 indicate that highest quarterly mean concentrations and maximum concentrations most often occur during the summer. In the western United States, highest quarterly mean values and maximum values occur mainly during the winter at a number of sites although there were exceptions to these general patterns. $PM_{2.5}$ and PM_{10} concentrations many urban areas have generally declined over the past few decades. However, they appear to have leveled off in the past few years.

6 - The median $PM_{2.5}$ concentration across the United States during 1999, 2000, and 2001, the first three years of operation of the $PM_{2.5}$ FRM network, was 13 $\mu g/m^3$, with a 95th percentile value of 18 $\mu g/m^3$. The corresponding median $PM_{10-2.5}$ concentration was 10 $\mu g/m^3$, with a 95th percentile value of 21 $\mu g/m^3$.

7 - Although $PM_{2.5}$ concentrations within a given Metropolitan Statistical Area (MSA) can be highly correlated between sites, there can still be significant differences in their concentrations. The degree of spatial uniformity in $PM_{2.5}$ concentrations and the strength of site to site correlations in urban areas varies across the country. These factors should be considered in using data obtained by the $PM_{2.5}$ FRM network to approximate community-scale human exposures, and caution should be exercised in extrapolating conclusions as to spatial uniformity or correlations obtained in one urban area to another. Limited information also suggests that the spatial variability in urban source contributions is likely to be larger than for regional source contributions to $PM_{2.5}$ and for $PM_{2.5}$, itself.

8 - Data for $PM_{10-2.5}$ concentrations are not as abundant as they are for $PM_{2.5}$. The difference method used in their derivation is subject to the effects of uncertainties in measuring both PM_{10} and $PM_{2.5}$. As a result, estimates of $PM_{10-2.5}$ concentrations, at times, come out as negative values, based on currently available data (e.g., in the EPA AIRS Database). In most cities where significant data is available, $PM_{10-2.5}$ is spatially less uniform than $PM_{2.5}$.

9 - Ambient PM contains both primary and secondary components. The results of ambient monitoring studies and receptor modeling studies indicate that $PM_{2.5}$ is dominated by secondary components in the eastern United States. General statements about the origin of OC in ambient $PM_{2.5}$ samples cannot yet be made and so the contribution of secondary components throughout the rest of the United States is still highly uncertain. Primary constituents represent a smaller but still important component of $PM_{2.5}$. Crustal materials,

which are primary constituents, constitute the largest measured fraction of $PM_{10-2.5}$ throughout the United States. Data for the concentration of bioaerosols in both the $PM_{2.5}$ and $PM_{10-2.5}$ size ranges are sparse.

- Recent but limited information about policy-relevant background concentrations have not provided sufficient evidence to warrant any changes in estimates of the annual average background concentrations given in the 1996 PM AQCD. These are: 1 to 4 $\mu g/m^3$ in the West and 2 to 5 $\mu g/m^3$ in the East for $PM_{2.5}$; and approximately 3 $\mu g/m^3$ in both the East and the West for $PM_{10-2.5}$, with a range of 0 to 9 $\mu g/m^3$ in the West and 0 to 7 $\mu g/m^3$ in the East. Such concentrations are likely to be highly variable both spatially and temporally. Further information regarding the frequency distribution of 24-hour concentrations based on analyses of observations at relatively remote monitoring sites and on source apportionment analyses has become available and can be used for selected sites.

E.2.6 Human Exposure to PM

- Personal exposure to PM mass or its constituents results when individuals come in contact with particulate pollutant concentrations in locations or microenvironments that they frequent during a specific period of time. Various PM exposure metrics can be defined according to its source (i.e., ambient, nonambient) and the microenvironment where exposure occurs.

- Most people spend most of their time indoors where they are exposed to indoor-generated PM and ambient PM that has infiltrated indoors.

- Indoor-generated and ambient PM differ in sources, sizes, chemical composition, and toxicity.

- The ambient PM concentration and the indoor PM concentration can be measured by outdoor and indoor monitors. The total personal exposure can be measured by a personal exposure monitor carried by the person. However, the concentrations of indoor-generated PM and ambient PM that has infiltrated indoors and the related values of ambient and nonambient PM exposures must be estimated.

17 - The intercept of a regression of individual, daily values of total personal exposure on daily PM concentrations, gives the average nonambient PM exposure; and the slope gives the average attenuation factor (the ratio of ambient PM exposure to ambient PM concentration).

18 - Similarly, the intercept of a regression of individual, daily values of indoor PM concentration on daily ambient concentrations, gives the average concentration of indoor-generated PM; and the slope gives the average infiltration factor (concentrations of ambient PM that has infiltrated indoors/ambient PM concentration).

19 - The attenuation factor and the infiltration factor depend on the penetration coefficient, the fraction of ambient PM that penetrates through the walls, doors, windows, etc.; the deposition or removal rate, a measure of how rapidly PM within the indoor microenvironment is removed by deposition to surfaces or by filtration in a heating/cooling system; and the air exchange rate, a measure of how rapidly indoor air is replaced by outdoor air. The attenuation factor also depends on the fraction of time spent outdoors.

20 - The air exchange rate is an important variable for determining the concentration of ambient PM found indoors. It can be measured by release and measurement of an inert tracer gas indoors. The air exchange rate increases with opening of windows or doors or operation of window or attic fans. It also increases as the indoor/outdoor temperature difference increases. For closed homes, i.e., no open windows or doors, the air exchange rate does not appear to be a function of wind speed or direction.

21 - The penetration coefficient and the deposition rate can be estimated from measurements of outdoor and indoor concentrations under conditions when there are no indoor sources (night time or unoccupied home). These parameters are functions of particle size. The penetration coefficient is high and the deposition rate is low for accumulation mode particles (0.1 to 1.0 μm). The penetration coefficient is lower and the deposition rate is higher for ultrafine particles (< 0.1 μm) and coarse mode particles (> 1.0 μm). The attenuation factor and the

infiltration factor are higher for particles in the accumulation mode than for ultrafine or coarse particles.

22 - The attenuation factor and the infiltration factor will vary as the air exchange rate does, and, therefore, will vary with season and housing characteristics. These factors will increase with increased opening of windows and doors. For closed homes, these factors will increase with an increase of the indoor/outdoor temperature difference; but they do not appear to be affected by wind speed or direction.

23 - The regression technique is useful for finding average values of the attenuation factor and the nonambient exposure and possibly for estimating the distribution of individual, daily values of the nonambient PM exposure.

24 - Individual, daily values of the ambient PM exposure, the nonambient PM exposure, and the attenuation factor may be determined from individual, daily values of the total PM personal exposure and daily ambient PM concentrations by several techniques:

25 - *Mass balance technique.* Direct measurement of the air exchange rate, measurement of the fraction of time spent outdoors by a diary of the subject's activity pattern, and use of the equilibrium mass balance equation for the attenuation factor with estimated values of the penetration coefficient and the deposition rate.

26 - *Sulfate ratio technique.* Individual, daily values of the attenuation factor (for $PM_{2.5}$) will be given by individual, daily values of personal exposure to sulfate / the daily ambient sulfate concentration provided there are no indoor sources of sulfate and sulfate and $PM_{2.5}$ have similar particle size distributions.

27 - *Recursive technique.* Indoor-generated emissions, which tend to be episodic, can be removed from a continuous record of indoor PM concentration, allowing separation of indoor-generated PM and ambient PM that has infiltrated indoors.

28 - In pooled studies (different subjects measured on different days), individual, daily values of total PM exposure are usually not well correlated with daily ambient PM concentrations.

In longitudinal studies (each subject measured for multiple days), individual, daily values of total PM personal exposure and daily ambient PM concentrations are highly correlated for some, but not all subjects.

29 - Only one study has reported estimated individual, daily values of ambient and nonambient PM exposure. Individual, daily values of total PM personal exposure and daily ambient PM concentrations were poorly correlated. However, individual, daily values of ambient PM exposure and daily ambient PM concentrations were highly correlated. Individual daily values of ambient and nonambient PM exposure were not well correlated. Individual daily values of nonambient PM exposure and daily ambient PM concentrations were also not well correlated.

30 - As long as the nonambient PM exposure is not correlated with the ambient PM exposure, it will not bias the estimated health effect of PM. However, the effect per µg/ambient PM concentration will be biased low compared to the health effect per µg/ambient PM exposure by the attenuation factor. This effect probably explains some of the heterogeneity in PM_{10} effects observed in multicity epidemiology studies, as indicated by a correlation of PM effects in different cities with air conditioning use in those cities (i.e., the higher the air conditioning use, the lower the health effect estimate per $\mu g/m^3$ of ambient PM).

31 - Exposure relationships also provide some insight into the issue of confounding. While the data base is small, concentrations of gaseous co-pollutants, NO_2, O_3, and SO_2 (and probably CO) are likely poorly correlated, and sometimes not significantly correlated, with personal exposure to the respective co-pollutant. However, they are frequently significantly correlated with both the ambient PM concentration and the ambient PM exposure. Thus, in a regression, where associations are found between gaseous co-pollutants and a health effect, it may be because they are a surrogate for PM rather than a confounder. That is, the health effect due to PM is transferred to the gaseous pollutant because of the positive correlation between the ambient concentration of the gas and the ambient PM exposure.

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E.3 DOSIMETRY OF PARTICULATE MATTER

- Dosimetry establishes the relationship between PM exposure and the dose of inhaled PM delivered to and retained at the target site. Deposition, clearance, translocation, and retention comprise the essential elements of dosimetry.

- Dosimetric information is critical to extrapolating effects found in controlled exposure studies of laboratory animals to those observed in human exposure studies and for relating effects in normal healthy persons to those in potentially susceptible persons.

- Dosimetry separates the respiratory tract into three regions, extrathoracic (ET), tracheobronchial (TB), and alveolar (A), based on anatomical features and particle deposition and clearance phenomena that occur within each region.

- Particles in the accumulation mode size range (0.1 to 1.0 μm D_p) have the lowest deposition fraction in all three regions.

- Coarse and ultrafine particles have higher fractional deposition. For coarse particles, fractional deposition peaks between 5 and 10 μm D_p for the TB region and 2.5 and 5 μm D_p for the A region.

- For ultrafine particles, fractional deposition peaks between 0.0025 and 0.005 μm D_p for the TB region and between 0.01 and 0.05 for the A region.

- A significant fraction of ultrafine and coarse particles, but not particles in the accumulation-mode size range, are deposited in the ET region.

- Such transport could provide a mechanism whereby particles could affect cardiovascular function as reported in the epidemiologic studies

- Fractional deposition, as a function of particle size, depends on lung size, tidal volume, and breathing rate. Exercising subjects receive higher doses of particles per cm^2 of lung surface than subjects at rest.

- Airway structure and physiological function vary with age. Such variations may alter the deposition patterns for inhaled particles. Airflow distribution is very uneven in diseased lungs, and deposition can be enhanced locally in areas of active ventilation. Total lung deposition is generally increased by obstructed airways so that particle deposition can be enhanced in people with chronic lung disease. Unfortunately, deposition studies in another susceptible population, the elderly, are still lacking.

- Particles depositing on airway surfaces may be completely cleared from the respiratory tract or translocated to other sites within this system by regionally specific clearance mechanisms. Clearance is either absorptive (dissolution) or nonabsorptive (transport of intact particles). Deposited particles may be dissolved in body fluids, taken up by phagocytic cells, or transported by the mucociliary system. Retained particles tend to be small (< 2.5 μm) and poorly soluble (e.g., silica, metals). Ultrafine particles can be rapidly cleared from the lungs into the systemic circulation where they can be transported to extrapulmonary regions.

- Tracheobronchial clearance has both a fast and a slow component. In the fast phase particles deposited in the TB region clear out rapidly during the first several hours and continue to clear out for 24 hours. A small remaining portion may clear out over several days (slow phase). Translocation of poorly soluble PM to the lymph nodes takes a few days and is more rapid for smaller (< 2 μm) particles; elimination rates of these retained particles are on the order of years. People with COPD have increased particle retention partly because of increased initial deposition and impaired mucociliary clearance and use cough to augment mucociliary clearance.

- Alveolar clearance takes months to years. Particles may be taken up by alveolar macrophages within 24 hours, but some phagocytosed macrophages translocate into the interstitium or lymphatics whereas some remain on the alveolar surface. Penetration of uningested particles into the interstitium increases with increasing particle load and results in increased translocation to lymph nodes.

- Acute effects of PM are probably best related to deposited dose; whereas chronic effects may be related to cumulative or retained dose. Retention of particles is a function of deposition site, clearance of particles by macrophages or the mucociliary system, and particle characteristics, especially solubility. Chronic effects may also arise from recurring cycles of pulmonary injury and repair.

- Computational models allow calculation of fractional deposition and dose per cm^2 of lung surface as a function of particle size and respiratory parameters for humans and some animals (including the laboratory rat). Such calculations can be used to predict the exposures needed to produce comparable doses for animal to human extrapolation. Computational models have been improved in recent years but experimental validation of model predictions is still required.

E.4 TOXICOLOGY OF PARTICULATE MATTER IN HUMANS AND LABORATORY ANIMALS

E.4.1 Health Effects of Specific PM Components

- There is relatively little new information on the effects of acid aerosols, and the conclusions of the 1996 PM AQCD, i.e., Air Quality Criteria for Particulate Matter (U.S. Environmental Protection Agency, 1996a), are unchanged. It was previously concluded that acid aerosols cause little or no change in pulmonary function in healthy subjects, but asthmatics may develop small changes in pulmonary function. Although pulmonary effects of acid aerosols have been the subject of extensive research in past decades, the cardiovascular effects of acid aerosols have received little attention and should not be ruled out as possible mediators of PM health effects.

- Health effects of particle-associated soluble metals have been demonstrated by in vivo and in vitro studies using residual oil fly ash (ROFA) or soluble transition metals. Although there are some uncertainties about differential effects of one transition metal versus another, water soluble metals leached from ROFA or ambient filter extracts have been shown consistently (albeit at high concentrations) to cause cell injury and inflammatory changes in vitro and in vivo.

- 1 Even though it is clear that combustion particles that have a high content of soluble metals can cause lung injury and even death in compromised animals and correlate well with epidemiologic findings in some cases (e.g., Utah Valley Studies), it has not been fully established that the small quantities of metals associated with ambient PM are sufficient to cause health effects. Moreover, it cannot be assumed that metals are the only or the primary toxic component of ambient PM, rather than there possibly being many different toxic agents contributing to ambient PM health effects.

- 2 There is growing toxicological evidence that diesel exhaust particles exacerbate the allergic response to inhaled antigens. The organic fraction of diesel exhaust has been linked to eosinophil degranulation and induction of cytokine production, suggesting that the organic constituents of diesel PM are the responsible part for the immune effects. It is not known whether the adjuvant-like activity of diesel PM is unique or whether other combustion particles have similar effects. It is important to compare the immune effects of other source-specific emissions, as well as concentrated ambient PM, to diesel PM to determine the extent to which exposure to diesel exhaust may contribute to the incidence and severity of allergic rhinitis and asthma.

- 3 Published research on the acute effects of particle-associated organic carbon constituents is conspicuous by its relative absence, except for diesel exhaust particles.

- 4 Studies with ultrafine particles have demonstrated a significantly greater inflammatory response than that seen with fine particles of the same chemical composition at similar mass doses. In other more limited studies, ultrafines also have generated greater oxidative stress in experimental animals. However, when the particle surface area is used as a dose metric, the inflammatory response to both fine and ultrafine particles may be basically the same. Thus, it may be the higher surface area of ultrafine particles is the important factors contributing to health effects.

- 5 Concentrated ambient particle (CAPS) studies should be among the most relevant in helping to understand the characteristics of PM producing toxicity, susceptibility of individuals to PM, and the underlying mechanisms. Studies have used collected urban PM for intratracheal administration to healthy and compromised animals. Despite the difficulties in extrapolating from the bolus delivery used in such studies, they have provided strong evidence that the chemical composition of ambient particles can have a major influence on toxicity.

- Ambient particle concentrators, that concentrate particles in situ, provide particles for inhalation studies. The concentration of particles without collection avoids the changes in size and composition that occur during collection during collection and resuspension. Studies with inhaled CAPs have observed cardiopulmonary changes in rodents and dogs at high concentrations of PM between 0.15 and 2.5 µm diameter. A new generation of ambient particle concentrators that allow separation and concentration of coarse-mode, accumulation-mode, and ultrafine particle separately will permit the direct toxicological comparison of these various ambient particle sizes.

- Recent studies support the conclusion of the 1996 PM AQCD, which stated that bioaerosols, at concentrations present in the ambient environment, cannot account for the reported health effects of ambient PM. However, it is possible that bioaerosols could contribute to the health effects of PM.

E.4.2 Mechanisms of Action

E.4.2.1 Cardiovascular Effects

- Changes in heart rate, heart rate variability, and conductance associated with ambient PM exposure have been reported in animal studies, in several human panel studies, and in a reanalysis of data from the MONICA study. Some of these studies included endpoints related to respiratory effects but few significant adverse respiratory changes were detected. This raises the possibility that ambient PM may have effects on the heart that are independent of adverse changes in the lung.

- Inhaled particulate matter affects the heart by uptake of particles into the circulation or release of a soluble substances into the circulation.

- Inhaled particulate matter affects autonomic control of the heart and cardiovascular system.

E.4.2.2 Respiratory Effects

- Particularly compelling evidence pointing towards ambient PM causing lung injury and inflammation derives from the study of ambient PM materials on filter extracts collected from community air monitors before, during the temporary closing of a steel mill in Utah Valley, and after its reopening. Intratracheal instillation of filter extract materials in human volunteers provoked greater lung inflammatory responses for materials obtained before and after the temporary closing versus that collected during the plant closing. Further, the instillation in rats of extract materials from before and after the plant closing resulted in a 50% increase in air way hyperresponsiveness to acetylcholine compared to 17 or 25% increases with saline or extract materials for the period when the plant was closed, respectively. Analysis of the extract materials revealed notably greater quantities of metals for when the plant was opened suggesting that such metals (e.g., Cu, Zn, Fe, Pb, As, Mn, Ni) may be important contributors to the pulmonary toxicity observed in the controlled exposure studies, as well as to health effects shown epidemiologically to vary with PM exposures of Utah Valley residents before, during, and after the steel mill closing.

- Still other toxicological studies point towards lung injury and inflammation being associated with exposure of lung tissue to complex combustion-related PM materials, with metals again being likely contributors. Rats with SO_2-induced bronchitis and monocrotaline-treated rats have been reported to have a greater inflammatory response to concentrated ambient PM than normal rats. These studies suggest that exacerbation of respiratory disease by ambient PM may be caused in part by lung injury and inflammation.

- Particulate air pollution causes increased susceptibility to respiratory infections. Exposure of rats to ROFA and *L. monocytogenes*, a bacterial pathogen, led rats treated with saline or *L. monocytogenes* in the absence of ROFA. Preexposure of rats to ROFA significantly enhanced injury and delayed the pulmonary clearance of a subsequent challenge of *L. monocytogenes*, when compared to saline-treated control rats. Acute exposure to ROFA appeared to slow pulmonary clearance of *L. monocytogenes* and to alter AM function. Such changes could lead to increased susceptibility to lung infection in exposed populations.

- Particulate air pollution increases airway reactivity and exacerbates asthma. Diesel particulate matter (DPM) has been shown to increase production of antigen-specific IgE in mice and humans. In vitro studies have suggested that the organic fraction of DPM is involved in the increased IgE production. ROFA leachate also has been shown to enhance antigen-specific airway reactivity in mice, indicating that soluble metals can also enhance an allergic response.

E.4.2.3 Systemic Effects Secondary to Lung Injury

- Lung injury from inhaled PM causes impairment of oxygenation and increased work of breathing that adversely affects the heart.
- Lung inflammation and cytokine production cause adverse systemic hemodynamic effects.
- Lung inflammation from inhaled PM causes increased blood coagulability that increases the risk of heart attacks and strokes.
- Interaction of PM with the lung affects hematopoiesis.

E.4.3 Susceptibility

- Older animals or animals with certain types of compromised health, either genetic or induced, are more susceptible to instilled or inhaled particles, although the increased animal-to-animal variability in these models has created greater uncertainty for the interpretation of the findings. Moreover, because PM seems to affect broad categories of disease states, ranging from cardiac arrhythmias to pulmonary infection, it can be difficult to know what disease models to use in evaluating the biological plausibility of adverse health effects of PM. Nevertheless, particularly interesting new findings point toward ambient PM exacerbation of allergic airway hyperresponsiveness and/or antigen-induced immune responses. Both metals and diesel particles have been implicated, with an expanding array of new studies showing DPM in particular as being effective in exacerbating allergic asthma responses.

E.5 EPIDEMIOLOGY OF HUMAN HEALTH EFFECTS ASSOCIATED WITH AMBIENT PARTICULATE MATTER

Chapter 8 of this document assesses the extensive PM epidemiologic data base that has become newly available since the 1996 PM AQCD. The most important types of additions to the epidemiologic database beyond that assessed in the 1996 PM AQCD include the following:

- New multi-city studies on a variety of endpoints which provide more precise estimates of the average PM effect sizes than most smaller-scale individual city studies;
- More studies of various health endpoints using ambient PM_{10} and/or closely related mass concentration indices (e.g., PM_{13} and PM_7), which substantially lessen the need to rely on non-gravimetric indices (e.g., BS or CoH);
- New studies evaluating relationships of a variety of health endpoints to the ambient PM coarse fraction ($PM_{10-2.5}$), the ambient fine-particle fraction ($PM_{2.5}$), and even ambient ultrafine particles measures ($PM_{0.1}$ and smaller), using direct mass measurements and/or estimated from site-specific calibrations;
- A few new studies in which the relationship of some health endpoints to ambient particle number concentrations were evaluated;
- Many new studies which evaluated the sensitivity of estimated PM effects to the inclusion of gaseous co-pollutants in the model;
- Preliminary attempts to evaluate the effects combinations or mixtures of air pollutants including PM components, based on factor analysis or source profiles;
- Numerous new studies of cardiovascular endpoints, with particular emphasis on assessment of cardiovascular risk factors as well as symptoms;
- Additional new studies on asthma and other respiratory conditions potentially exacerbated by PM exposure;
- New analyses of lung cancer associations with long-term exposures to ambient PM;

- New studies of infants and children as a potentially susceptible population.

In addition, Chapter 8 discusses statistical issues posed by use of General Additive Mode (GAM) analyses involving default convergence criteria in widely used commercially-available software employed in time-series analyses of ambient PM-health effects relationship reported in a few published studies assessed in the 1996 PM AQCD and in numerous more recent studies assessed in the present PM AQCD. This includes discussion of the following key points:

- Use of GAM analyses with default convergence criteria (GAM default) has variable impacts on PM effect size estimates from study to study, depending on many factors (numbers of observations, numbers of potential effect modifiers or potential confounders included, specific "smoothing" approaches used to control for their effects, numbers of degrees of freedom used, etc.). The effect of GAM (default) use tends most often to be some (unusually only slight) overestimation of the PM effect size compared to results obtained with use of GAM with stringent convergence criteria or other appropriate modeling approaches, e.g., general linear models (GLM).

- The results of EPA-encouraged reanalyses of a number of (> 35) of important PM time-series analyses comparing PM effect sizes and standard error (confidence interval) estimates from GAM (default) analyses versus GAM (stringent) or other appropriate statistical approaches (GLM). These reanalyses appear in a Health Effects Institute Special Report (HEI, 2003) that includes not only short communications on the GAM reanalyses by the original investigators, but also commentaries on the reanalyses and their implications for interpreting the PM time-series analyses results by a special peer-review panel convened by HEI at EPA's request.

E.5.2 Key Epidemiologic Findings

The epidemiologic studies discussed in Chapter 8 demonstrate biologically-plausible responses in humans exposed at ambient concentrations. These observational study findings are further enhanced by supportive findings of causal studies from other scientific disciplines (dosimetry, toxicology, etc.), in which other factors could be experimentally controlled, as discussed in Chapters 6 and 7. The most salient findings derived from the PM epidemiologic studies include the following:

- A large and reasonably convincing body of epidemiology evidence confirms earlier associations between short- and long-term ambient PM_{10} exposures (inferred from stationary community air monitor measures) and mortality/morbidity effects and suggest that PM_{10} (or one or more PM_{10} components) is a probable contributing cause of adverse human health effects.

- There appears to be some spatial heterogeneity in city-specific excess risk estimates for the relationships between short-term ambient PM_{10} concentrations and acute health effects. The reasons for such variation in effects estimates are not well understood at this time but do not negate ambient PM's likely causative contribution to observed PM-mortality and/or morbidity associations in many locations. Possible factors contributing to the apparent heterogeneity include geographic differences in air pollution mixtures, composition of PM components, and personal and sociodemographic factors affecting PM exposure (such as use of air conditioners, education, and so on).

- A growing body of epidemiologic studies confirm associations between short- and long-term ambient $PM_{2.5}$ exposures (inferred from stationary air monitor measures) and adverse health effects and suggest that $PM_{2.5}$ (or one or more $PM_{2.5}$ components) is a probable contributing cause of observed PM-associated health effects. Some new epidemiologic findings also suggest that health effects are associated with mass or number concentrations of ultrafine (nuclei-mode) particles, but not necessarily more so than for other ambient fine PM components.

- A smaller body of evidence appears to support an association between short-term ambient thoracic coarse fraction ($PM_{10-2.5}$) exposures (inferred from stationary air monitor measures) and short-term health effects in epidemiologic studies. This suggests that $PM_{10-2.5}$, or some constituent component(s) of $PM_{10-2.5}$, may be a contributory cause of adverse health effects in some locations. Reasons for differences among findings on coarse-particle health effects reported for different cities are still poorly understood, but several of the locations where significant $PM_{10-2.5}$ effects have been observed (e.g., Phoenix, Mexico City, Santiago) tend to be in drier climates and may have contributions to observed effects due to higher levels of organic particles from biogenic processes (endotoxins, molds, etc.) during warm months. Other studies suggest that particles of crustal origin are generally unlikely to exert notable health effects under most ambient exposure conditions. Also, in some western U.S. cities where $PM_{10-2.5}$ is a large part of PM_{10}, the relationship between hospital admissions and PM_{10} may be an indicator of response to coarse thoracic particles from wood burning.

7 - Long-term PM exposure durations, on the order of months to years, as well as on the order of a few days, are statistically associated with serious human health effects (indexed by mortality, hospital admissions/medical visits, etc.). More chronic PM exposures, on the order of years or decades, appear to be associated with life shortening well beyond that accounted for by the simple accumulation of the more acute effects of short-term PM exposures (on the order of a few days). Substantial uncertainties remain regarding the magnitude of and mechanisms underlying chronic health effects of long-term PM exposures and the relationship between chronic exposure and acute responses to short-term exposure.

8 - Recent investigations of the public health implications of such chronic PM exposure-mortality effect estimates were also reviewed. Life table calculations by Brunekreef (1997) found that relatively small differences in long-term exposure to airborne PM of ambient origin can have substantial effects on life expectancy. For example, a calculation for the 1969-71 life table for U.S. white males indicated that a chronic exposure increase of 10 $\mu g/m^3$ PM was associated with a reduction of 1.3 years for the entire population's life expectancy at age 25. Also, new evidence of associations of PM exposure with infant mortality and/or intrauterine growth retardation and consequent increase risk for many serious health conditions associated with low birth weight, if further substantiated, would imply that life shortening in the entire population from long-term PM exposure could well be significantly larger than that estimated by Brunekreef (1997).

9 - Considerable coherence exists among effect size estimates for ambient PM health effects. For example, results derived from several multi-city studies, based on pooled analyses of

data combined across multiple cities (thought to yield the most precise estimates of mean effect size), show the percent excess total (non-accidental) deaths estimated per 50 μg/m^3 increase in 24-h PM_{10} to be ~1.4% in the 90 largest U.S. cities with the estimate for the Northeast being the largest (approximately twice the nationwide estimate); ~3.4% in 10 large U.S. cities; ~3.6% in the 8 largest Canadian cities; and ~3.0% in western European cities. These combined estimates are consistent with the range of PM_{10} estimates previously reported in the 1996 PM AQCD. These and excess risk estimates from many other individual-city studies, generally falling in the range of ca. 1.5 to 8.0% per 50 μg/m^3 24-h PM_{10} increment, also comport well with numerous new studies confirming increased cause-specific cardiovascular- and respiratory-related mortality. They are also coherent with larger effect sizes reported for cardiovascular and respiratory hospital admissions and visits, as would be expected for these morbidity endpoints versus those for PM_{10}-related mortality.

10 - Several independent panel studies (but not all) that evaluated temporal associations between PM exposures and measures of heart beat rhythm in elderly subjects provide generally consistent indications of decreased heart rate variability (HRV) being associated with ambient PM exposure (decreased HRV being an indicator of increased risk for serious cardiovascular outcomes, e.g., heart attacks). Other studies point toward changes in blood characteristics (e.g., C-reactive protein levels) related to increased risk of ischemic heart disease also being associated with ambient PM exposures. However, these heart rhythm and blood characteristics findings should currently be viewed as providing only limited or preliminary support for PM-related cardiovascular effects.

11 - Notable new evidence now exists which substantiates positive associations between ambient PM concentrations and increased respiratory-related hospital admissions, emergency department, and other medical visits, particularly in relation to PM_{10} levels. Of much interest are new findings tending to implicate not only fine particle components but also coarse thoracic (e.g., $PM_{10-2.5}$) particles as likely contributing to exacerbation of asthma conditions. Also of much interest are emerging new findings indicative of likely increased occurrence of chronic bronchitis in association with (especially chronic) PM exposure. Also of particular interest are reanalyses or extensions of earlier prospective cohort studies of

long-term ambient PM exposure effects which demonstrate substantial evidence for association of increased lung cancer risk with such PM exposures, especially exposure to fine PM or its subcomponents.

12 - One major methodological issue affecting epidemiologic studies of both short-term and long-term PM exposure effects is that ambient PM of varying size ranges is typically found in association with other air pollutants, including gaseous criteria pollutants (e.g, O_3, NO_2, SO_2, CO), air toxics, and/or bioaerosols. Available statistical methods for assessing potential confounding arising from these associations may not yet be fully adequate. The inclusion of multiple pollutants often produces statistically unstable estimates. Omission of other pollutants may incorrectly attribute their independent effects to PM. Second-stage regression methods may have certain pitfalls that have not yet been fully evaluated. Much progress in sorting out relative contributions of ambient PM components versus other co-pollutants is nevertheless being made and, overall, tends to substantiate that observed PM effects are at least partly due to ambient PM acting alone or in the presence of other covarying gaseous pollutants. However, the statistical association of health effects with PM acting alone or with other pollutants should not be taken as an indicator of a lack of effect of the other pollutants.

13 - It is possible that differences in observed health effects will be found to depend on site-specific differences in chemical and physical composition characteristics of ambient particles and on factors affecting exposure (such as air conditioning) as well as on differences in PM mass concentration. For example, epidemiologic Utah Valley studies showed that PM_{10} particles, known to be richer in metals during exposure periods while the steel mill was operating, were more highly associated with adverse health effects than was PM_{10} during the PM exposure reduction while the steel mill was closed. In contrast, PM_{10} or $PM_{2.5}$ was relatively higher in crustal particles during windblown dust episodes in Spokane and in three central Utah sites than at other times, but was not associated with higher total mortality. These differences require more research that may become more feasible as the $PM_{2.5}$ sampling network produces air quality data related to speciated samples.

1 - The above reasons suggest it is inadvisable to pool PM epidemiologic studies for different locations or time periods, with different population sub-groups, or different health endpoints (as is often done in "meta-analyses"), without careful assessment of potential causes and consequences of these differences and appropriate caveating of results. Published multi-city analyses using common data bases, measurement methods, analytical strategies, and extensive independent external review (as carried out in the APHEA and NMMAPS studies) are useful. Pooled analyses of more diverse collections of independent studies of different cities, using varying methodology and/or data quality or representativeness, are likely less credible and should not, in general, be used without careful assessment of their underlying scientific comparability.

2 - It may be possible that different PM size components or particles with different composition or sources produce effects by different mechanisms manifested at different lags or that different preexisting conditions may lead to different delays between exposure and effect. Thus, although maximum effect sizes for PM effects have often been reported for 0-1 day lags, evidence is also beginning to suggest that more consideration should be given to lags of several days. Also, if it is considered that all health effects occurring at different lag days are all real effects, so that the risks for each lag day should be additive, then overall risks may exist that are higher than implied by maximum estimates for any particular single or two-day lags. In that case, multi-day averages or distributed lag models may provide more accurate estimate of the total impact of PM on the population.

3 - Certain classes of ambient particles may be distinctly less toxic than others and may not exert human health effects at typical ambient exposure concentrations or only under special circumstances. Coarse thoracic particles of crustal origin, for example, may be relatively non-toxic under most circumstances compared to those of combustion origin such as wood burning. However, crustal particles may be sufficiently toxic to cause human health effects under some conditions; resuspended crustal particles, for example, may carry toxic trace elements and other components from previously deposited fine PM, e.g., metals from smelters (Phoenix) or steel mills (Steubenville, Utah Valley), PAH's from automobile exhaust, or pesticides from administration to agricultural lands. Likewise, fine particles

from different sources have different effect sizes. More research is needed to identify conditions under which one or another class of particles may cause little or no adverse health effects, as well as conditions under which different classes of particles may cause relatively more notable effects.

4 - Certain epidemiologic evidence from "intervention studies" suggests that reducing ambient PM_{10} concentrations may reduce a variety of health effects on a time scale from a few days to a few months, as found in epidemiologic studies of "natural experiments" such as in the Utah Valley, and supported by toxicology studies using particles extracts from ambient community sampling filters from the Utah Valley. Recent studies in Germany and in the Czech Republic also tend to support a hypothesis that reductions in particle-related air pollution are associated with reductions in the incidence of adverse health effects.

5 - Studies that combine the features of cross-sectional and cohort studies provide the best evidence for chronic effects of PM exposure. Gauderman et al. (2000; 2002) have found significant decreases in lung function growth related to PM_{10} levels using these techniques.

6 - Adverse health effects in children reported in a limited number of more recent studies are emerging as an important area of more concern than was the case in the 1996 PM AQCD. Unfortunately, relatively little is known about the relationship of PM to the most serious health endpoints, neonatal and infant mortality, emergency hospital admissions and mortality in older children, as well as low birth weight and preterm birth.

7 - Little is yet known about involvement of PM exposure in the progression from less serious childhood conditions, such as asthma and respiratory symptoms, to more serious disease endpoints later in life. This is an important health issue because childhood illness or death may cost a very large number of productive life-years.

8 - Lastly, new epidemiologic studies of ambient PM associations with increased non-hospital medical visits (physician visits) and asthma effects suggest likely much larger health effects and costs to society due to ambient PM than just those indexed by mortality and/or hospital admissions/visits.

E.6 ENVIRONMENTAL EFFECTS OF PM

E.6.1 Vegetation and Ecosystem Effects

- Deposition of particulate matter from the atmosphere has the potential to alter ecosystem structure and function. Human existence on this planet depends on the essential life-support services that ecosystem structure and functions provide. Concern has risen in recent years regarding the consequences of changing the biological diversity of ecosystems because human activities are creating disturbances that are altering the structure (complexity and stability) and functioning (producing changes in the processes of energy and water flow and nutrient cycling) of ecosystems.

- Human-induced changes in biotic diversity and alterations in the structure and ecosystems processes are the two most dramatic ecological trends in the past century. Biodiversity encompasses all levels of biological organization, including individuals, populations, species, and ecosystems. For this reason, there is a need to understand the effects of PM deposition on vegetation and ecosystems and biodiversity.

- Ecosystem functions maintain clean water, pure air, biodiversity, and impart the following benefits: fixation of solar energy, absorption and breakdown of pollutants, cycling of nutrients, binding of soil, degradation of organic wastes, maintenance of a balance of atmospheric gases, regulation of radiation balance, and climate.

- The deposition of PM onto vegetation and soil, depending on its chemical composition (acid/base, trace metal, or nutrients, e.g., nitrates or sulfates), can produce direct or indirect responses within an ecosystem.

- Ecosystem response to pollutant deposition is a direct function of the level of sensitivity of the ecosystem and its ability to ameliorate resulting changes. Changes in ecosystem structural patterns and the functioning of ecological processes must be scaled in both time and space and propagated to the more complex levels of community interaction to produce observable ecosystem changes.

1 - The major effect of atmospheric PM on ecosystems is indirect and occurs through the deposition of nitrates and sulfates and the acidifying effects of the associated H^+ ion in wet and dry deposition in the soil environment. In the soil, they have the potential to inhibit nutrient uptake, alter the ecological processes of energy flow and nutrient cycling, change ecosystem structure, and affect ecosystem biodiversity. Most nitrate is not deposited or measured as PM but is a combination of wet and dry deposition.

2 - The soil environment, one of the most dynamic sites of biological interaction, is inhabited by communities of bacteria, fungi, and actinomycetes. Bacteria, as essential components of the nitrogen and sulfur cycles, and fungi in the uptake of mineral nutrients play an important role in plant nutrition. Their actions make these elements available for plant uptake. Fungi form mycorrhizae, a mutualistic symbiotic relationship with plant roots that is integral to the uptake of mineral nutrients. Changes in the soil environment resulting from deposition of nitrates and sulfates that alter the role of the bacteria in the nutrient cycles and mycorrhizal fungi in making minerals available for plant utilization, determine plant and, ultimately, ecosystem response.

3 - Although nitrogen as molecular nitrogen (N_2) is the most abundant element in the atmosphere, it only becomes available to support plant growth after its conversion into reactive forms. In nature, nitrogen may be divided into two groups: reactive (Nr) and nonreactive (N_2). Reactive nitrogen or Nr includes the inorganic reduced forms of nitrogen (e.g., ammonia [NH_3] and ammonium [NH_4^+]), inorganic oxidized forms (e.g., nitrogen oxides [NO_x], nitric acid [HNO_3], nitrous oxide [N_2O], and nitrate [NO_3^-]), and organic compounds (e.g., urea, amine, proteins, and nucleic acids).

4 - Reactive nitrogen can be widely dispersed and accumulate in the environment when the rates of its formation exceed the rates of removal via denitrification. As a result of human food production, it is now accumulating in the environment on all spatial scales – local, regional and global; and its creation and accumulation is projected to increase as per capita use of resources by human populations increases.

1 • The major changes in the nitrogen cycle can be both beneficial and detrimental to the health and welfare of humans and ecosystems. The cascade of environmental effects resulting from reactive nitrogen accumulation include the following: (1) production of tropospheric ozone and aerosols that induce human health and ecosystem problems; (2) increases in the productivity in forests and grasslands followed by decreases wherever Nr deposition increases significantly and exceeds critical thresholds; (3) reactive nitrogen additions probably decrease biodiversity in many natural habitats; (4) in association with sulfur is responsible for acidification and loss of biodiversity in lakes and streams in many regions of the world; (5) eutrophication, hypoxia, loss of biodiversity, and habitat degradation in coastal ecosystems. [Eutrophication is now considered the biggest pollution problem in coastal waters.], and (6) contributes to global climate change and stratospheric ozone depletion, which can in turn affect ecosystems and human health.

2 • "Nitrogen saturation" results when reactive nitrogen concentrations exceed the capacity of a system to utilize it. Saturation implies that some resource other than nitrogen is limiting biotic function. Water and phosphorus for plants and carbon for microorganisms are most likely to be the secondary limiting factors. The appearance of nitrogen in soil solution is an early symptom of excess nitrogen. In the final stage, disruption of ecosystem structure becomes visible.

3 • Possible ecosystem responses to nitrogen saturation include (1) a permanent increase in foliar nitrogen and reduced foliar phosphorus and lignin caused by the lower availability of carbon, phosphorus, and water; (2) reduced productivity in conifer stands because of disruptions of physiological function; (3) decreased root biomass and increased nitrification and nitrate leaching; (4) reduced soil fertility, resulting from increased cation leaching and increased nitrate and aluminum concentrations in streams, (5) decreased water quality, and (6) changes in soil microbial communities from predominantly fungal (mycorrhizal) communities to those dominated by bacteria during saturation.

- Intensive research over nearly a decade indicates that, although the soils of most North American forests are nitrogen limited, severe symptoms of nitrogen saturation have been observed in the high-elevation, non-aggrading spruce-fir ecosystems in the Appalachian Mountains; the eastern hardwood watersheds at the Fernow Experimental Forest near Parsons, WV; forests in southern California; the southwestern Sierra Nevada in Central California; and the Front Range in northern Colorado. The mixed conifer forest and chaparral watershed with high smog exposure in the Los Angeles Air Basin exhibit the highest stream water NO_3^- concentrations in wilderness areas of North America.

- Increases in soil nitrogen play a selective role in ecosystems. Plant succession patterns and biodiversity are affected significantly by chronic nitrogen additions in some North American ecosystems. Long-term nitrogen fertilization studies in both New England and Europe suggest that some forests receiving chronic inputs of nitrogen may decline in productivity and experience greater mortality. Declining coniferous forest stands with slow nitrogen cycling may be replaced by deciduous fast-growing forests that rapidly cycle nitrogen.

- In experimental studies nitrogen deposition over a 12-year period Minnesota grasslands dominated by native warm-season grasses shifted to low-diversity mixtures dominated by cool-season grasses.

- Excess nitrogen inputs to unmanaged heathlands in the Netherlands has resulted in nitrophilous grass species replacing slower growing heath species. Over the past several decades the composition of plants in the forest herb layers has been shifting toward species commonly found in nitrogen-rich areas. It also was observed that the fruiting bodies of mycorrhizal fungi had decreased in number, indicating that formation of mycorrhizae were affected.

- Soil nitrogen enrichment of the soil significantly alters the composition and richness of the arbuscular mycorrhizal fungal community and markedly decreases overall diversity of the mycorrhizal community. Decline in the coastal sage scrub in southern California was directly linked to the decline of arbuscular mycorrhizal fungal community.

- The effects of excessive deposition of nitrogen, particularly NH_3 and NH_4^+, have led to changes in Dutch heathlands via: (1) acidification of the soil and the loss of cations of K^+, Ca^{2+} and Mg^{2+}; and (2) nitrogen enrichment, which results in increased plant growth rates and altered competitive relationships. Alteration of any of a number of parameters (e.g., increased nitrogen) can alter ecosystem structure and function.

- Notable effects of excess nitrogen deposition have been observed with regard to aquatic systems. Atmospheric nitrogen deposition onto soils in watershed areas feeding into estuarine sound complexes (e.g., the Pamlico Sound of North Carolina) appear to contribute to excess nitrogen flows in runoff (especially during and after heavy rainfall events such as hurricanes) from agricultural practices or other uses (e.g., fertilization of lawns or gardens). Massive influxes of such nitrogen into watersheds and sounds can lead to algae blooms, which, upon degradation, deplete oxygen and cause extensive fish kills and damage to commercial fish and sea food harvesting.

- Acidic precipitation, a critical environmental stress that affects forest landscapes and aquatic ecosystems in North America, Europe, and Asia, is linked to the effects associated with the deposition of Nr and sulfates and the associated hydrogen ion. The resulting soil acidity can lead to nutrient deficiencies and to high aluminum-to-nutrient ratios that limit uptake of calcium and magnesium and create a nutrient deficiency adversely affect tree growth. Calcium is essential in the formation of wood and the maintenance of the primary plant tissues necessary for tree growth.

- The critical loads concept is useful for estimating the amounts of pollutants (e.g., reactive nitrogen and acidic precipitation) that sensitive ecosystems can absorb on a sustained basis without experiencing measurable degradation. The estimation of ecosystem critical loads requires an understanding of how an ecosystem will respond to different loading rates in the long term and can be of special value for ecosystems receiving chronic deposition of Nr and sulfur independently and as acidic deposition when in combination.

- The biological effect of PM is determined by the amount deposited during the wet and dry deposition onto the plant surfaces or soil in the vicinity of the roots. The three major routes involved are (1) precipitation scavenging in which particles are deposited in rain and snow; (2) occult (fog, cloud water, and mist interception); and (3) dry deposition, a much slower, yet more continuous removal to place surfaces.

- Few heavy metals (e.g., copper, nickel, zinc) have been documented to have direct phytoxicity under field conditions. Ecosystems immediately downwind of major emissions sources such as power generating, industrial, or urban complexes can receive locally heavy inputs. Heavy metal accumulation in the richly organic forest floor where biological activity is greatest by affecting litter decomposition present the greatest potential for influencing nutrient cycling. The presence of cadmium, copper and nickel have been observed to affect the symbiotic activity of fungi, bacteria, and actinomycetes.

- Phytochelatins produced by plants as a response to sublethal concentrations of heavy metals, are indicators of metal stress and can be used to indicate that heavy metals are involved in forest decline. Increasing concentrations of phytochelatins with increasing altitude, and their increases across regions that show increased levels of forest injury, have implicated them in forest decline.

- Secondary organics formed in the atmosphere have been variously subsumed under the following terms: toxic substances, pesticides, hazardous air pollutants (HAPS), air toxics, semivolatile organic compounds (SOCs), and persistent organic pollutants (POPS). Such substances are controlled under CAA Sect.112, Hazardous Air Pollutants (not as criteria pollutants controlled by NAAQS under CAA Sections 108 and 109). Their possible effects on humans and ecosystems are discussed in many other government documents and publications. They are noted in this document because, in the atmosphere, many of the chemical compounds are partitioned between gas and particle phases and are deposited as particulate matter. As particles, they become airborne and can be distributed over a wide area and affect remote ecosystems. Some are also of concern to humans because they may reach toxic levels in food chains of both animals and humans; whereas others may tend to maintain or decrease some toxicity as they move through the food chain.

E.6.2 Visibility

Chapter 4 of this document includes information supplementary to several other significant reviews of the science of visibility, including the 1991 report of the National Acid Precipitation Assessment Program, the National Research Council's *Protecting Visibility in National Parks and Wilderness Areas* (1993), and EPA's 1995 *Interim Findings on the Status of Visibility Research*. The following points are made in Chapter 4 and/or in the above referenced documents.

- The relationships between air quality and visibility are well understood. Ambient fine particles are the major cause of visibility impairment. Significant scientific evidence exists showing that reducing fine particle concentrations will improve visibility.

- The National Research Council defines visibility qualitatively as "the degree to which the atmosphere is transparent to visible light." This definition may be expressed quantitatively in terms of contrast transmittance. The EPA has defined visibility impairment as a reduction in visual range (the farthest distance at which a large black object can be distinquished against the horizontal sky is the visual range) and/or atmospheric discoloration.

- Light, as it passes through the atmosphere from a scene to an observer, is both scattered and absorbed. The rate of loss of transmitted light intensity with distance is measured by the light-extinction coefficient, which may be expressed as the sum of the coefficients for: (a) light scattering due to gases; (b) light scattering due to particles; (c) light absorption by gases, and; (d) light absorption by particles. Light scattering by particles is the major component of light extinction. Light absorption by gases is almost entirely due to NO_2, and is typically significant only near NO_2 sources. Light absorption by particles is primarily caused by elemental carbon.

- Light scattering efficiency depends on particle size, falling off rapidly for particles below 0.3 or above 1.0 μm in diameter. Therefore, particles in the accumulation mode (of the fine particle mode) are most effective in scattering light and are more important in visibility degradation than either nuclei-mode or coarse-mode particles. Light absorption is not a strong function of particle size. Under exceptional circumstances, such as dust storms, coarse particles can dominate scattering.

1 - In addition to reducing the intensity of light carrying information about a scene (transmitted radiance), particles also scatter light into the observer's view. This extraneous light, called air light or path radiance, carries no information about the scene. The competition between these two sources of light, expressed as the ratio of transmitted radiance from the scene to path radiance, determines the contrast transmittance and the visual quality of the view.

2 - Visibility at any location is affected by air quality and non-air quality related effects. The visibility effects of atmospheric constituents are dependant upon not just the mass of pollutants, but on the size distribution and refractive index of particles, which are strongly influenced by relative humidity. Non-air quality effects include the angle between the sun and the observer's sight path, location of clouds, and reflectivity of the ground. These effects are independent of effects due to changes in atmospheric constituents. Lighting and scene effects can be accounted for by defining a range of these effects when estimating visibility changes due to air quality influences.

3 - The relationship between air pollution and the appearance of a scenic view is well understood. Models exist that, given an adequate description of the air quality and non-air quality variables, can produce a simulated photograph that accurately depicts a cloud-free scene as it would appear to a human observer.

4 - There are several potential quantitative indicators of visibility, including: (a) fine particle mass and composition (fine particle mass alone provides less of both types of information); (b) scattering by dried ambient particles; (c) scattering by particles under ambient conditions; (d) extinction (calculated from measurements of scattering plus absorption); (e) light extinction measured directly; and (f) contrast transmittance.

5 - A new index, the deciview *(dv),* is now being used as a quantitative measure of haziness. It is related to the light extinction coefficient, b_{ext}, by $Haziness\ (dv) = 10\ ln(b_{ext}/10\ Mn)$. The deciview is more nearly linearly related to perceived changes in haze level than either visual range or light extinction. A change of 1 or 2 *dv* in uniform haze under many viewing conditions will be seen as a small but noticeable change in the appearance of a scene regardless of the initial haze condition.

- Visibility in the United States is best in the western, intermountain region. Visibility impairment or haziness is greatest in the eastern United States and southern California. Haziness in the eastern United States is caused primarily by atmospheric sulfate. Haziness in southern California is primarily caused by nitrate and organic PM. Nitrates contribute about 40% to the total light extinction in southern California. Nitrates account for 10 to 20% of the total extinction in other areas of the United States.

- Organics are the second largest contributors to light extinction in most areas in the United States. Organic carbon is the greatest cause of light extinction in the Pacific Northwest, Oregon, Idaho, and Montana, accounting for 40 to 45% of the total extinction. Organic carbon contributes between 15 to 20% to the total extinction in most of the western United States and 20 to 30% in the remaining areas of the United States.

- Light absorption by carbon is relatively insignificant but is highest in the Pacific Northwest (up to 15%) and in the eastern United States (3%).

- High dust concentrations transported from southern California and the subtropics have contributed to regional haze in the Grand Canyon and other Class I areas in the southwestern United States.

E.6.3 Particulate Matter-Related Effects on Materials

Atmospheric PM and SO_2 exert effects on materials that are related both to aesthetic appeal and physical damage. Studies have demonstrated particles, primarily consisting of carbonaceous compounds, cause soiling of commonly used building materials and culturally important items such as statues and works of art. Physical damage from the dry deposition of SO_2, particles, and the absorption or adsorption of corrosive agents on deposited particles can also result in the acceleration of the weathering of manmade building and naturally occurring cultural materials.

- The natural process of metal corrosion from exposure to environmental elements (wind, moisture, sun, temperature fluctuations, etc.) is enhanced by exposure to anthropogenic pollutants, in particular SO_2.

- Dry deposition of SO_2 enhances the effects of environmental elements on calcereous stones (limestone, marble, and carbonated cemented) by converting the calcium carbonate (calcite) in the stone to calcium sulphate dihydrate (gypsum). The rate of deterioration is determined by the SO_2 concentration, the stone's permeability and moisture content, and the deposition rate.

- Sulfur dioxide limits the life expectancy of paints by causing discoloration, loss of gloss, and loss of thickness of the paint film layer.

- A significant detrimental effect of particulate pollution is the soiling of painted surfaces and other building materials. Soiling is a degradation process requiring remediation by cleaning or washing, and depending on the soiled surface, repainting. Soiling decreases the reflectance of a material and reduces the transmission of light through transparent materials. Soiling may reduce the life usefulness of the material soiled.

E.6.4 Effects of Atmospheric Particulate Matter on Global Warming Processes and Transmission of Solar Ultraviolet Radiation

- The physical processes (i.e., scattering and absorption) responsible for airborne particle effects on transmission of solar visible and ultraviolet radiation are the same as those responsible for visibility degradation. Scattering of solar radiation back to space and absorption of solar radiation determine the effects of an aerosol layer on solar radiation.

- Atmospheric particles greatly complicate projections of future trends in global warming processes because of emissions of greenhouse gases; consequent increases in global mean temperature; resulting changes in regional and local weather patterns; and mainly deleterious (but some beneficial) location-specific human health and environmental effects. The body of available evidence, ranging from satellite to in situ measurements of aerosol effects on radiation receipts and cloud properties, is strongly indicative of an important role in climate for aerosols. This role, however, is poorly quantified. No significant advances have been made in reducing the uncertainties assigned to forcing estimates provided by the IPCC for aerosol-related forcing, especially for black carbon-containing aerosol. The IPCC characterizes the scientific understanding of greenhouse gas-related forcing as “high” in contrast to that for aerosol, which it describes as “low” to “very low.”

- 9 Quantification of the effect of anthropogenic aerosol on hydrological cycles requires more information than is presently available regarding ecosystems responses to reduced solar radiation and other changes occurring in the climate system. However, several global scale studies indicate that aerosol cooling alone can slow down the hydrological cycle, while cooling plus the nucleation of additional cloud droplets can dramatically reduce precipitation rates.

- 10 In addition to direct climate effects through the scattering and absorption of solar radiation, particles also exert indirect effects on climate by serving as cloud condensation nuclei, thus affecting the abundance and vertical distribution of clouds. The direct and indirect effects of particles appear to have significantly offset global warming effects caused by the buildup of greenhouse gases on a globally-averaged basis. However, because the lifetime of particles is much shorter than that required for complete mixing within the Northern Hemisphere, the climate effects of particles generally are felt much less homogeneously than are the effects of long-lived greenhouse gases.

- 11 Any effort to model the impacts of local alterations in particle concentrations on projected global climate change or consequent local and regional weather patterns would be subject to considerable uncertainty.

- 12 Atmospheric particles also complicate estimation of potential future impacts on human health and the environment projected as possible to occur because of increased transmission of solar ultraviolet radiation (UV-B) through the Earth’s atmosphere, secondary to stratospheric ozone depletion due to anthropogenic emissions of chlorofluorcarbons (CFCs), halons, and certain other gases. The transmission of solar UV-B radiation is affected strongly by atmospheric particles. Measured attenuations of UV-B under hazy conditions range up to 37% of the incoming solar radiation. Measurements relating variations in PM mass directly to UV-B transmission are lacking.

- Particles also can affect the rates of photochemical reactions occurring in the atmosphere, e.g., those involved in catalyzing tropospheric ozone formation. Depending on the amount of absorbing substances in the particles, photolysis rates either can be increased or decreased. Thus, atmospheric particle effects on UV-B radiation, which vary depending on size and composition of particles, can differ substantially over different geographic areas and from season to season over the same area. Any projection of effects of location-specific airborne PM alterations on increased atmospheric transmission of solar UV radiation (and associated potential human health or environmental effects) due to stratospheric ozone-depletion would, therefore, also be subject to considerable uncertainty.

E.7 KEY CONCLUSIONS

- Epidemiologic studies show consistent positive associations of exposure to ambient PM with health effects, including mortality and morbidity. The observed associations of ambient PM exposure with health effects must take into account the effects of other environmental or demographic factors, depending on whether the effects are acute or chronic. Effect-size estimates for PM-attributable excess relative risk for a given health outcome vary somewhat depending on specific analytic models used, but nevertheless have shown reasonable quantitative consistency across different studies.

- Issues surrounding potential bias in PM risk estimates from time-series studies using generalized additive models analyses and default convergence criteria were recently raised. Reanalyses of some important studies were included in an HEI Special Report (2003) that generally confirmed that PM effect estimates generally decline somewhat when using more stringent convergence criteria, as compared to the default GAM analyses, with the new estimates being well within confidence intervals of the original estimates. Overall, the absolute effect was relatively small, and the basic direction of effect and conclusions regarding the significance of the PM effect on mortality and hospital admissions remained unchanged in these analyses when the GAM convergence requirement was made more stringent. A modeling issue of particular importance highlighted by HEI (2003) is the sensitivity of all models to the degrees of freedom allotted to potentially confounding weather variables and time. The HEI panel recommended further exploration of the sensitivity of these studies to a wider range of alternative degrees of smoothing and to alternative specifications of weather variables in time-series models.

6 - Individuals with cardiovascular or pulmonary disease, especially if they are elderly, are more likely to suffer severe health effects (mortality or hospitalization) related to PM exposure than are healthy young adults. Children and asthmatics are also susceptible to certain PM effects, e.g., increased respiratory symptoms and decreased lung function. Smokers also constitute a population group at increased risk for ambient PM exposure effects.

7 - Daily ambient fine particle concentrations measured at a community air-monitoring site are useful surrogates for daily personal exposures to ambient fine particles. This is consistent, for example, with observed high correlations of personal sulfate exposures with ambient sulfate concentrations. The relationship between personal exposure to thoracic coarse particles and the ambient concentration of thoracic coarse fraction particles is not as strong, making effects due to coarse fraction particles harder to detect in epidemiologic studies.

8 - Development of a comprehensive biologically based exposure-dose-response model to aid health risk assessment requires further dosimetry data characterizing differences among species in percent deposition and regional deposition patterns including differences in inhalability, airway geometry, and clearance rates. More information is also needed on mechanism(s) of clearance, pathological processes affecting deposition and clearance of particles, and factors influencing the response(s) of respiratory tract tissues to particle burden.

9 - The percent deposition and regional patterns of deposition depend strongly on particle size. Percent deposition is higher in smaller lungs (children; women), during exercise, and in the functioning parts of the lungs in people with compromised lungs (e.g., those with chronic obstructive lung disease).

10 - Estimation of public health impacts of ambient airborne particle exposures in the United States would most credibly combine information on exposure-response relationships derived

for particular U.S. urban areas, in combination with estimates of exposures to ambient particle concentrations for the general population and/or specific susceptible subgroups (e.g., the elderly) those particular areas. At this time, risk assessment is necessarily limited to use of available information from concentration-response relationships relating ambient concentrations to health effects in populations. In view of geographic differences in ambient PM mixtures and demographics, broad generalization of some single "best estimate" of relative risk for a given increment in concentration of a given particle indicator (e.g., PM$_{10}$, PM$_{25}$, etc.) would be subject to much uncertainty.

11 • Toxicological studies of PM using controlled inhalation exposure of humans and laboratory animals, intratracheal instillation in humans and animals, and exposure of human and animal cells grown in culture find numerous biological effects which may be related to adverse health effects. Newer studies are finding different biological effects for a variety of different particle components. Newer studies also are beginning to identify biological mechanisms whereby PM deposited in the lung can produce adverse effects on the cardiovascular and respiratory systems.

12 • Epidemiologic studies indicate increased health risks associated with exposure to PM, alone or in combination with other air pollutants. PM-related increases in individual health risks are small, but likely significant from an overall public health perspective because of the large numbers of individuals in susceptible risk groups that are exposed to ambient PM.

13 • Numerous new studies, including multicity studies, continue to show a consistent association of PM$_{10}$ exposure with mortality and various morbidity endpoints, thus substantiating the relationship of PM exposure with various health effects. However, some new studies using PM$_{2.5}$ as an indicator find higher statistical significance and higher excess risk for PM$_{2.5}$ compared to PM$_{10}$. Several studies have also observed statistically associations of PM$_{10\text{-}2.5}$ with health effects.

14 • Epidemiologic studies, in which factors identified with source categories or individual chemical components of PM have been used as indicators, also show significant associations

with nitrates, sulfates, various indicators of elemental carbon, the organic component of PM, and some elements. PM-related source category factors, such as regional sulfate, vehicular traffic, fossil fuel combustion, vegetative combustion, and oil burning have also been found to be significantly associated with mortality.

15 • Data from multicity studies, comparisons of effects found in single and multiple regressions, exposure relationships, and toxicity suggest that the gaseous co-pollutants (CO, NO_3, SO_2,O_3) are not responsible for the relationships observed with PM indicators in community, time-series epidemiology. This does not, however, necessarily imply lack of an independent association of gaseous co-pollutants with health effects.

16 • Fine and thoracic coarse PM, indexed respectively by $PM_{2.5}$ and $PM_{10-2.5}$, should be considered as separate subclasses of PM. Considerations of emissions sources, atmospheric chemistry, physical behavior, exposure relationships, respiratory deposition, toxicologic findings, and epidemiologic observations argue for monitoring fine and thoracic coarse particles separately.

17 • Assessment of health risk in epidemiologic studies of ambient air pollutants, including PM, has relied largely on studies that focus on changes in health risks that occur in relation to normal changes in ambient air pollutant concentrations. Further evidence of the effects of air pollution on health may be deduced from intervention studies, i.e, studies of changes in health effects that occur when air pollution concentrations have been temporarily or permanently reduced through regulatory action, industrial shutdown, or other intervening factor(s). Only a few epidemiologic intervention studies are available; however, taken together, these studies lend confidence that further reduction of ambient air pollution exposures in the U.S. would reduce both respiratory and cardiovascular health effects. Available studies also give reason to expect that further reductions in both particulate and gaseous air pollutants would benefit health. Furthermore, experimental studies of Utah Valley filter extracts points to PM-associated metals as a likely cause or promoter of at least some of the health disorders associated with ambient PM.

- The overall weight of evidence, based on information concerning PM exposure, dosimetry, toxicology, and epidemiology, supports the conclusion that PM, especially fine PM, is the primary contributor to a variety of adverse health effects associated with air pollution. However, difficult technical issues still remain in further separating the effects of fine and coarse particles and in delineating respective contributions of PM acting along or in combination with gaseous co-pollutants in increasing risks of health effects anticipated to occur in response to exposures to contemporary particle-containing ambient air mixes in the United States.

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1. INTRODUCTION

This document is an update of "Air Quality Criteria for Particulate Matter" published by the U.S. Environmental Protection Agency (EPA) in 1996, and it will serve as the basis for Congressionally-mandated periodic review of the National Ambient Air Quality Standards (NAAQS) for particulate matter (PM). The present document critically assesses the latest scientific information relative to determining the health and welfare effects associated with the presence of various concentrations of PM in ambient air. The document builds upon the assessment in the previous 1996 EPA Air Quality Criteria Document for Particulate Matter (PM AQCD) by focusing on assessment and integration of information most relevant to PM NAAQS criteria development, based on pertinent peer-reviewed literature published or accepted for publication mainly through April 2002. This introductory chapter presents a brief summary of legislative requirements and history of the PM NAAQS, provides an overview of issues addressed and procedures utilized in the preparation of the present document, and provides orientation to the general organizational structure of the document.

1.1 LEGISLATIVE REQUIREMENTS

As indicated in U.S. Code (1991), the U.S. Clean Air Act (CAA), Sections 108 and 109 (42 U.S.C. Sections 7408 and 7409) govern the establishment, review, and revision of National Ambient Air Quality Standards (NAAQS). Section 108(a) directs the EPA Administrator to list pollutants, which, in the Administrator's judgement, cause or contribute to air pollution which may reasonably be anticipated to endanger either public health or welfare and to issue air quality criteria for them. The air quality criteria are to reflect the latest scientific information useful in indicating the kind and extent of all identifiable effects on public health and welfare that may be expected from the presence of the pollutant in ambient air.

Section 109 directs the Administrator of EPA to propose and promulgate "primary" and "secondary" NAAQS for pollutants identified under Section 108. Section 109(b)(1) defines a primary standard as a level of air quality, the attainment and maintenance of which, in the judgement of the Administrator, based on the criteria and allowing for an adequate margin of safety, is requisite to protect the public health. Section 109(b)(2) defines a secondary standard as one which, in the judgement of the Administrator, based on the criteria, is requisite to protect public welfare from any known or anticipated adverse effects associated with the presence of such pollutants. Welfare effects, defined in Section 302(h), include, but are not limited to, effects on soils, water, crops, vegetation, man-made materials, animals, wildlife, weather, visibility and climate, damage to and deterioration of property, and hazards to transportation, as well as effects on economic values and personal comfort and well-being. Section 109(d)(1) requires periodic review and, as appropriate, revision of existing criteria and standards. Section 109(d)(2) requires an independent committee of non-EPA experts, the Clean Air Scientific Advisory Committee (CASAC), to provide advice and recommendations to the EPA Administrator regarding the scientific soundness and appropriateness of criteria and NAAQS for PM and other "criteria air pollutants" (i.e., ozone, nitrogen dioxide, sulfur oxides, carbon monoxide, lead) regulated under CAA Sections 108-109.

1.2 HISTORY OF PREVIOUS PM CRITERIA AND NAAQS REVIEWS

"Particulate matter" is the generic term for a broad class of physically and chemically diverse substances that exist in ambient air as discrete particles (liquid droplets or solids) over a wide range of sizes. These airborne particles originate from a variety of stationary and mobile sources. Primary particles are emitted directly into ambient air; whereas secondary particles are formed in the atmosphere by transformation of gaseous emissions such as sulfur oxides (SO_x), nitrogen oxides (NO_x), and volatile organic compounds (VOCs). The physical and chemical properties of PM vary greatly with time, region, meteorology, and source category, thus complicating assessment of ambient PM health and welfare effects. Particles in ambient air are usually distributed bimodally in two somewhat overlapping size categories: (1) fine (diameter generally less than 2.5 mm) and (2) coarse (diameter generally greater than 1.0 µm). Particles in these two size fractions tend to differ in terms of formation mechanisms, sources of origin, composition, and behavior in the atmosphere and human respiratory tract.

EPA first promulgated primary and secondary NAAQS for PM on April 30, 1971 (Federal Register, 1971). These standards measured PM as "total suspended particulate" (TSP), which refers to ambient PM up to a nominal size of 25 to 45 micrometers (µm). The primary standards for PM (measured as TSP) were 260 µg/m^3 (24-h average), not to be exceeded more than once per year, and 75 µg/m^3 (annual geometric mean). The secondary standard (measured as TSP) was 150 µg/m^3 (24-h average), not to be exceeded more than once per year.

EPA completed the next review of PM air quality criteria and standards in July 1987, revising the 1971 standards to protect against adverse health effects of inhalable airborne particles which can be deposited in the lower (thoracic) regions of the human respiratory tract, with "PM_{10}" as the indicator (i.e., those particles collected by a sampler with a specified penetration curve yielding an upper 50% cut-point of 10-µm aerodynamic diameter (Federal Register, 1987). EPA established identical primary and secondary PM_{10} standards for two averaging times: 150 µg/m^3 (24-h average), with no more than one expected exceedance per year and 50 µg/m^3 (expected annual arithmetic mean), averaged over three years.

1.2.1 The 1997 PM NAAQS Revision

The last previous review of the air quality criteria and standards for PM was initiated in April 1994 by EPA announcing its intention to develop revised Air Quality Criteria for Particulate Matter. Several workshops were held by EPA's Environmental Criteria and Assessment Office in Research Triangle Park, NC (ECAO-RTP) in November 1994 and January 1995 to discuss important new health effects information useful in preparing initial PM AQCD draft materials. Also, plans for review of the PM criteria and standards under a highly accelerated, court-ordered schedule were presented by EPA at a public meeting of the CASAC in December 1994. A court order entered in *American Lung Association v. Browner*, CIV-93-643-TUC-ACM (U.S. District Court of Arizona, 1995), as subsequently modified, required publication of EPA's final decision on the review of the PM NAAQS by July 19, 1997.

Several external review drafts of the revised PM AQCD were prepared by the RTP Division of EPA's newly created National Center for Environmental Assessment (i.e., by NCEA-RTP, the successor office to ECAO-RTP), and each were made available for public comment followed by CASAC review (at public meetings held in August 1995, December 1995, and February 1996). The CASAC came to closure on its review of the PM AQCD in early 1996, advising the EPA Administrator in a March 15, 1996 closure letter (Wolff, 1996) that "although our understanding of the health effects of PM is far from complete, a revised Criteria Document which incorporates the Panel's latest comments will provide an adequate review of the available scientific data and relevant studies of PM." Revisions made in response to public and CASAC comments were then incorporated by NCEA-RTP, as appropriate, into the final 1996 PM AQCD (U.S. Environmental Protection Agency, 1996a). A PM Staff Paper (SP), prepared by the Office of Air Quality Planning and Standards (OAQPS) within EPA's Office of Air and Radiation (OAR), drew upon the 1996 PM AQCD and other exposure and risk assessments to pose options for PM NAAQS decisions. Drafts of the PM SP also underwent public comment and CASAC review, with consequent revision into the final 1996 PM SP (U.S. Environmental Protection Agency, 1996b).

The 1996 PM AQCD and the 1997 PM SP (U.S. Environmental Protection Agency, 1997a,b) provide detailed information on atmospheric formation, ambient concentrations, and health effects of ambient air PM, as well as quantitative estimates of human health risks associated with exposure to ambient PM. The principal focus of these documents was on recent epidemiologic evidence reporting associations between ambient concentrations of PM and a range of serious health effects. Special attention was given to several size-specific classes of particles, including PM_{10} and the principal fractions of PM_{10}, referred to as the fine ($PM_{2.5}$) and coarse ($PM_{10-2.5}$) fractions. $PM_{2.5}$ refers to those particles collected by samplers having penetration curves yielding an upper 50% cut point of 2.5 μm aerodynamic diameter. $PM_{10-2.5}$ refers to those particles in an aggregate sample having an upper 50% cut point of 10 μm and a lower 50% cut point of 2.5 μm aerodynamic diameter. In other words, the coarse fraction ($PM_{10-2.5}$) refers to the inhalable particles that remain if fine ($PM_{2.5}$) particles are removed from a sample of PM_{10} particles. As discussed in the 1996 PM AQCD, fine and coarse fraction particles can be differentiated by their sources and formation processes and by their chemical and physical properties, including behavior in the atmosphere.

Taking into account information and assessments presented in the 1996 PM AQCD and PM SP, advice and recommendations of CASAC, and public comments received on proposed revisions to the PM NAAQS published in December 1996 (Federal Register, 1996), the EPA Administrator promulgated significant revisions to the PM NAAQS in July 1997 (Federal Register, 1997). In that decision, the PM NAAQS were revised in several respects. While it was determined that the PM NAAQS should continue to focus on particles less than or equal to 10 μm in diameter, it was also determined that the fine and coarse fractions of PM_{10} should be considered separately. New standards were added, using $PM_{2.5}$ as the indicator for fine particles, and PM_{10} standards were retained for the purpose of regulating coarse-fraction particles. Two new $PM_{2.5}$ standards were set: an annual standard of 15 $\mu g/m^3$, based on the 3-year average of annual arithmetic mean $PM_{2.5}$ concentrations from single or multiple community-oriented monitors; and a 24-hour standard of 65 $\mu g/m^3$, based on the 3-year average of the 98th percentile of 24-hour $PM_{2.5}$ concentrations at each population-oriented monitor within an area. To continue to address coarse-fraction particles, the annual PM_{10} standard was retained, and the form, but not the level, of the 24-hour PM_{10} standard was revised to be based on the 99th percentile of 24-hour PM_{10} concentrations at each monitor in an area. The secondary standards were revised by making them identical in all respects to the primary standards.

Following promulgation of the revised PM NAAQS, legal challenges were filed by a large number of parties, addressing a broad range of issues. In May 1998, the U.S. Court of Appeals for the District of Columbia Circuit issued an initial opinion that upheld EPA's decision to establish fine particle standards, holding that such standards were amply justified by the growing body of empirical evidence demonstrating a relationship between fine particle pollution and adverse health effects. American Trucking Associations v. Browner, 175 F. 3d 1027, 1055-56 (D.C. Cir. 1999) (rehearing granted in part and denied in part, 195 F. 3d 4 (D.C. Cir. 1999b), affirmed in part and reversed in part, Whitman v. American Trucking Associations, 531 U.S. 457 (2001). Further, the court found "ample support" for EPA's decision to regulate coarse fraction particles, although it vacated the revisions to the 1987 PM_{10} standards on the basis of PM_{10} being a "poorly matched indicator for coarse particulate pollution" because PM_{10} includes fine particles. Id. at 1053-55. As a result of this aspect of the court's ruling, which EPA did not appeal, the 1987 PM_{10} standards remain in effect.

In addition, the court broadly held that EPA's approach to establishing the level of the standards in its 1997 decisions on both the PM and ozone NAAQS (which were promulgated on the same day and considered together by the court in this aspect of its opinion) effected "an unconstitutional delegation of legislative authority." Id. at 1034-40. EPA appealed this aspect of the court's ruling to the United States Supreme Court. In February 2001, the U.S. Supreme Court unanimously reversed the Court of Appeals' ruling on the constitutional issue, and sent the case back to the Court of Appeals for resolution of any remaining issues that had not been addressed in that court's earlier rulings. Whitman v. American Trucking Associations, 531 U.S. 457, 475-76 (2001). In March 2002, the Court of Appeals rejected all remaining challenges to the standards, finding that the 1997 $PM_{2.5}$ standards were reasonably supported by the record and were not "arbitrary or capricious." American Trucking Associations v. EPA, 283 F. 3d 355, 369-72 (D.C. Cir. 2002). Thus, the 1997 $PM_{2.5}$ standards are in effect.

1.2.2 Coordinated Particulate Matter Research Program

Shortly after promulgation of the 1997 PM NAAQS decisions, NCEA-RTP published a PM Health Risk Research Needs Document (U.S. Environmental Protection Agency, 1998a) that identified research needed to improve scientific information supporting future reviews of the PM NAAQS. The document provided a foundation for PM research coordination among Federal agencies and other research organizations and also provided input to later National Research Council (NRC) deliberations on PM research. The Office of Research and Development (ORD) of EPA also moved quickly to broaden its ongoing PM research activities by developing, in partnership with other Federal agencies, a coordinated interagency PM research program. This interagency program has and continues to focus mainly on expanding scientific knowledge of ambient PM exposure and health effects, as well as including development of improved monitoring methods and cost-effective mitigation strategies. The interagency effort also promotes substantially expanded coordination with other research organizations, including the Health Effects Institute (HEI) and other state-, university-, and industry-sponsored research groups. Beginning in the fall of 1997, public participation was and continues to be encouraged through workshops and review of EPA's PM Research Program documentation.

In response to Congressional requirements in EPA's Fiscal Year 1998 Appropriation, the NRC established its Committee on Research Priorities for Airborne Particulate Matter in January 1998. This NRC PM Research Committee's charge is to identify the most important research priorities relevant to setting PM NAAQS, to develop a conceptual plan for PM research, and to monitor EPA's research progress toward improved understanding of the relationship between PM and public health. The Committee issued its first report in early 1998 (National Research Council, 1998), a second one in 1999 (National Research Council, 1999), and a third one in 2001 (National Research Council, 2001). In the above-noted series of reports, the NRC PM Research Committee recommended that expanded PM research efforts be planned and carried out in relation to a general conceptual framework as shown in Figure 1-1. That framework essentially calls for research aimed at: (a) identifying sources of airborne particles or gaseous precursor

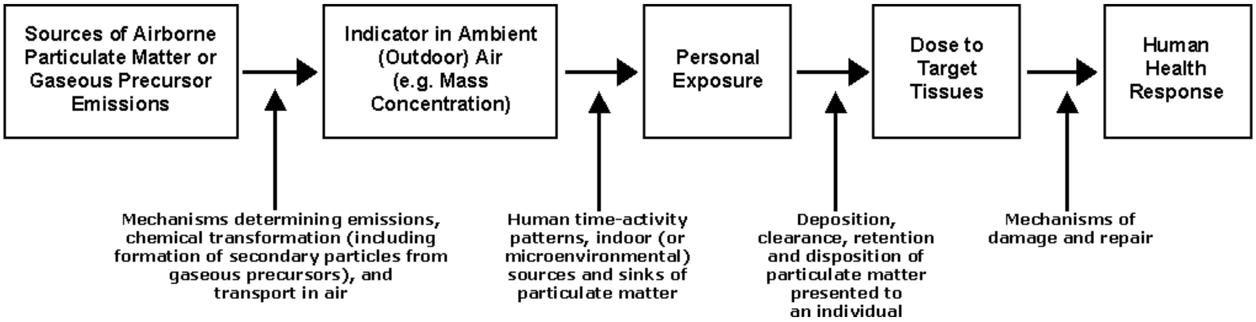

Figure 1-1. A general framework for integrating particulate-matter research. Note that this figure is not intended to represent a framework for research management. Such a framework would include multiple pathways for the flow of information.

Source: National Research Council (2001).

emissions and characterization of processes involved in atmospheric transformation, transport, and fate of ambient PM; (b) delineation of temporal and spatial patterns of air quality indicators (e.g., $PM_{2.5}$, $PM_{10-2.5}$, PM_{10} mass concentrations) of ambient PM and apportionment of observed variations in such ambient PM indicators to various emission sources; (c) characterization of human exposures to ambient PM as one important component of total personal exposure to particles, as modified by time-activity patterns and varying microenvironmental exposure to particles of indoor or ambient origin; (d) characterization of resulting respiratory tract deposition, clearance, retention, and disposition of inhaled particles, as determinants of dose to target tissues (e.g., locally in the lungs or via systemic translocation to the heart or other organs); (e) delineation of mechanisms of damage and repair plausibly leading to (f) human health responses, as extrapolated from or quantified by experimental animal or human exposure (toxicology) studies and/or observational (epidemiology) studies.

Research conducted under a PM Research Program structured in relation to the conceptual framework shown in Figure 1-1 would be expected (a) to reduce key scientific uncertainties regarding interrelationships between PM sources, ambient concentrations, exposures, dose to target tissues, and resulting health effects and (b) thereby improve the scientific underpinnings for both current and future periodic PM NAAQS reviews. Table 1-1 highlights some types of key uncertainties identified by the NRC PM Research Committee in relation to elements of the

TABLE 1-1. KEY SCIENTIFIC UNCERTAINTIES RELATED TO THE SOURCE-TO-RESPONSE FRAMEWORK

Source → **Concentration (or other indicator)**

- Contribution of various emission sources to ambient and indoor particulate matter concentrations
- Relative contribution of various sources to the most toxic components of particulate matter

Concentration (indicator) → **Exposure**

- Relationship between ambient (indoor) particulate matter and the composition of particles to which people are exposed
- Contribution of ambient particulate matter to total personal exposure for:
  - Susceptible subpopulations
  - General population
- Variation in relationship of ambient particulate matter concentrations to human exposure by place
- Variation in contribution of ambient particulate matter concentrations to total human exposure over time
- Covariance of particulate matter exposures with exposures to other pollutants
- Relationships between outdoor ambient and personal exposures for particulate matter and co-pollutants

Exposure → **Dose**

- Relationship between inhaled concentration and dose of particulate matter and constituents at the tissue level in susceptible subjects
  - Asthma
  - Chronic obstructive pulmonary disease (COPD)
  - Heart disease
  - Age: infants and elderly
  - Others

Dose → **Response**

- Mechanisms linking morbidity and mortality to particulate matter dose to or via the lungs
  - Inflammation
  - Host defenses
  - Neural mechanisms

Source: National Research Council (2001).

source-to-response conceptual framework illustrated in Figure 1-1. The NRC Committee went on to delineate a series of 10 research topics that they recommended be addressed in an expanded PM research program aimed at answering a set of broadly stated questions, as shown in Table 1-2.

The EPA PM Research Program, structured to address topics shown in Table 1-2 includes, for example, studies to improve understanding of the formation and composition of fine PM, improved measurements and estimation of population exposures to ambient PM, the characteristics or components of PM that are responsible for its health effects, factors increasing susceptibility to PM effects in some subpopulations, and mechanisms by which these effects are produced. The results from these efforts, and related efforts by other Federal agencies and the general scientific community during the past several years, have substantially enhanced the scientific and technical bases for future decisions on the PM NAAQS.

1.3 CURRENT PM CRITERIA AND NAAQS REVIEW

1.3.1 Key Milestones

As with other NAAQS reviews, rigorous assessment of relevant scientific information is presented in this updated, revised PM AQCD. As shown in Table 1-3, development of the document has involved substantial external peer review through (a) public workshops involving the general aerosol scientific community, (b) iterative reviews of successive drafts by CASAC, and (c) comments from the public. The final document will reflect input received through these reviews and will serve to evaluate and integrate the latest available scientific information to ensure that the review of the PM standards is based on rigorous evaluation of the available science.

An earlier (October 1999) First External Review Draft of this updated document was released in the fall of 1999 for public comment and CASAC review. A Second External Review Draft (March 2001) took into account earlier public comments and the December 1999 CASAC review and was reviewed by CASAC in July 2001. A Third External Review Draft similarly took into account prior public comments and CASAC recommendations and was released in early May 2002 for a 60-day public comment period; CASAC reviewed it at a public meeting in July 2002.

TABLE 1-2. RESEARCH TOPICS AND QUESTIONS RECOMMENDED BY NATIONAL RESEARCH COUNCIL (NRC) TO BE ADDRESSED BY EXPANDED PM RESEARCH PROGRAM

RESEARCH TOPIC 1.	**OUTDOOR MEASURES VERSUS ACTUAL HUMAN EXPOSURES**	• *What are the quantitative relationships between concentrations of particulate matter and gaseous co-pollutants measured at stationary outdoor air monitoring sites and the contributions of these concentrations to actual personal exposures, especially for subpopulations and individuals?*
RESEARCH TOPIC 2.	**EXPOSURES OF SUSCEPTIBLE SUBPOPULATIONS TO TOXIC PARTICULATE MATTER COMPONENTS**	• *What are the exposures to biologically important constituents and specific characteristics of particulate matter that cause responses in potentially susceptible subpopulations and the general population?*
RESEARCH TOPIC 3.	**CHARACTERIZATION OF EMISSION SOURCES**	• *What are the size distribution, chemical composition, and mass-emission rates of particulate matter emitted from the collection of primary-particle sources in the United States, and what are the emissions of reactive gases that lead to secondary particle formation through atmospheric chemical reactions?*
RESEARCH TOPIC 4.	**AIR-QUALITY MODEL DEVELOPMENT AND TESTING**	• *What are the linkages between emission sources and ambient concentrations of the biologically important components of particulate matter?*
RESEARCH TOPIC 5.	**ASSESSMENT OF HAZARDOUS PARTICULATE MATTER COMPONENTS**	• *What is the role of physicochemical characteristics of particulate matter in eliciting adverse health effects?*
RESEARCH TOPIC 6.	**DOSIMETRY: DEPOSITION AND FATE OF PARTICLES IN THE RESPIRATORY TRACT**	• *What are the deposition patterns and fate of particles in the respiratory tract of individuals belonging to presumed susceptible subpopulations?*
RESEARCH TOPIC 7.	**COMBINED EFFECTS OF PARTICULATE MATTER AND GASEOUS POLLUTANTS**	• *How can the effects of particulate matter be disentangled from the effects of other pollutants? How can the effects of long-term exposure to particulate matter and other pollutants be better understood?*
RESEARCH TOPIC 8.	**SUSCEPTIBLE SUBPOPULATIONS**	• *What subpopulations are at increased risk of adverse health outcomes from particulate matter?*
RESEARCH TOPIC 9.	**MECHANISMS OF INJURY**	• *What are the underlying mechanisms (local pulmonary and systemic) that can explain the epidemiologic findings of mortality/morbidity associated with exposure to ambient particulate matter?*
RESEARCH TOPIC 10.	**ANALYSIS AND MEASUREMENT**	• *To what extent does the choice of statistical methods in the analysis of data from epidemiologic studies influence estimates of health risks from exposures to particulate matter? Can existing methods be improved? What is the effect of measurement error and misclassification on estimates of the association between air pollution and health?*

Source: National Research Council (2001).

TABLE 1-3. SCHEDULE FOR DEVELOPMENT OF THE CURRENT REVISED PARTICULATE MATTER AIR QUALITY CRITERIA DOCUMENT (PM AQCD)

Major Milestones	Target Dates
PM NAAQS Review Plan to CASAC	October 1997
Prepare AQCD Development Plan	November 1997 to January 1998
Begin Literature Search	February 1998
Federal Register Call for Information/Sources Sought	April 1998
CASAC Meeting on AQCD Development Plan	May 1998
Prepare Workshop Drafts of Chapters	May to December 1998
Peer Review Workshop	April 1999
Prepare External Review Draft AQCD	March to September 1999
First External Review Draft	October 1999
Public Comment Period on Draft AQCD	October 1999 to January 2000
CASAC Meeting on First Draft AQCD	December 1999
Second External Review Draft	March 2001
Public Comment Period on Second Draft	April to July 2001
CASAC Meeting on Second Draft	July 2001
Third External Review Draft	April 2002
Public Comment Period on Third Draft	May to July 2002
CASAC Meeting on Third Draft	July 2002
Final PM AQCD	Oct/Nov 2002

Shortly after EPA released the Third External Review Draft in May 2002, the Health Effects Institute (HEI) announced that researchers at Johns Hopkins University had discovered problems with applications of statistical software used in a number of important studies on links between ambient air particulate matter (PM) and death and disease. In response to the surfacing of such statistical issues, which affected numerous PM time-series studies that used General Additive Models (GAM) and were published post-1995, EPA took steps in consultation with CASAC to encourage researchers to reanalyze affected studies and to submit them expeditiously for peer review by a special expert panel convened by HEI. The results of reanalyses for more than 30 studies of likely importance in informing U.S. standard setting decisions for ambient PM have now been peer-reviewed and are included, along with commentary by the HEI expert peer-review panel, in a recently released HEI Special Report (Health Effects Institute, May 2003). The subject statistical issues and reanalyses results are discussed in more detail in Chapter 8 of this document. After a 60-day public comment period, starting in June 2003, and CASAC review of this Fourth Draft, the final version of this PM AQCD is targeted for issuance by December 31, 2003.

After CASAC review of the First External Review Draft of this revised PM AQCD in December 1999, EPA's OAQPS started to prepare the associated PM Staff Paper (SP). A preliminary draft SP was made available to the public and was discussed at a July 2001 CASAC meeting; and additional consultations have been held via teleconference with CASAC to obtain feedback on proposed approaches to be used in conducting analyses to be included in the First External Review Draft of the PM SP due to be released in the summer of 2003. The draft PM SP will draw on the updated findings and conclusions from this draft PM AQCD and will also undergo public comment and CASAC review (now being scheduled for November, 2003). Ultimately drawing on information in the final version of this newly revised PM AQCD, the PM SP will evaluate policy implications of the key studies and scientific findings contained in the AQCD, present related staff analyses of air quality and human health risk, and identify critical elements that EPA staff believes should be considered in reviewing the PM standards. The PM SP is intended to bridge the gap between the scientific review in the AQCD and the public health and welfare policy judgements required of the Administrator in reviewing the PM NAAQS. In doing so, the PM SP will include staff conclusions and recommendations of options for the Administrator's consideration.

Based on the final versions of the PM AQCD and the PM SP, and on the advice of CASAC, the Administrator will propose decisions as to whether to retain or revise the current PM NAAQS and provide opportunities for public and CASAC comments on the proposed decisions. Taking into account comments on the proposed decisions, the Administrator will then make final decisions on the PM NAAQS, which are now expected to be published around the end of 2005.

1.3.2 Methods and Procedures for Document Preparation

The procedures for developing this revised PM AQCD build on the experience and methods derived from the most recent previous PM, Ozone, and CO AQCD preparation efforts. Briefly, the respective responsibilities for production of the present PM AQCD are as follows. An NCEA-RTP PM Team was formed and is responsible for developing and implementing the project plan for preparation of the PM AQCD, taking into account inputs from individuals in other EPA program and policy offices identified as part of the EPA PM Work Group. The resulting project plan (i.e., the PM Document Development Plan) was discussed with CASAC in May 1998 and was appropriately revised. An ongoing literature search has continued to be conducted to identify, to the extent possible, all pertinent PM literature published since early 1996. Additionally, EPA published in the Federal Register (1) a request for information asking for recently available research information on PM that may not yet be published and (2) a request for individuals with the appropriate type and level of expertise to contribute to the writing of PM AQCD materials to identify themselves (U.S. Environmental Protection Agency, 1998b). The specific authors of chapters or sections of the proposed document were selected on the basis of their expertise on the subject areas and their familiarity with the relevant literature; these include both EPA and non-EPA scientific experts. The project team defined critical issues and topics to be addressed by the authors and provided direction in order to emphasize evaluation of those studies most clearly identified as important for standard setting. It should be noted that materials contributed by non-EPA authors are incorporated and, at times, modified by EPA PM team staff to reflect internal and/or external review comments, e.g., by the public or CASAC, and that EPA is responsible for the ultimate content of the PM AQCD.

The main focus of this revised criteria document is the evaluation and interpretation of pertinent atmospheric science information, air quality data, human exposure information, and health and welfare effects information newly published since that assessed in the 1996 PM AQCD and likely to be useful in deriving criteria for U.S. EPA PM NAAQS decisions. Initial draft versions of AQCD chapters were evaluated via expert peer-review workshop discussions and/or written peer reviews that focused on the selection of pertinent studies included in the chapters, the potential need for additional information to be added to the chapters, and the quality of the summarization and interpretation of the literature. The authors of the draft chapters then revised them on the basis of workshop and/or written expert review recommendations. These and other integrative summary materials were incorporated into the First External Review Draft of the PM AQCD (October 1999), which underwent public comment and was the subject of consultation with CASAC at a December 1999 public meeting.

In order to foster timely presentation and publication of newly emerging PM research findings, EPA co-sponsored an Air and Waste Management Association International Speciality Conference, entitled “PM 2000: Particulate Matter and Health,” held in January 2000 in Charleston, SC. The conference was co-sponsored in cooperation with several other government agencies and/or private organizations that also fund PM research. Topics covered included new research results concerning the latest advances in PM atmospheric sciences (e.g., PM formation, transport, transformation), PM exposure, PM dosimetry and extrapolation modeling, PM toxicology (e.g., mechanisms, laboratory animal models, human clinical responses), and PM epidemiology. The main purpose of the conference was to facilitate having the latest scientific information available in time for incorporation as quickly as possible into the Second External Review Draft of this revised PM AQCD. Hence, arrangements were made for scientists to submit written manuscripts on papers or posters presented at the PM 2000 Conference for expedited peer-review by several major journals, so that decisions on acceptance for publication could be made by mid-2000. The evaluations and findings set forth in the Second External Review Draft (March 2001) of the revised PM AQCD included consideration of such published PM 2000 papers and extensive additional information published elsewhere since the previous First External Review Draft; and the Second Draft was reviewed by CASAC in July 2001.

Further revisions were then incorporated into the Third External Review Draft (April 2002) to reflect both public comment and CASAC review of the Second Draft, as well as assessment of additional extensive new information published since that addressed in the Second Draft. This Fourth Draft AQCD incorporates changes made in response to earlier public comments and CASAC reviews; and it includes pertinent peer-reviewed literature published or accepted for publication mainly through April 2002. The final PM AQCD will include revisions made in response to public comment and CASAC review of this draft document.

1.3.3 Approach

An initial step in development of this revised PM AQCD was to focus on selection of pertinent issues to include in the document as the basis for the derivation of PM NAAQS criteria. Preliminary issues were identified by the NCEA PM Team via inputs from other EPA program and policy offices, as derived from the 1996 PM AQCD and SP, their CASAC and public reviews, from the 1997 standard promulgation process, and from the 1998 PM Research Needs Document (alluded to in Section 1.2.2). Still further identification and refinement of issues resulted from NRC review and reports on PM research priorities (also discussed in Section 1.2.2 above). The CASAC review of the PM AQCD Development Plan and public comments on earlier draft AQCD materials at various stages of their development also provided important inputs regarding issue identification.

In developing draft materials for inclusion in the revised PM AQCD, detailed review of key new research was undertaken as a first step. However, instead of presenting a comprehensive review of all the literature, emphasis in this revised AQCD is placed on (1) first, the concise summary of key findings derived from previous PM criteria reviews (especially the 1996 PM AQCD) and, then, (2) evaluation of the most pertinent new key information, with greater emphasis on more interpretive assessment — an approach reflecting CASAC recommendations. To aid in the development of a more concise document than the 1996 PM AQCD, compilation of summary tables of relevant new literature published since completion of that previous document and selective text discussion of such new literature has been undertaken, with increased emphasis being placed in text discussions on interpretive evaluation and integration of key points derived from the newly summarized research results.

1.4 DOCUMENT ORGANIZATION AND CONTENT

The present draft document attempts to critically review and assess relevant scientific literature on PM published, since early 1996, including materials accepted for publication mainly through April 2002 (and thus appearing mostly during 2002). Limited coverage of some more recent studies is also included as deemed appropriate in light of its special importance. For example, information derived from the recently released HEI Special Report (Health Effects Institute, May 2003), discussed above in Section 1.3.1, is being integrated into this assessment.

Literature discussed in detail in the 1996 EPA PM AQCD (U.S. Environmental Protection Agency, 1996a) generally is not discussed in depth in this document; rather key findings from that 1996 review are summarized as appropriate. Limited treatment is included, however, for some earlier studies judged to be of particular importance in the review of the PM NAAQS. Key literature is mainly summarized in tables; and the text mainly attempts to integrate and discuss overall interpretive points. An attempt is made to present alternative points of view where scientific controversy exists.

Emphasis is placed in the document on studies conducted at or near PM pollutant concentrations found in ambient air. However, although emphasis has been placed on studies in the range of current ambient levels, studies examining effects of higher concentrations have been included if they contain unique data or documentation of a previously unreported effect or mechanism.

The present document, basically organized to assess information related to topics along the same flow of issues presented in the NRC conceptual framework shown in Figure 1-1, includes an Executive Summary and nine chapters presented in two volumes. Volume I contains the Executive Summary, this general introduction (Chapter 1), and Chapters 2 through 5. Chapters 2 and 3 provide background information on physical and chemical properties of PM and related compounds; sources and emissions; atmospheric transport, transformation, and fate of PM; methods for the collection and measurement of PM; and U.S. ambient air PM concentrations. Chapter 4 assesses PM environmental effects on vegetation and ecosystems, visibility, man-made materials, and climate-related effects (including effects on atmospheric transmission of solar radiation), and includes limited information on economic impacts of some welfare effects. Chapter 5 discusses factors affecting exposure of the general population to ambient PM.

The second volume contains Chapters 6 through 9. Chapter 6 evaluates information concerning dosimetry of inhaled particles in the respiratory tract. Chapter 7 assesses the toxicology of specific types of PM constituents and potential mechanisms of action, based on both laboratory animal studies and controlled human exposure studies. Chapter 8 discusses observational, i.e., epidemiologic, studies. Lastly, Chapter 9 integrates key information on exposure, dosimetry, and critical health risk issues derived from studies reviewed in the prior chapters, as well as highlighting key points regarding important welfare effects associated with ambient PM.

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2. PHYSICS, CHEMISTRY, AND MEASUREMENT OF PARTICULATE MATTER

Chapter 3 of the 1996 EPA document Air Quality Criteria for Particulate Matter (1996 PM AQCD; U.S. Environmental Protection Agency, 1996a) contained an extensive review of the physics and chemistry of airborne particulate matter (PM). Chapter 2 of this revised version of the PM AQCD also provides background information on the physics and chemistry of atmospheric particles, information useful in aiding the understanding of subsequent chapters. Those subsequent chapters are basically organized to follow the sequence of key elements comprising the risk assessment framework described in Chapter 1 (Section 1.2.2), beginning with sources and continuing to effects as shown in Figure 1-1. Thus, this chapter provides new information useful in evaluating PM effects of PM on human health and welfare and in preparing related risk assessments used to support PM standard-setting decisions. Information important for implementation of PM standards, but not essential to the standard setting process, is not the focus in this chapter. The reader is referred to the NARSTO Fine Particle Assessment (NARSTO, 2003) for information relevant to air quality management for PM.

Unlike other criteria pollutants (O_3, CO, SO_2, NO_2, and Pb), PM is not a specific chemical entity but is a mixture of particles from different sources and of different sizes, compositions, and properties. Emphasis is placed here on discussion of differences between fine and coarse particles and differences between ultrafine particles and accumulation-mode particles within fine particles.

PM is defined quantitatively by the measurement techniques employed. Therefore, it will be useful to discuss our understanding of the relationship between PM suspended in the atmosphere, PM inhaled by people, and PM measured by various sampling and analytical techniques. Chapter 4 of the 1996 PM AQCD (U.S. Environmental Protection Agency, 1996a) contained a review of the state-of-the-art of PM measurement technology. Since that time, considerable progress has been made in understanding problems in the measurement of PM mass, chemical composition, and physical parameters. There also has been progress in developing new and improved measurement techniques, especially for continuous measurements. Therefore, a more extensive survey on measurement problems and on newly developed measurement techniques is included in Section 2.2. For more detail and older references, the reader is referred to Chapters 3 and 4 of the 1996 PM AQCD (U.S. Environmental Protection Agency, 1996a).

2.1 PHYSICS AND CHEMISTRY OF PARTICULATE MATTER

2.1.1 Basic Concepts

Atmospheric particles originate from a variety of sources and possess a range of morphological, chemical, physical, and thermodynamic properties. Examples of atmospheric particles include combustion-generated particles, such as diesel soot or fly ash; photochemically produced particles, such as those found in urban haze; salt particles formed from sea spray; and soil-like particles from resuspended dust. Some particles are liquid; some are solid. Others may contain a solid core surrounded by liquid. Atmospheric particles contain inorganic ions, metallic compounds, elemental carbon, organic compounds, and crustal compounds. Some atmospheric particles are hygroscopic and contain particle-bound water. The organic fraction is especially complex, containing hundreds (probably thousands) of organic compounds. (See Appendix 3C for information on the composition of the organic fraction and the concentration of specific organic compounds.) Primary particles are emitted directly from sources; whereas secondary particles are formed from gases through chemical reactions in the atmosphere involving atmospheric oxygen (O_2) and water vapor (H_2O); reactive species such as ozone (O_3); radicals such as the hydroxyl (•OH) and nitrate (•NO_3) radicals; and pollutants such as sulfur dioxide (SO_2), nitrogen oxides (NO_X), and organic gases from natural and anthropogenic sources. The particle formation process includes nucleation of particles from low-vapor pressure gases emitted from sources or formed in the atmosphere by chemical reactions, condensation of low-vapor pressure gases on existing particles, and coagulation of particles. Thus, any given particle may contain PM from many sources. Because a particle from a given source is likely to be composed of a mixture of chemical components and particles from different sources may coagulate to form a new particle, atmospheric particles may be considered a mixture of mixtures.

The composition and behavior of particles are fundamentally linked with those of the surrounding gas. An aerosol may be defined as a suspension of solid or liquid particles in air. The term aerosol includes both the particles and all vapor or gas phase components of air.

However, the term aerosol is sometimes used to refer to the suspended particles only. In this document, “particulate” is used only as an adjective, as in particulate matter.

A complete description of the atmospheric aerosol would include an accounting of the chemical composition, morphology, and size of each particle and the relative abundance of each particle type as a function of particle size (Friedlander, 1970). However, the physical and chemical characteristics of particles are usually measured separately. Size distributions by particle number, used to calculate surface area and volume distributions, often are determined by physical means, such as electrical mobility, aerodynamic behavior, or light scattering. Chemical composition usually is determined by analysis of collected samples although some species can be measured in situ. The mass and average chemical composition of particles, segregated according to aerodynamic diameter by cyclones or impactors, can also be determined. However, recent developments in single particle analysis techniques by electron microscopy with X-ray analysis of single particles (but not agglomerates) collected on a substrate or by mass spectroscopy of individual suspended particles provide elemental composition of individual particles by particle size and, thus, are bringing the description envisioned by Friedlander closer to reality.

2.1.2 Physical Properties and Processes

2.1.2.1 Definitions of Particle Diameter

The diameter of a spherical particle may be determined by optical or electron microscopy, by light scattering and Mie theory, by its electrical mobility, or by its aerodynamic behavior. However, atmospheric particles often are not spherical. Therefore, their diameters are described by an “equivalent” diameter (i.e., the diameter of a sphere that would have the same physical behavior). An optical diameter is the diameter of a spherical particle, with the same refractive index as the particle used to calibrate the optical particle sizer, that scatters the same amount of light into the solid angle measured. Diffusion and gravitational settling are important physical behaviors for particle transport, collection, and removal processes, including deposition in the respiratory tract. Different equivalent diameters are used depending on which process is more important. For smaller particles diffusion is more important and the Stokes diameter is often used. For larger particles gravitational setting is more important and the aerodynamic diameter is often used.

The Stokes diameter, D_p, describes particle size based on the aerodynamic drag force imparted on a particle when its velocity differs from that of the surrounding fluid. For a smooth, spherically shaped particle, D_p exactly equals the physical diameter of the particle. For irregularly shaped particles, D_p is the diameter of an equivalent sphere that would have the same aerodynamic resistance. Electrical mobility analyzers classify particles according to their electrical mobility. Particles of equal Stokes diameters that carry the same electric charge will have the same electrical mobility. Hence, for spherical particles, the electrical mobility diameter would equal the Stokes diameter. The mobility diameter can be considered the diameter of a spherical particle that would have the same electrical mobility. The particle mobility can be related to the particle diffusion coefficient and Brownian diffusion velocity through the Stokes-Einstein equation. Thus, the Stokes diameter is the appropriate parameter for particle behavior governed by diffusion. The Stokes diameter, D_p, is used in size distributions based on light scattering and mobility analysis. The Stokes diameter is independent of density.

The aerodynamic diameter, D_a, however, depends on particle density. It is defined as the diameter of a spherical particle with an equal gravitational settling velocity but a material density of 1 g/cm^3. Cascade impactors separate particles based on their aerodynamic diameter and aerodynamic particle sizers measure the aerodynamic diameter. Respirable, thoracic, and inhalable sampling and $PM_{2.5}$ and PM_{10} sampling are based on particle aerodynamic diameter. For particles greater than about 0.5 µm, the aerodynamic diameter is generally the quantity of interest. For smaller particles, the Stokes diameter may be more useful. Particles with the same physical size and shape but different densities will have the same Stokes diameter but different aerodynamic diameters.

Aerodynamic diameter, D_a, is related to the Stokes diameter, D_p, by:

$$D_a = \left(\frac{\rho C_p}{C_a} \right)^{1/2} D_p \qquad (2\text{-}1)$$

where ρ is the particle density, and C_p and C_a are the Cunningham slip factors evaluated for the particle diameters D_p and D_a respectively. The slip factor is a function of the ratio between particle diameter and mean free path of the suspending gas (0.066 µm for air at one atmosphere pressure and 20 °C). C is an empirical factor that accounts for the reduction in the drag force on particles due to the "slip" of the gas molecules at the particle surface. It is important for particles less than 1 μm in diameter, for which the surrounding air cannot be modeled by a continuous fluid. For large particles ($D_p > 5$ μm) $C = 1$; while for smaller particles $C > 1$.

For particles with diameters greater than the mean free path, λ, the aerodynamic diameter given by equation (2-1) is approximated by:

$$D_a = (\rho)^{1/2}\, D_p \qquad (D_p \gg \lambda) \tag{2-2}$$

This expression, which shows that aerodynamic diameter is directly proportional to the square root of the particle density, is often used for particles as small as 0.5 μm. For particles with diameters much smaller than the mean free path, the slip factor must be taken into account. In this case the aerodynamic diameter is directly proportional to the particle density,

$$D_a = (\rho)\, D_p \ (D_p \ll \lambda) \tag{2-3}$$

Detailed definitions of the various sizes and their relationships are given in standard aerosol textbooks (e.g., Friedlander [2000], Reist [1984, 1993], Seinfeld and Pandis [1998], Hinds [1999], Vincent [1989, 1995], Willeke and Baron [1993], Baron and Willeke [2002], and Fuchs [1964, 1989]).

2.1.2.2 Aerosol Size Distributions

Particle size as indexed by one of the "equivalent" diameters is an important parameter in determining the properties, effects, and fate of atmospheric particles. The atmospheric deposition rates of particles and therefore their residence times in the atmosphere are a strong function of their Stokes and aerodynamic diameters. The diameter also influences deposition patterns of particles within the lung. Because light scattering is strongly dependent on the optical particle size, the amount of light scattering per unit PM mass will be dependent on the size distribution of atmospheric particles. Therefore, the effects of atmospheric particles on visibility, radiative balance, and climate will be influenced by the size distribution of the particles. Studies using cascade impactors or cyclones measure the particle-size distribution directly in aerodynamic diameter. The diameters of atmospheric particles range from 1 nm to 100 µm, spanning 5 orders of magnitude. A variety of different instruments, measuring a variety of equivalent diameters, are required to cover this range.

Older particle counting studies used optical particle counters to cover the range of 0.3 to 30 µm diameter. Diameters of particles below 0.5 µm were measured as mobility diameters. The particle diameters used in size distribution graphs from these studies usually are given as physical or Stokes diameters rather than aerodynamic diameters. In recent years, aerodynamic particle sizers have been developed that give a direct measurement of the aerodynamic diameter in the range of approximately 0.7 to 10 µm diameter. These instruments have been used with electrical mobility analyzers that measure the mobility diameter of particles from 3 nm to approximately 0.5 µm (McMurry, 2000). Unfortunately, there is no agreed-upon technique for combining the various equivalent diameters. Some workers use various assumptions to combine the various measurements into one presentation; others report each instrument separately. Therefore, the user of size distribution data should be careful to determine exactly which equivalent diameter is reported.

Particle Size Distribution Functions

The distribution of particles with respect to size is an important physical parameter governing their behavior. Because atmospheric particles cover several orders of magnitude in particle size, size distributions often are expressed in terms of the logarithm of the particle diameter on the X-axis and the measured differential concentration on the Y-axis: $\Delta N/\Delta(\log D_p)$ = the number of particles per cm^3 of air having diameters in the size range from $\log D_p$ to $\log(D_p + \Delta D_p)$. Because logarithms do not have dimensions, it is necessary to think of the distribution as a function of $\log(D_p/D_{p0})$, where the reference diameter D_{p0} = 1 µm is not explicitly stated. If $\Delta N/\Delta(\log D_p)$ is plotted on a linear scale, the number of particles between D_p and $D_p + \Delta D_p$ is proportional to the area under the curve of $\Delta N/\Delta(\log D_p)$ versus $\log D_p$. Similar considerations apply to distributions of surface, volume, and mass. When approximated by a function, the distributions are usually given as $dN/d(\log D_p)$ rather than $\Delta N/\Delta(\log D_p)$.

Atmospheric Aerosol Size Distributions

In 1978, Whitby (1978) published an analysis of over 1000 particle size distributions measured at various locations in the U.S. Figure 2-1 shows the number, surface area, and volume distributions for the grand average continental size distribution. Volume, surface area, and number distributions are plotted on an arithmetic scale such that the volume, surface area, or number of particles in any specified size range is proportional to the corresponding area under the curve. These distributions show that most of the particles are quite small, below 0.1 µm; whereas most of the particle volume (and therefore most of the mass) is found in particles > 0.1 µm. Other averaged atmospheric size distributions are shown in Figure 2-2 and 2-3 (Whitby, 1978; Whitby and Sverdrup, 1980). Figure 2-2a and b describe the number of particles as a function of particle diameter for rural, urban-influenced rural, urban, and freeway-influenced urban aerosols. For some of the same data, the particle volume distributions are shown in Figure 2-3a and b. Whitby (1978) observed that the size distributions typically had three peaks which he called “modes.” The entire size distribution could be characterized well by a trimodal model consisting of three additive log-normal distributions. The mode with a peak between 5 and 30 µm diameter, formed by mechanical processes, was named the coarse particle mode; the mode with a peak between 0.15 and 0.5 µm, formed by condensation and coagulation, was called the accumulation mode; and the mode with a peak between 0.015 and 0.04 µm, whose size was influenced by nucleation as well as by condensation and coagulation, was called the transient nuclei or Aiken nuclei range, subsequently shortened to the nuclei mode. The nuclei mode could be seen in the number and surface distribution but only in special situations was it noticeable in the mass or volume distributions. The accumulation and nuclei modes taken together were called fine particles. An idealized size distribution showing modes and formation mechanisms is shown in Figure 2-4.

Whitby (1978) concluded

> The distinction between “fine particles” and “coarse particles” is a fundamental one. There is now an overwhelming amount of evidence that not only are two modes in the mass or volume distribution usually observed, but that these fine and coarse modes are usually chemically quite different. The physical separation of the fine and coarse modes originates because condensation produces fine particles while mechanical processes produce mostly coarse particles . . . the dynamics of fine particle growth ordinarily operate to prevent the fine

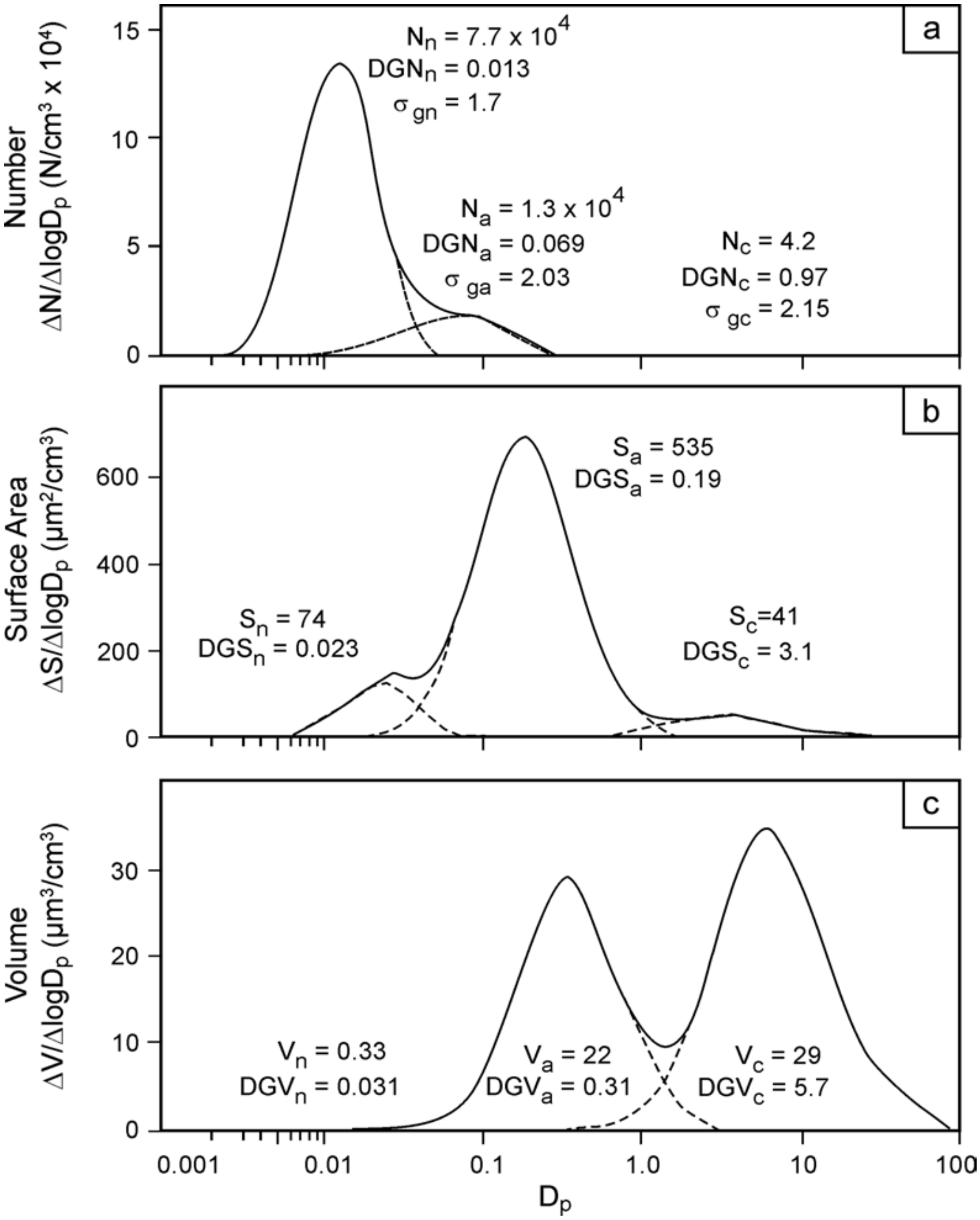

Figure 2-1. Distribution of coarse (c), accumulation (a), and nuclei (n) mode particles by three characteristics, a) number (N), b) surface area (S) and c) volume (V) for the grand average continental size distribution. DGV = geometric mean diameter by volume; DGS = geometric mean diameter by surface area; DGN = geometric mean diameter by number; D_p = particle diameter.

Source: Whitby (1978).

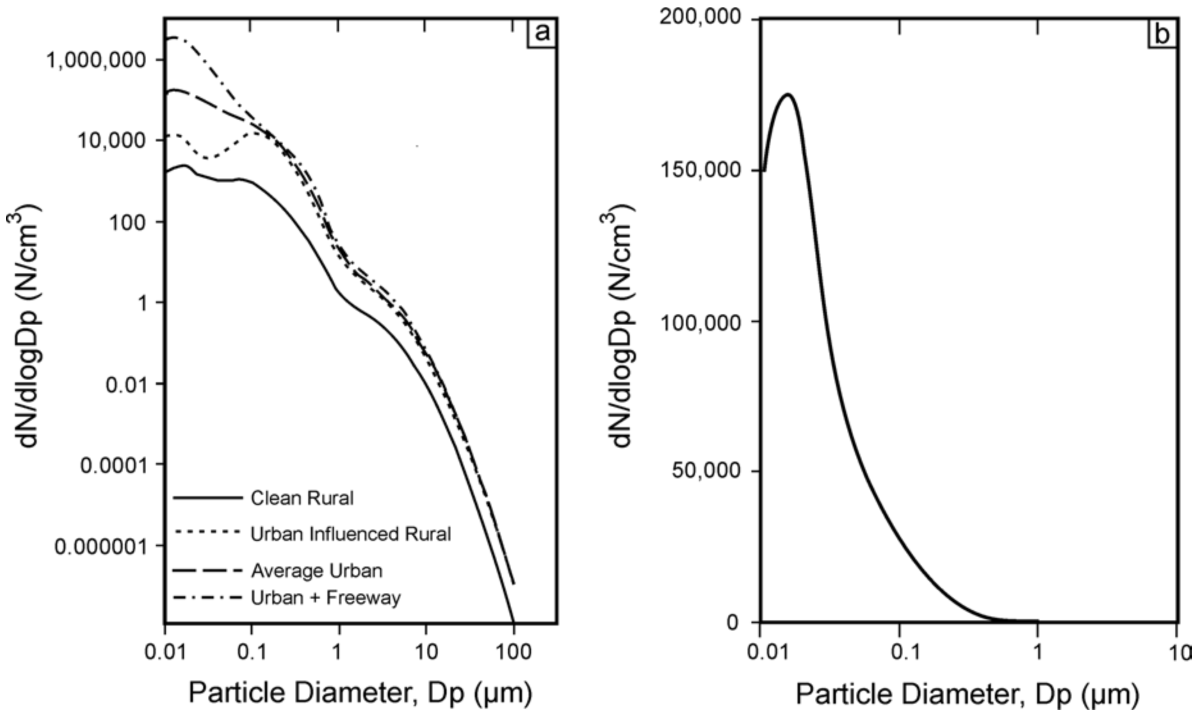

Figure 2-2. Particle size distributions by number, (a) number concentrations are shown on a logarithmic scale to display the wide range by site and size; (b) number concentrations for the average urban distribution are shown on a linear scale. For the linear scale, the area under any part of the curve is proportional to particle number in that size range.

Source: Whitby (1978); Whitby and Sverdrup (1980).

> particles from growing larger than about 1 µm. Thus, the fine and coarse modes originate separately, are transformed separately, are removed separately, and are usually chemically different . . . practically all of the sulfur found in atmospheric aerosol is found in the fine particle fraction. Thus, the distinction between fine and coarse fractions is of fundamental importance to any discussion of aerosol physics, chemistry, measurement, or aerosol air quality standards.

Whitby's (1978) conclusions were based on extensive studies of size distributions in a number of western and midwestern locations during the 1970s (Whitby et al., 1974; Willeke and Whitby, 1975; Whitby, 1978; Wilson et al., 1977; Whitby and Sverdrup, 1980). No size-distribution studies of similar scope have been published since then. Newer results

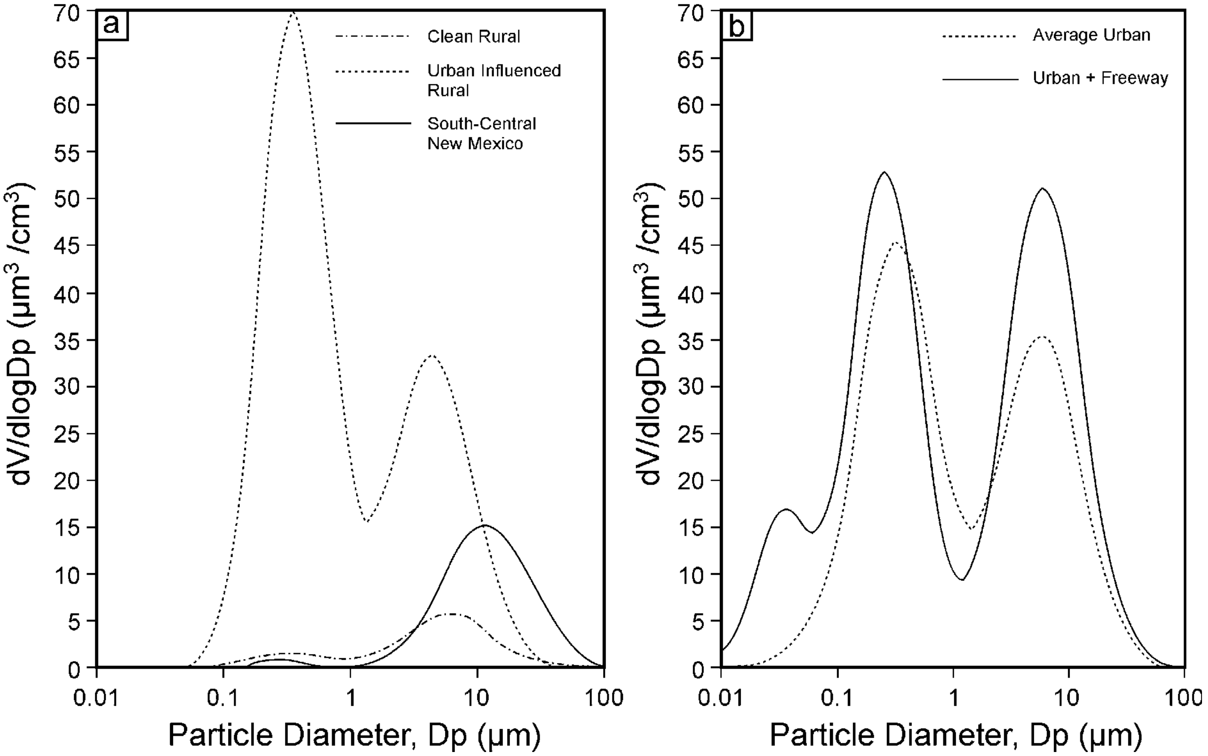

Figure 2-3. Size distribution by volume (a) for the averaged rural and urban-influenced rural number distributions shown in Figure 2-2a and a distribution from south central New Mexico, and (b) for the averaged urban and freeway-influenced urban number distributions shown in Figure 2-2a.

Source: Whitby and Sverdrup (1980); Kim et al. (1993) south central New Mexico.

from particle counting and impactor techniques, including data from Europe (U.S. Environmental Protection Agency, 1996a) and Australia (Keywood et al., 1999, 2000), show similar results for the accumulation and coarse modes. Extensive measurements of particle size distributions, as part of EPA's Supersites program, are providing much new data for analysis.

Whitby's (1978) conclusions have held up remarkably well. However, ideas about the sub-0.1 μm diameter range have changed somewhat as newer instruments provided measurements extending to smaller sizes and with greater resolution in size and time (McMurry et al., 2000). Depending on the source, temperature, saturated vapor pressure of the components, and the age of the aerosol, size distributions have been observed with peaks (including multiple peaks) throughout the sub-0.1 μm diameter size range. Sub-0.1 μm diameter peaks have been

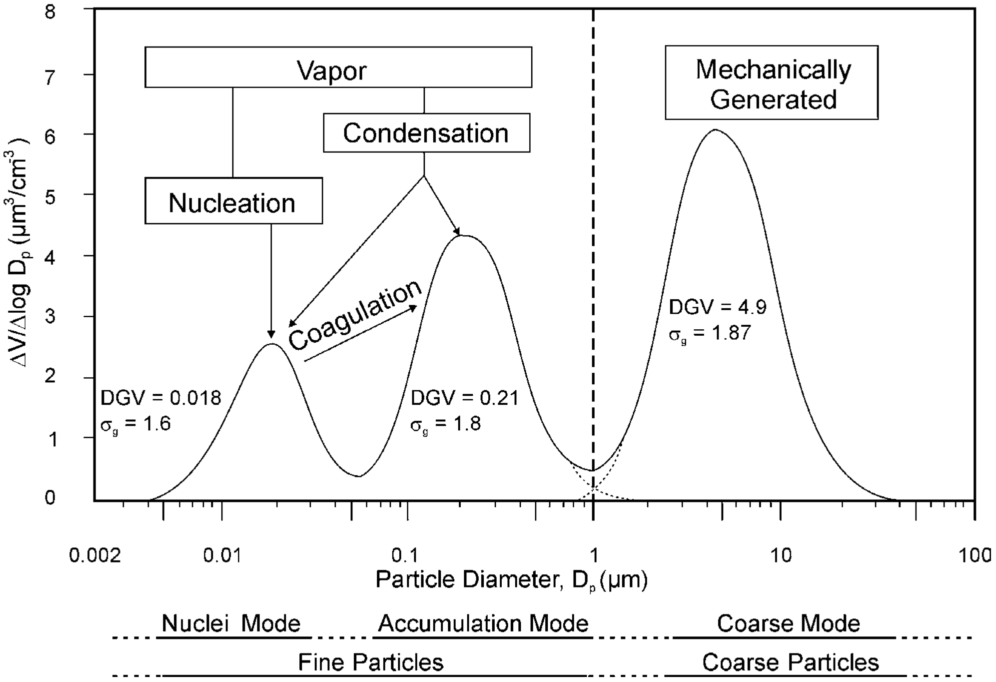

Figure 2-4. Volume size distribution, measured in traffic, showing fine and coarse particles and the nuclei and accumulation modes of fine particles. DGV (geometric mean diameter by volume, equivalent to volume median diameter) and σ_g (geometric standard deviation) are shown for each mode. Also shown are transformation and growth mechanisms (e.g., nucleation, condensation, and coagulation).

Source: Adapted from Wilson and Suh (1997).

observed in rural areas (O'Dowd, 2002) as well as for brief periods (nucleation bursts) in urban areas (Woo et al., 2001a). Based on these and other observations, discussed in detail in Section 2.1.2.3, aerosol scientists now classify particles in the sub-0.1 µm size range as ultrafine particles and divide this size range into a nucleation region (< 10 nm) and an Aitkin (nuclei) region (10-100 nm), as shown in Figure 2-5. Other studies, discussed in detail in the 1996 PM AQCD (U.S. Environmental Protection Agency, 1996a), have shown that in fog or clouds or at very high relative humidities the accumulation mode may split into a larger size (more hygroscopic or droplet) submode and a smaller size (less hygroscopic or condensation) submode.

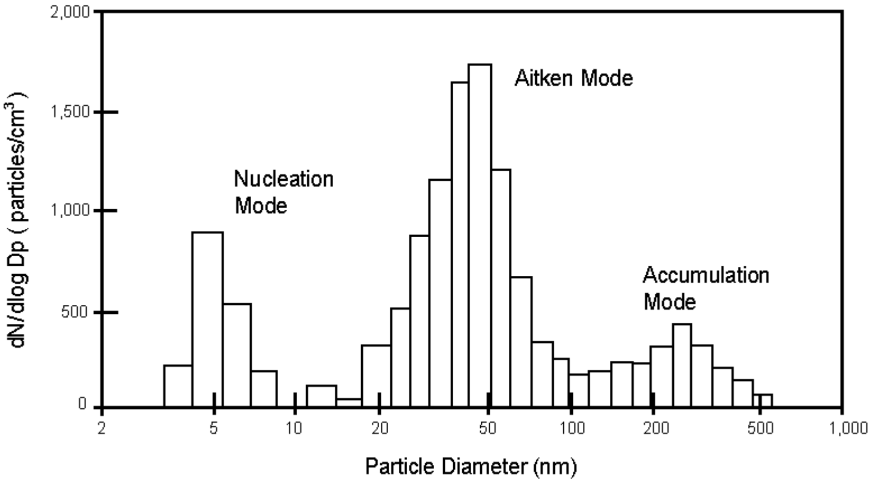

Figure 2-5. Submicron number size distribution observed in a boreal forest in Finland showing the tri-modal structure of fine particles. The total particle number concentration was 1011 particles/cm^3 (10 minute average).

Source: Mäkelä et al. (1997).

Definitions of Particle Size Fractions

In the preceding discussion several subdivisions of the aerosol size distribution were identified. Aerosol scientists use three different approaches or conventions in the classification of particles by size: (1) modes, based on the observed size distributions and formation mechanisms; (2) cut point, usually based on the 50% cut point of the specific sampling device, including legally specified, regulatory sizes for air quality standards; and (3) dosimetry or occupational health sizes, based on the entrance into various compartments of the respiratory system.

Modal. The modal classification as first proposed by Whitby (1978) is shown in Figures 2-1 and 2-4. New modes introduced since 1978 are shown in Figure 2-5. The nucleation and Aitkin modes are best observed in the number distribution. However, the Aitkin mode can be seen in the volume distribution in traffic or near traffic or other sources of ultrafine particles (Figures 2-3b and 2-4). The observed modal structure is frequently approximated by several log-normal distributions. Definitions of terms used to describe size distributions in modal terms are given below.

Nucleation Mode: Freshly formed particles with diameters below 10 nm, observed during active nucleation events. The lower limit, where particles and large molecules overlap, is uncertain. Current techniques limit measurements to particles 3 nm or greater.

Aitkin Mode: Larger particles with diameters between 10 and 100 nm. The Aitken mode may result from growth of smaller particles or nucleation from higher concentrations of precursors. Nucleation and Aitkin nuclei modes are normally observed in the number distribution.

Accumulation Mode: Particles with diameters from about 0.1 μm to just above the minimum in the mass or volume distributions which usually occurs between 1 and 3 μm. Accumulation-mode particles normally do not grow into the coarse mode. Nucleation-mode and Aitkin-mode particles grow by coagulation (two particles combining to form one) or by condensation (low-equilibrium vapor pressure gas molecules condensing on a particle) and "accumulate" in this size range.

Coarse Mode or Coarse Particles: Particles with diameters mostly greater than the minimum in the particle mass or volume distributions, which generally occurs between 1 and 3 μm. These particles are usually formed by mechanical breakup of larger particles or bulk material.

Fine Particles: Fine particles include the nucleation, Aitkin, and accumulation modes, i.e., particles from the lowest measurable size, currently about 3 nm, to just above the minimum in the mass or volume distribution which generally occurs between 1 and 3 μm. These particles are generated during combustion or formed from gases.

Ultrafine Particles: That portion of fine particles with diameters below about 0.1 μm (100 nm), i.e., the Aitkin and nucleation modes.

Modes are defined primarily in terms of their formation mechanisms but also differ in terms of sources, composition, age, and size. Nucleation mode applies to newly formed particles which have had little chance to grow by condensation or coagulation. Aitkin mode particles are also recently formed particles that are still actively undergoing coagulation. However, because of higher concentrations of precursors or more time for condensation and coagulation, the particles have grown to larger sizes. Accumulation mode applies to the final stage as particles, originally formed as nuclei, grow to a point where growth slows down. These three modes, which together are called fine particles, are formed primarily by combustion or chemical reactions of gases yielding products with low saturated vapor pressures. Fine particles include metals and elemental and organic carbon (primary PM) and sulfate, nitrate, ammonium ions, and organic compounds (secondary PM).

The coarse mode refers to particles formed by mechanical breakdown of minerals, crustal material, and organic debris. The composition includes primary minerals and organic material. The accumulation mode and the coarse mode overlap in the region between 1 and 3 µm (and occasionally over an even larger range). In this region, chemical composition of individual particles can usually, but not always, allow identification of a source or formation mechanism and so permit identification of a particle as belonging to the accumulation or coarse mode.

Sampler Cut Point. Another set of definitions of particle size fractions arises from considerations of size-selective sampling. Size-selective sampling refers to the collection of particles below or within a specified aerodynamic size range. Size fractions are usually specified by the 50% cut point size; e.g., $PM_{2.5}$ refers to particles collected by a sampling device that collects 50% of 2.5 µm particles and rejects 50% of 2.5 µm particles. However, size fractions are defined, not merely by the 50% cut point, but by the entire penetration curve. Examples of penetration curves are given in Figure 2-6. Thus, as shown by Figure 2-6, a $PM_{2.5}$ sampler, as defined by the Federal Reference Method, rejects 94% of 3 µm particles, 50% of 2.5 µm particles, and 16% of 2 µm. Samplers with the same 50% cut point but differently shaped penetration curves would collect different fractions of PM. Size-selective sampling has arisen in an effort to measure particle size fractions with some special significance (e.g., health, visibility, source apportionment, etc.), to measure mass size distributions, or to collect size-segregated particles for chemical analysis. Dichotomous samplers split the particles into smaller and larger

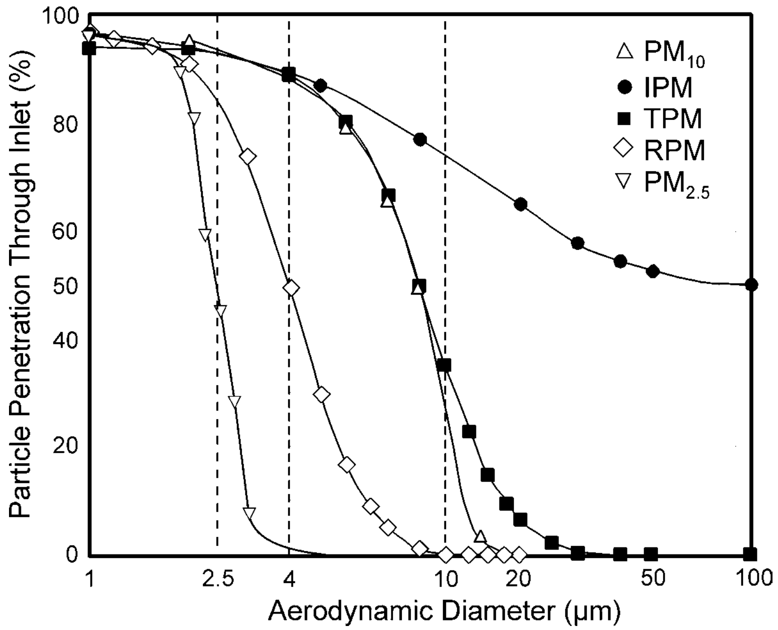

Figure 2-6. Specified particle penetration (size-cut curves) through an ideal (no-particle-loss) inlet for five different size-selective sampling criteria. Regulatory size cuts are defined in the Code of Federal Regulations; $PM_{2.5}$ (2001c), PM_{10} (2001a). $PM_{2.5}$ is also defined in the Federal Register (1997). Size-cut curves for inhalable particulate matter (IPM), thoracic particulate matter (TPM) and respirable particulate matter (RPM) size cuts are computed from definitions given by American Conference of Governmental and Industrial Hygienists (1994).

fractions that may be collected on separate filters. However, some fine particles ($\approx$10%) are collected with the coarse particle fraction. Cascade impactors use multiple size cuts to obtain a distribution of size cuts for mass or chemical composition measurements. One-filter samplers with a variety of upper size cuts are also used, e.g., $PM_{2.5}$, PM_{10}.

Regulatory size cuts are a specific example of size-selective sampling. In 1987, the NAAQS for PM were revised to use PM_{10}, rather than total suspended particulate matter (TSP), as the indicator for the NAAQS for PM (Federal Register, 1987). The use of PM_{10} as an indicator is an example of size-selective sampling based on a regulatory size cut (Federal Register, 1987). The selection of PM_{10} as an indicator was based on health considerations and was intended to focus regulatory concern on those particles small enough to enter the thoracic region of the human respiratory tract. The $PM_{2.5}$ standard set in 1997 is also an example of size-selective sampling based on a regulatory size cut (Federal Register, 1997). The $PM_{2.5}$ standard was based primarily on epidemiologic studies using concentrations measured with $PM_{2.5}$ samplers as an exposure index. However, the $PM_{2.5}$ sampler was not designed to collect all respirable particles; it was designed to collect fine particles because of their different sources and properties (Whitby et al., 1974). Thus, the need to attain a $PM_{2.5}$ standard will tend to focus regulatory concern on control of sources of fine particles.

Prior to 1987, the indicator for the NAAQS for PM was TSP. TSP is defined by the design of the High Volume Sampler (hivol) that collects all of the fine particles but only part of the coarse particles (Figure 2-7). The upper cut-off size of the hivol depends on the wind speed and direction and may vary from 25 to 40 µm. The Wide Range Aerosol Classifier (WRAC) was designed specifically to collect the entire coarse mode using an impaction system designed by Lundgren to collect particles up to 100 µm in diameter (Lundgren and Burton, 1995).

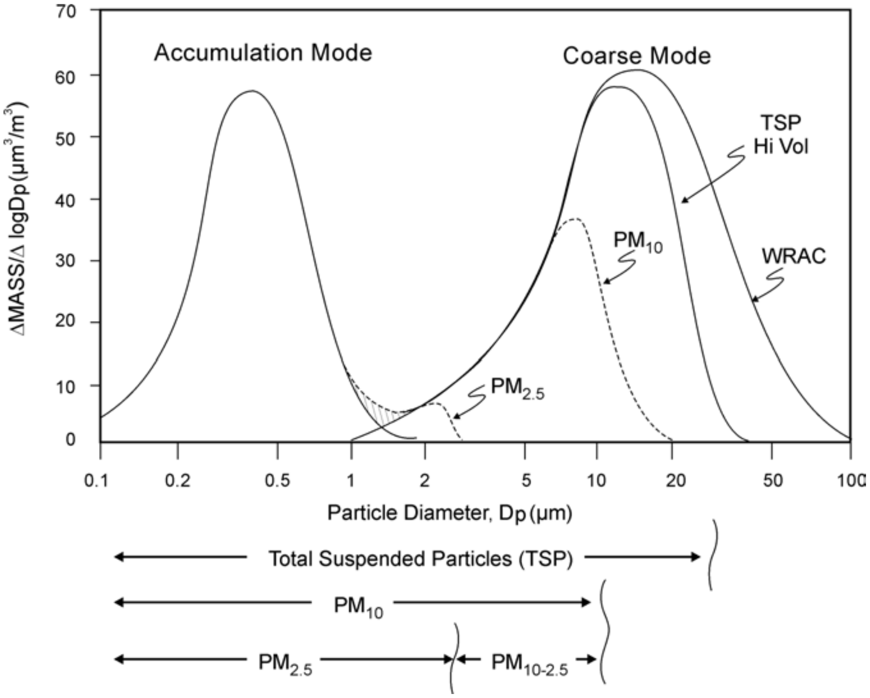

Figure 2-7. An idealized distribution of ambient particulate matter showing fine-mode particles and coarse-mode particles and the fractions collected by size-selective samplers. (WRAC is the Wide Range Aerosol Classifier which collects the entire coarse mode [Lundgren and Burton, 1995].)

Source: Adapted from Wilson and Suh (1997) and Whitby (1978).

An idealized distribution with the normally observed division of ambient aerosols into fine-mode particles and coarse-mode particles and the size fractions collected by the WRAC, TSP, PM_{10}, $PM_{2.5}$ and $PM_{10\text{-}2.5}$ samplers is shown in Figure 2-7. PM_{10} samplers, as defined in Appendix J to Title 40 Code of Federal Regulations (40 CFR) Part 50 (Code of Federal Regulations, 2001a; Federal Register, 1987), collect all of the fine-mode particles and part of the coarse-mode particles. The upper cut point is defined as having a 50% collection efficiency at 10 ± 0.5 μm aerodynamic diameter. The slope of the collection efficiency curve is defined in amendments to 40 CFR, Part 53, (Code of Federal Regulations, 2001b). An example of a PM_{10} size-cut curve is shown in Figure 2-6.

An example of a $PM_{2.5}$ size-cut curve is also shown in Figure 2-6. The $PM_{2.5}$ size-cut curve, however, is defined by the design of the Federal Reference Method (FRM) Sampler. The basic design of the FRM sampler is given in the Federal Register (1997, 1998) and as 40 CFR Part 50, Appendix L (Code of Federal Regulations, 2001c). Additional performance specifications are given in 40 CFR Parts 53 and 58 (Code of Federal Regulations, 2001b,d). In order to be used for measurement of $PM_{2.5}$ to determine compliance with the $PM_{2.5}$ NAAQS, each specific sampler design and its associated manual of operational procedures must be designated as a reference method under 40 CFR Part 53 in Section 1.2 of Appendix L (Code of Federal Regulations, 2001c). Thus $PM_{2.5}$ FRM samplers may have somewhat different designs (see Table 2-4 in Section 2.2.4.1.2).

Papers discussing PM_{10} or $PM_{2.5}$ frequently insert an explanation such as “PM_x (particles less than x μm diameter)” or “PM_x (nominally, particles with aerodynamic diameter $\leq$ x μm).” While these explanations may seem easier than “PM_X, (particles collected with an upper 50% cut point of x μm aerodynamic diameter and a specified penetration curve),” they are not entirely correct and may be misleading since they suggest an upper 100% cut point of x μm. Some countries use PM_{10} to refer not to samplers with a 50% cut at 10 μm D_a but to samplers with 100% rejection of all particles greater than 10 μm D_a. Such samplers miss a fraction of coarse thoracic PM. An example is shown in Figure 2-8.

PM_{10}, as defined by EPA, refers to particles collected by a sampler with an upper 50% cut point of 10 μm D_a and a specific, fairly sharp, penetration curve. $PM_{2.5}$ is analogously defined. Although there is not yet an FRM, $PM_{10\text{-}2.5}$ refers either to particles collected by a sampler with an upper 50% cut point of 10 μm D_a and a lower 50% cut point of 2.5 μm D_a or to the difference

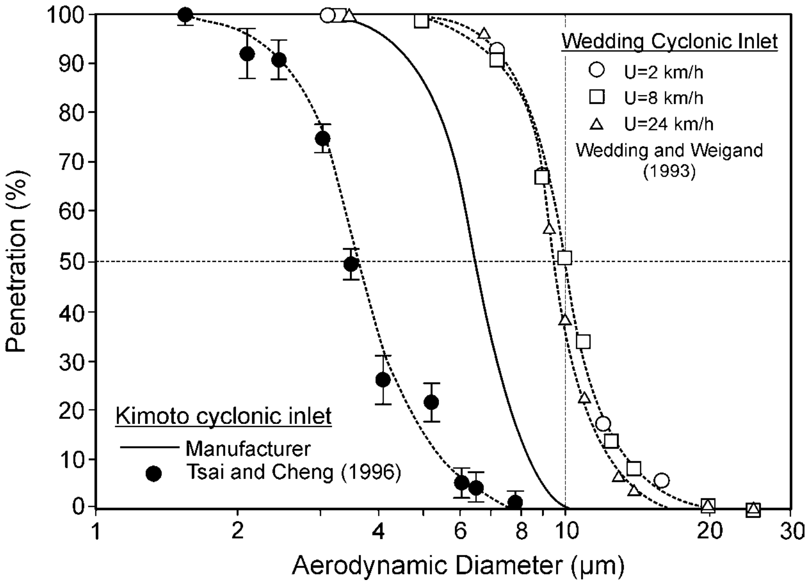

Figure 2-8. Comparison of penetration curves for two PM_{10} beta gauge samplers using cyclone inlets. The Wedding PM_{10} sampler uses the U.S. EPA definition of PM_x as x = 50% cut point. The Kimoto PM_{10} defines PM_x as x = the 100% cut point (or zero penetration).

Source: Tsai and Cheng (1996).

between the particle concentration measured by a PM_{10} monitor and a $PM_{2.5}$ monitor. In all cases, the fraction of PM collected depends on the entire penetration curve (or curves); i.e., for $PM_{2.5}$ some particles > 2.5 µm D_a are collected and not all particles < 2.5 µm D_a are collected.

In an analysis reported in 1979, EPA scientists endorsed the need to measure fine and coarse particles separately (Miller et al., 1979). Based on the availability of a dichotomous sampler with a separation size of 2.5 µm D_a, they recommended 2.5 µm D_a as the cut point between fine and coarse particles. Because of the wide use of this cut point, the $PM_{2.5}$ fraction is frequently referred to as “fine” particles. However, although the $PM_{2.5}$ sample will usually contain all of the fine particles, it may collect a small fraction of the coarse particles, especially in dry areas or during dry conditions. A $PM_{10\text{-}2.5}$ size fraction may be obtained from a dichotomous sampler or by subtracting the mass collected by a $PM_{2.5}$ sampler from the mass collected by a PM_{10} sampler. The resulting $PM_{10\text{-}2.5}$ mass, or $PM_{10\text{-}2.5}$, is sometimes called “coarse” particles. However, it would be more correct to call $PM_{2.5}$ an indicator of fine particles (because it contains some coarse particles) and $PM_{10-2.5}$ an indicator of the thoracic component of coarse particles (because it excludes some coarse particles below 2.5 µm D_a and above 10 µm D_a). It would be appropriate to call PM_{10} an indicator of thoracic particles. PM_{10} and thoracic PM, as shown in Figure 2-6, have the same 50% cut point. However, the thoracic cut is not as sharp as the PM_{10} cut; therefore, thoracic PM contains some particles between 10 and 30 µm diameter that are excluded from PM_{10}.

Over the years, the terms fine and coarse, as applied to particles, have lost the precise meaning given in Whitby's (1978) definition. In any given article, therefore, the meaning of fine and coarse, unless defined, must be inferred from the author's usage. In this document, fine particles means all particles in the nucleation, Aitken, and accumulation modes; and coarse particles means all particles in the coarse mode. $PM_{2.5}$ and fine particles are not equivalent terms.

Occupational Health or Dosimetric Size Cuts. The occupational health community has defined size fractions in terms of their entrance into various compartments of the respiratory system. This convention classifies particles into inhalable, thoracic, and respirable particles according to their upper size cuts. Inhalable particles enter the respiratory tract, including the head airways. Thoracic particles travel past the larynx and reach the lung airways and the gas-exchange regions of the lung. Respirable particles are a subset of thoracic particles that are more likely to reach the gas-exchange region of the lung. In the past, exact definitions of these terms have varied among organizations. As of 1993, a unified set of definitions was adopted by the American Conference of Governmental Industrial Hygienists (ACGIH, 1994), the International Standards Organization (ISO), and the European Standardization Committee (CEN). The curves which define inhalable (IPM), thoracic (TPM), and respirable (RPM) particulate matter are shown in Figure 2-6. These curves should not be taken to indicate that particles > 4 µm D_a do not reach the gas exchange regions or that particles < 4 µm D_a do not deposit in the bronchi. See Figure 6-13 for a graphical characterization of particle deposition in regions of the respiratory system as a function of particle size.

2.1.2.3 Ultrafine Particles

As discussed in Chapter 7 (Toxicology of Particulate Matter in Humans and Laboratory Animals) and in Chapter 8 (Epidemiology of Human Health Effects Associated with Ambient Particulate Matter), some scientists argue that ultrafine particles may pose potential health problems and that some health effects may be associated with particle number or particle surface area as well as or more closely than with particle mass. Some additional attention will be given to ultrafine particles because they contribute the major portion of particle number and a significant portion of particle surface area.

Formation and Growth of Fine Particles

Several processes influence the formation and growth of particles. New particles may be formed by nucleation from gas phase material. Particles may grow by condensation as gas phase material condenses on existing particles; and particles also may grow by coagulation as two particles combine to form one. Gas phase material condenses preferentially on smaller particles, and the rate constant for coagulation of two particles decreases as the particle size increases. Therefore, ultrafine particles grow into the accumulation mode; but accumulation-mode particles do not normally grow into the coarse mode (see Figure 2-4). More information and references on formation and growth of fine particles can be found in the 1996 AQCD PM (U.S. Environmental Protection Agency, 1996a).

Equilibrium Vapor Pressures

An important parameter in particle nucleation and in particle growth by condensation is the saturation ratio, S, defined as the ratio of the partial pressure of a species, p, to its equilibrium vapor pressure above a flat surface at a specified temperature, p_o: $S = p/p_o$. For either condensation or nucleation to occur, the species vapor pressure must exceed its equilibrium vapor pressure. For particles, the equilibrium vapor pressure is not the same as p_o. Two effects are important: (1) the Kelvin effect, which is an increase in the equilibrium vapor pressure above the surface due to its curvature (very small particles have higher vapor pressures and will not be stable to evaporation until they attain a critical size) and (2) the solute effect, which is a decrease in the equilibrium vapor pressure of the liquid due to the presence of other compounds in solution. Organic compounds may also be adsorbed on ultrafine carbonaceous particles.

For an aqueous solution of a nonvolatile salt, the presence of the salt decreases the equilibrium vapor pressure of the water over the droplet. This effect is in the opposite direction of the Kelvin effect, which increases the equilibrium vapor pressure above a droplet because of its curvature. The existence of an aqueous solution will also influence the vapor pressure of water-soluble species. The vapor pressure behavior of mixtures of several liquids or of liquids containing several solutes is complex.

New Particle Formation

When the vapor concentration of a species exceeds its equilibrium concentration (expressed as its equilibrium vapor pressure), it is considered condensable. Condensable species can either condense on the surface of existing particles or can nucleate to form new particles. The relative importance of nucleation versus condensation depends on the rate of formation of the condensable species and on the surface or cross-sectional area of existing particles (McMurry and Friedlander, 1979). In ambient urban environments, the available particle surface area is usually sufficient to rapidly scavenge the newly formed condensable species. Formation of new, ultrafine particles is usually not observable in mass or volume distributions except near sources of condensable species. Wilson et al. (1977) report observations of the Aitkin nuclei mode in traffic. However, bursts of new particle formation can be observed in urban areas in the number distribution (Woo et al., 2001a; McMurray et al., 2000). New particle formation also can be observed in cleaner, remote regions. Bursts of new particle formation in the atmosphere under clean conditions usually occur when aerosol surface area concentrations are low (Covert et al., 1992). High concentrations of nuclei mode particles have been observed in regions with low particle mass concentrations indicating that new particle formation is inversely related to the available aerosol surface area (Clarke, 1992).

Sources of Ultrafine Particles

Ultrafine particles are the result of nucleation of gas phase species to form condensed phase species with very low equilibrium vapor pressure. In the atmosphere there are four major classes of substances that yield particulate matter with equilibrium vapor pressures low enough to form nuclei mode particles:

(1) *Particles containing heavy metals*. Nuclei mode particles of metal oxides or other metal compounds are generated when metallic impurities in coal or oil are vaporized during combustion and the vapor undergoes nucleation. Metallic ultrafine particles also may be formed from metals in lubricating oil or fuel additives that are vaporized during combustion of gasoline or diesel fuels. Ultrafine metallic particles were discussed in Section 6.9 of the 1996 PM AQCD (U.S. Environmental Protection Agency, 1996a).

(2) *Elemental carbon or soot* (EC). EC particles are formed primarily by condensation of C_2 molecules generated during the combustion process. Because EC has a very low equilibrium vapor pressure, ultrafine EC particles can nucleate even at high temperatures (Kittelson, 1998; Morawska et al., 1998).

(3) *Organic carbon* (OC). Recent smog chamber studies and indoor experiments show that atmospheric oxidation of certain organic compounds found in the atmosphere can produce highly oxidized organic compounds with an equilibrium vapor pressure sufficiently low to result in nucleation (Kamens et al., 1999; Weschler and Shields, 1999).

(4) *Sulfates.* Sulfuric acid (H_2SO_4) molecules are generated in the atmosphere by conversion of sulfur dioxide (SO_2) to H_2SO_4. As H_2SO_4 is formed, it can either nucleate to form new ultrafine particles, or it can condense on existing ultrafine or accumulation mode particles (Clark and Whitby, 1975; Whitby, 1978). Nucleation theory allows calculation of nucleation rates for both binary nucleation, involving water and sulfuric acid (Easter and Peters, 1994) or ternary nucleation, which requires sulfuric acid, ammonia (NH_3), and water (Korhonen et al., 1999). Kulmala et al. (2000) compared nucleation rates of binary and ternary nucleation and concluded that the ternary rate is 1,000 times the binary rate. Results from an aerosol dynamics model with a ternary nucleation scheme indicate that nucleation in the troposphere should be ubiquitous and yield a reservoir of thermodynamically stable sulfate clusters 1-3 nm in diameter. The growth of these clusters to a detectable size (> 3 nm diameter) is limited by the availability of condensable vapor. Observations of atmospheric particle formation and growth from a continental and a coastal site suggest that a growth process including ternary nucleation is

responsible for the formation of cloud condensation nuclei. Nucleation processes in the atmosphere may also involve organic compounds as well as sulfuric acid, ammonia, and water. However, current formulations of nucleation theory only include the three inorganic components. (The possible formation of ultrafine NH_4NO_3 by reaction of NH_3 and nitric acid (HNO_3) vapor has not been investigated.)

Vehicle engine exhaust may include all these substances. Ultrafine particles are observed in the emissions from spark, diesel, and jet engines (Kittelson, 1998). In these cases it seems likely that elemental carbon, organic compounds, ammonia and sulfuric acid from sulfur in the fuel, as well as metal additives in the fuel or fuel oil, may contribute to the formation of ultrafine particles (Tobias et al., 2001). An example of particles from a diesel engine showing number and volume distributions is given in Figure 2-9.

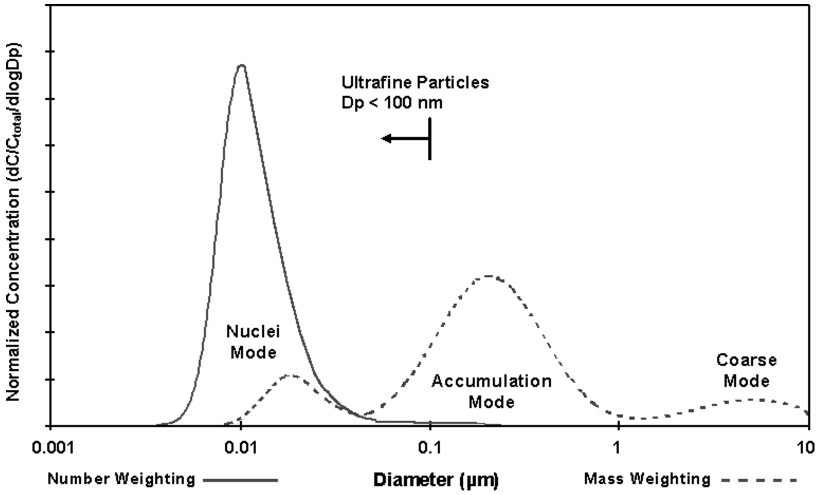

Figure 2-9. Typical engine exhaust size distribution.

Source: Kittelson (1998).

Recent Measurements of Ultrafine Particles

Instruments, developed during the past decade, permit measurement of size distributions down to 3 nm diameter particles. Use of these techniques have led to new information on the formation of new particles by nucleation. Such measurements have been carried out during intensive field measurement campaigns, during continuous measurements in urban areas in several European cities, and in the U.S. as a part of the Supersite program (McMurry et al., 2000; Woo et al., 2001a). Nucleation has been observed in the free troposphere (Weber et al., 1999; Clarke, 1992; Schröder and Ström, 1997; Raes et al., 1997); in outflows of evaporating convective clouds (Clarke et al., 1998; Hegg et al., 1990, 1991; Radke and Hobbs, 1991; Perry and Hobbs, 1994); in the marine boundary layer (Covert et al., 1992; Hoppel et al., 1994; Van Dingenen et al., 1995; Weber et al., 1998; Clarke et al., 1998); downwind of coastal regions during low tide (McGovern et al., 1996; McGovern, 1999); on mountains (Weber et al., 1995, 1997; Raes et al., 1997; Wiedensohler et al., 1997); over forests (MäKelä et al., 1997; Kulmala et al., 1998; O'Dowd et al., 2002); downwind of certain biogenic emissions (Weber et al., 1998); in urban areas (Birmili and Wiedensohler, 1998; McMurry et al., 2000; Woo et al., 2001a); near freeways (Zhu et al., 2002a,b); in engine exhaust (Kittelson, 1998; Tobias et al., 2001); and in homes (Wallace and Howard-Reed, 2002). Nucleation events in outdoor air almost always occur during daylight, indicating that photochemistry plays a role in producing the gas phase precursors of new particles.

The number size distributions observed over a boreal forest in Finland before and during the initial stages of a nucleation event are shown in Figure 2-10. The Aitken and accumulation modes can be seen clearly before the nucleation event. The nucleation mode, with a peak between 3 and 7 nm, appears during the event. Figure 2-11 shows the variety of size distributions that may be observed as nuclei are formed and grow, based on size distributions measured in the Arctic marine boundary layer (Covert et al., 1996). These distributions all show a trimodal distribution within the fine particle size range. The changes in size distribution due to coagulation (and dilution) immediately downwind of a freeway (Zhu et al., 2002b) are shown in Figure 2-12(a)-(g). At 30 m downwind the nucleation mode is larger than the Aitken mode, but by 60 m downwind coagulation has removed particles from the nucleation mode and added particles to the Aitken mode so that the Aitken mode is larger than the nucleation mode.

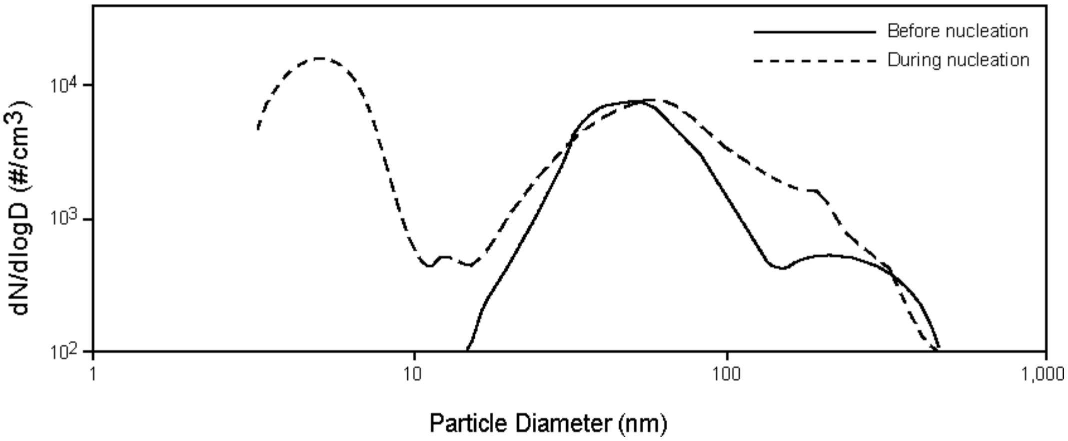

Figure 2-10. Number size distributions showing measurement of a nucleation burst made in a boreal forest in Finland.

Source: O'Dowd et al. (2002).

There is strong evidence that sulfuric acid vapor often participates in nucleation. However, condensation of sulfuric acid and its associated water and ammonium ions typically can account for only 10% to 20% of the observed growth rates for freshly nucleated particles. Therefore, organic compounds may account for much of the formation and growth of freshly nucleated particles. Evidence of nucleation of organic particles comes from smog chamber studies (Kamens et al., 1999) and from field studies over forests (MäKelä et al., 1997; Kulmala et al., 1998; O'Dowd et al., 2002). Nucleation of organic particles may also occur indoors due to the reaction of infiltrated ozone with indoor terpenes from air fresheners or cleaning solutions (Weschler and Shields, 1999). The observation of bursts of nuclei-mode particles in Atlanta (Woo et al., 2001a), perhaps due to unusually high rates of production of condensable species, suggests that high concentrations of ultrafine particles may be a normal occurrence in polluted urban areas.

Concentration of Ultrafine Particles: A Balance Between Formation and Removal

Nuclei-mode particles may be removed by dry deposition or by growth into the accumulation mode. This growth takes place as other low vapor pressure material condenses on the particles or as nuclei-mode particles coagulate with themselves or with accumulation mode

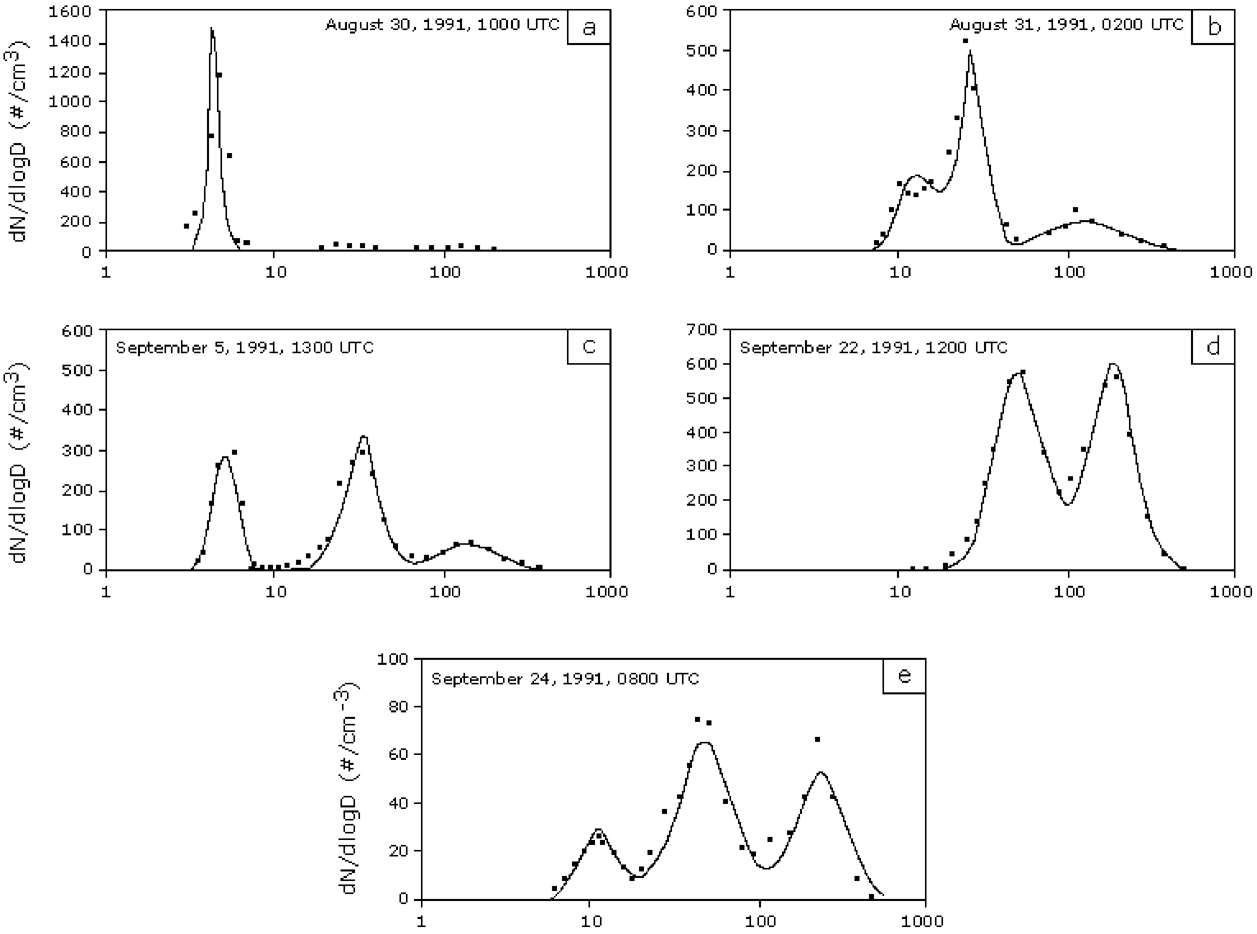

Figure 2-11. Examples of the measured one hour average particle number size distributions and the log normal fits to the modes of the data. Squares are measured data, solid lines are the fitted log normal modes determined by DistFit^{TM}. These modes, nucleation between 3 and 20 nm, Aitken between 20 and 100 nm, and accumulation above 100 nm can be observed in most examples.

Source: Covert et al. (1996).

particles. Because the rate of coagulation would vary with the concentration of accumulation-mode particles, it might be expected that the concentration of nuclei-mode particles would increase with a decrease in accumulation-mode mass. On the other hand, the concentration of particles would be expected to decrease with a decrease in the rate of generation of particles by reduction in emissions of metal and carbon particles or a decrease in the rate of generation of H_2SO_4 or condensable organic vapor. The rate of generation of H_2SO_4 depends on the

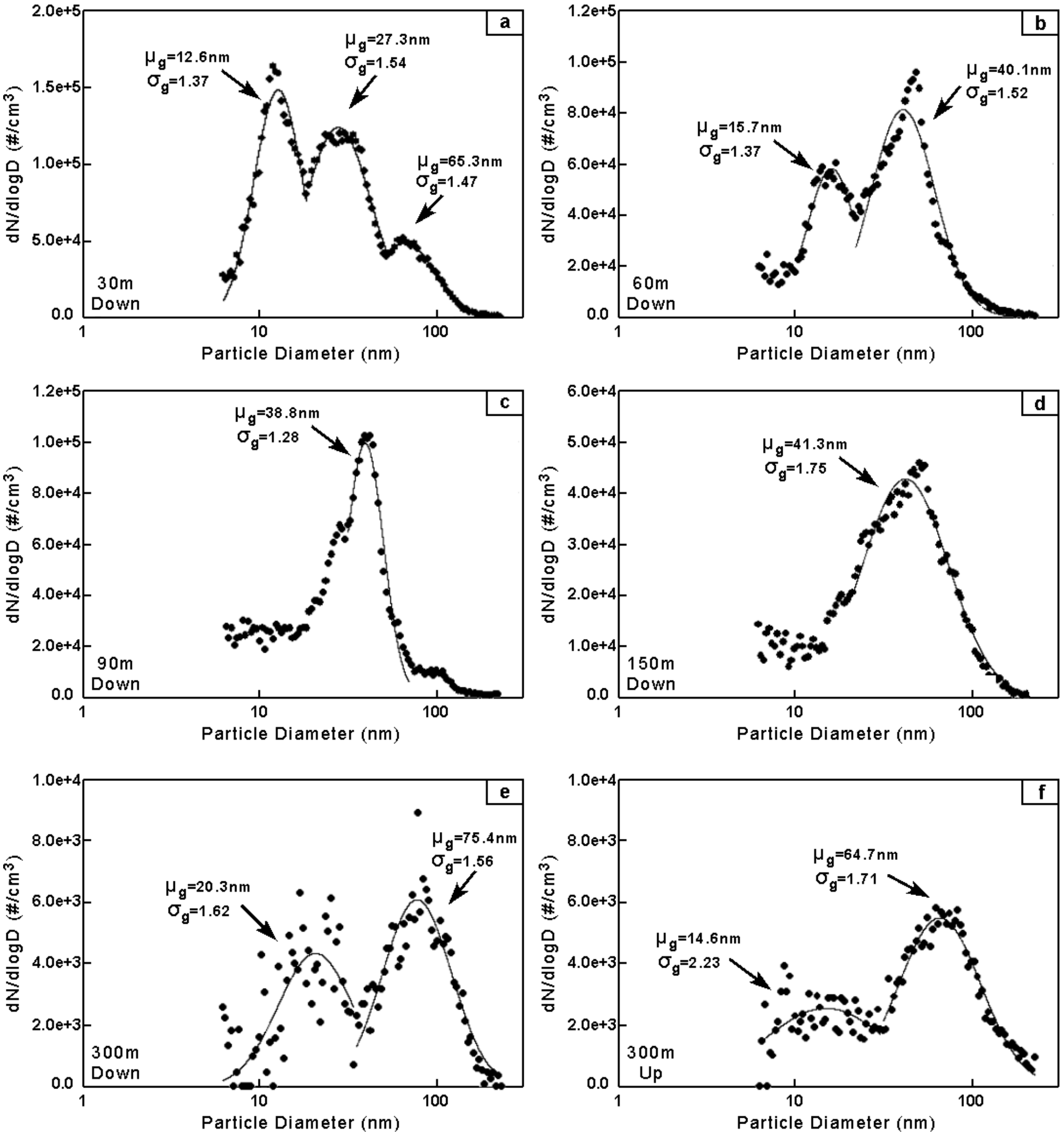

Figure 2-12(a-f). **Fitted multi-model particle size distribution at different sampling distances from freeway 405 (a) 30 m downwind, (b) 60 m downwind, (c) 90 m downwind, (d) 150 m downwind, (e) 300 m downwind, (f) 300 m upwind. Size distributions were normalized to the control CPC's reading. Note different scales for dN/d log D_p axis. Modal parameters given are: geometric mean diameter, μ_g; and geometric standard deviation, σ_g.**

Source: Zhu et al. (2002b).

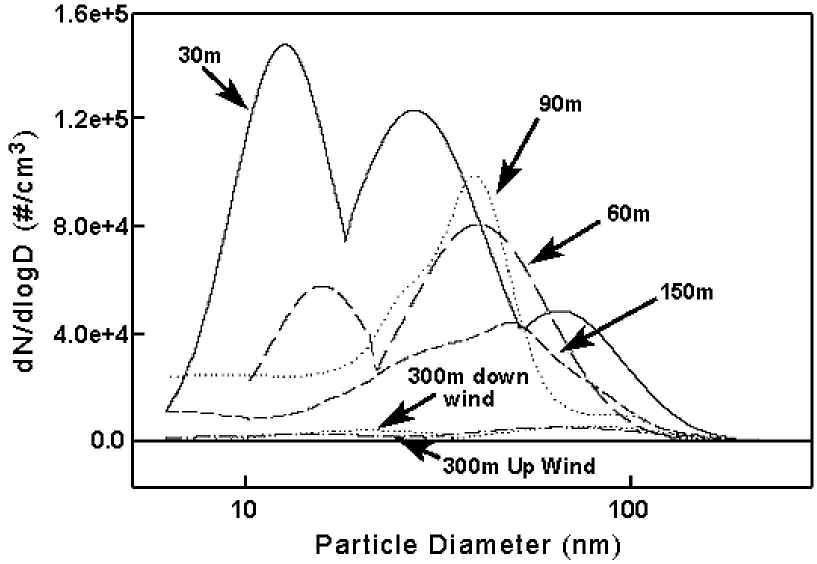

Figure 2-12(g). (Combination of a-e with dN/d logD_p scale.) Ultrafine particle size distribution at different sampling locations near the 405 freeway in Los Angeles, CA.

Source: Zhu et al. (2002b).

concentration of SO_2 and hydroxyl radical (•OH), which is generated primarily by reactions involving ozone (O_3). Thus, reductions in SO_2 and O_3 would lead to a decrease in the rate of generation of H_2SO_4 and condensable organic vapor and to a decrease in the concentration of nuclei-mode particles. The balance between formation and removal is uncertain. However, these processes can be modeled using a general dynamic equation for particle size distribution (Friedlander, 2000) or by aerosol dynamics modules in newer air quality models (Binkowski and Shanker, 1995; Binkowski and Ching, 1995).

2.1.3 Chemistry of Atmospheric Particulate Matter

The major constituents of atmospheric PM are sulfate, nitrate, ammonium, and hydrogen ions; particle-bound water; elemental carbon; a great variety of organic compounds; and crustal material. Atmospheric PM also contains a large number of elements in various compounds and concentrations. More information and references on the composition of PM measured in a large number of studies in the United States, may be found in 1996 PM AQCD (U.S. Environmental

Protection Agency, 1996a). In this document, the composition and concentrations of PM are discussed in Chapter 3, Section 3.1, Patterns and Trends in Ambient $PM_{2.5}$ Concentrations and ambient data for concentrations and composition of $PM_{2.5}$ are given in Appendices 3A, 3B, and 3C.

2.1.3.1 Chemical Composition and Its Dependence on Particle Size

Studies conducted in most parts of the United States indicate that sulfate, ammonium, and hydrogen ions; elemental carbon, secondary organic compounds and primary organic species from cooking and combustion; and certain transition metals are found predominantly in the fine particle mode. Crustal materials such as calcium, aluminum, silicon, magnesium, and iron are found predominately in the coarse particles. Some primary organic materials such as pollen, spores, and plant and animal debris are also found predominantly in the coarse mode. Some components such as potassium and nitrate may be found in both the fine and coarse particle modes but from different sources or mechanisms. Potassium in coarse particles comes from soil. Potassium also is found in fine particles in emissions from burning wood or cooking meat. Nitrate in fine particles comes primarily from the reaction of gas-phase nitric acid with gas-phase ammonia to form particulate ammonium nitrate. Nitrate in coarse particles comes primarily from the reaction of gas-phase nitric acid with preexisting coarse particles.

2.1.3.2 Primary and Secondary Particulate Matter

Particulate material can be primary or secondary. PM is called “primary” if it is in the same chemical form in which it was emitted into the atmosphere. PM is called “secondary” if it is formed by chemical reactions in the atmosphere. Primary coarse particles are usually formed by mechanical processes. This includes material emitted in particulate form such as wind-blown dust, sea salt, road dust, and combustion-generated particles such as fly ash and soot. Primary fine particles are emitted from sources either directly as particles or as vapors that rapidly condense to form ultrafine or nuclei-mode particles. This includes soot from diesel engines, a great variety of organic compounds condensed from incomplete combustion or cooking, and compounds of As, Se, Zn, etc., that condense from vapor formed during combustion or smelting. The concentration of primary particles depends on their emission rate, transport and dispersion, and removal rate from the atmosphere.

Secondary PM is formed by chemical reactions of free, adsorbed, or dissolved gases. Most secondary fine PM is formed from condensable vapors generated by chemical reactions of gas-phase precursors. Secondary formation processes can result in either the formation of new particles or the addition of particulate material to pre-existing particles. Most of the sulfate and nitrate and a portion of the organic compounds in atmospheric particles are formed by chemical reactions in the atmosphere. Secondary aerosol formation depends on numerous factors including the concentrations of precursors; the concentrations of other gaseous reactive species such as ozone, hydroxyl radical, peroxy radicals, or hydrogen peroxide; atmospheric conditions including solar radiation and relative humidity (RH); and the interactions of precursors and pre-existing particles within cloud or fog droplets or in the liquid film on solid particles. As a result, it is considerably more difficult to relate ambient concentrations of secondary species to sources of precursor emissions than it is to identify the sources of primary particles.
A significant effort is currently being directed toward the identification and modeling of organic products of photochemical smog including the conversion of gases to particulate matter. More information of the transformation of precursor gases into secondary PM is given in Chapter 3, Section 3.3.1, Chemistry of Secondary PM Formation.

Particle strong acidity is due almost entirely to H_2SO_4 or NH_4HSO_4. Thus, the acidity of atmospheric particles depends on both the amount of SO_2 that is oxidized to SO_3 and subsequently forms H_2SO_4 and the amount of ammonia available to react with the sulfuric acid. Nitric acid is more volatile than sulfuric acid. Thus, if gas phase SO_3 or sulfuric acid or particles containing H_2SO_4 or NH_4HSO_4 contact particles containing NH_4NO_3, nitric acid gas will be released with the remaining ammonia contributing to further neutralization of the acid. Little NH_4NO_3 is found in atmospheres containing significant particle strong acidity. However, as SO_2 emissions are reduced to the point that there is more than enough ammonia to neutralize the sulfuric acid, NH_4NO_3 particles will begin to form. Thus, ammonia emissions and concentrations relative to those of SO_2 and H_2SO_4 are important in determining the strong acidity in the atmosphere and the concentration of particulate NH_4NO_3. Therefore, once SO_2 emissions have been reduced to the point that ammonia and sulfate are in balance to form $(NH_4)_2SO_4$, further reductions in SO_2 will not result in an equivalent reduction in airborne PM because one $(NH_4)_2SO_4$ unit will be replaced by two NH_4NO_3 units.

2.1.3.3 Particle-Vapor Partitioning

Several atmospheric aerosol species, such as ammonium nitrate and certain organic compounds, are semivolatile and are found in both gas and particle phases. A variety of thermodynamic models have been developed to predict the temperature and relative humidity dependence of the ammonium nitrate equilibria with gaseous nitric acid and ammonia. However, under some atmospheric conditions, such as cool, cold, or very clean air, the relative concentrations of the gas and solid phases are not accurately predicted by equilibrium considerations alone, and transport kinetics can be important. The gas-particle distribution of semivolatile organic compounds depends on the equilibrium vapor pressure of the compound, total particle surface area, particle composition, atmospheric temperature, and relative humidity. Although it generally is assumed that the gas-particle partitioning of semivolatile organics is in equilibrium in the atmosphere, neither the equilibria nor the kinetics of redistribution are well understood. Diurnal temperature fluctuations cause gas-particle partitioning to be dynamic on a time scale of a few hours and can cause semivolatile compounds to evaporate during the sampling process. The pressure drop across the filter can also contribute to the loss of semivolatile compounds. The dynamic changes in gas-particle partitioning caused by changes in temperature, pressure, and gas-phase concentration, both in the atmosphere and after collection, cause serious sampling problems that are discussed in Section 2.2.3, Measurement of Semivolatile Particulate Matter.

Equilibria with Water Vapor

As a result of the equilibrium of water vapor with liquid water in hygroscopic particles, many ambient particles contain liquid water (particle-bound water). Unless removed, this particle-bound water will be measured as a component of the particle mass. Particle-bound water is important in that it influences the size of the particles, and in turn, their light scattering properties and their aerodynamic properties, which are important for deposition to surfaces, to airways following inhalation, and in sampling instrumentation. The aqueous solution provides a medium for reactions of dissolved gases including reactions that do not take place in the gas phase. The aqueous solutions also may act as a carrier to convey soluble toxic species to the gas-exchange regions of the respiratory system, including species that would be removed by deposition in the upper airways if the particles had remained in the gas phase (Friedlander and

Yeh, 1998; Kao and Friedlander, 1995; Wilson, 1995). An extensive review of equilibrium with water vapor as it pertains to ambient aerosols was given in Chapter 3 of the 1996 PM AQCD (U.S. Environmental Protection, Agency, 1996a).

The interaction of particles with water vapor may be described briefly as follows. As relative humidity increases, particles of crystalline soluble salts, such as $(NH_4)_2SO_4$, NH_4HSO_4, or NH_4NO_3, undergo a phase transition to become aqueous solution particles. According to the phase rule, for particles consisting of a single component, this phase transition is abrupt, taking place at a relative humidity that corresponds to the vapor pressure of water above the saturated solution (the deliquescence point). With a further increase in relative humidity, the solution particle adds water (and the concentration of the solute decreases) so that the vapor pressure of the solution is maintained equal to that of the surrounding relative humidity; thus, the solution particle tends to follow the equilibrium growth curve. As relative humidity decreases, the solution particle follows the equilibrium curve to the deliquescence point. However, rather than crystallizing at the deliquescence relative humidity, the solute remains dissolved in a supersaturated solution to considerably lower relative humidities. Ultimately the solution particle abruptly loses its water vapor (efflorescence) and typically returns to the initial crystalline form.

For particles consisting of more than one component, the solid to liquid transition will take place over a range of relative humidities with an abrupt onset at the lowest deliquescence point of the several components and with subsequent growth as crystalline material in the particle dissolves according to the phase diagram for the particular multicomponent system. Under such circumstances, a single particle may undergo several more or less abrupt phase transitions until the soluble material is fully dissolved. At decreasing relative humidity, such particles tend to remain in solution to relative humidities well below the several deliquescence points. In the case of the sulfuric acid-ammonium sulfate-water system, the phase diagram is fairly well understood. For particles of composition intermediate between NH_4HSO_4 and $(NH_4)_2SO_4$, this transition occurs in the range from 40% to below 10%, indicating that for certain compositions the solution cannot be dried in the atmosphere. At low relative humidities, particles of this composition would likely be present in the atmosphere as supersaturated solution droplets (liquid particles) rather than as solid particles. Thus, they would exhibit hygroscopic rather than deliquescent behavior during relative humidity cycles.

Other pure compounds, such as sulfuric acid, are hygroscopic (i.e., they form aqueous solutions at any relative humidity and maintain a solution vapor pressure over the entire range of relative humidity). Soluble organic compounds may also contribute to the hygroscopicity of the atmospheric aerosol (Saxena et al., 1995; Saxena and Hildeman, 1996), but the equilibria involving organic compounds and water vapor, and, especially for mixtures of salts, organic compounds, and water, are not so well understood. These equilibrium processes may cause an ambient particle to significantly increase its diameter at relative humidities above about 40% (Figure 2-13). A particle can grow to five times its dry diameter as the RH approaches 100% (Figure 2-14). The Federal Reference Methods, for filter measurements of $PM_{2.5}$ and PM_{10} mass, require equilibration at a specified, low relative humidity after collection (for $PM_{2.5}$, between 30 and 40% RH with control of ±5% RH [Code of Federal Regulations, 2001a]). This equilibration removes much of the particle-bound water and provides a relatively stable PM mass for gravimetric measurements (see Section 2.2 for details and references). Otherwise, particle mass would be a function of relative humidity, and the particle mass would be largely particle-bound water at higher relative humidities. However, some particle-bound water may be retained even after equilibration. Recent studies have shown that significant amounts of particle-bound water are retained in particles collected on impaction surfaces even after equilibration and that the amount of retained particle-bound water increases with relative humidity during collection (Hitzenberger et al., 1997).

The retention of particle-bound water is a greater problem for continuous monitors that measure changes in mass collected on a filter over long sampling times. If particle-bound water is not removed, changes in relative humidity would cause changes in the mass of PM collected over previous hours or days. These changes could be much greater than amount of PM mass added in one hour. Therefore, continuous monitoring techniques generally attempt to remove particle-bound water before measurement either by heating or dehumidification. However, other semivolatile materials (e.g., ammonium nitrate and organic compounds) that may be partially lost during sampling or equilibration of an unheated filter are certainly lost when the collected sample is heated above ambient temperature. These changes in particle size with relative humidity also mean that particle measurements such as surface area or volume, or composition as a function of size, should be made at the same RH in order for the results are to be

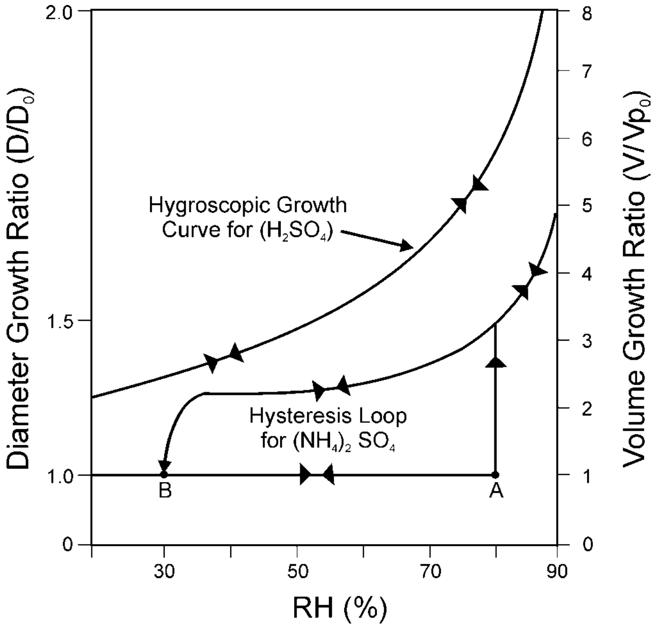

Figure 2-13. Particle growth curves showing fully reversible hygroscopic growth of sulfuric acid (H_2SO_4) particles, deliquescent growth of ammonium sulfate [$(NH_4)_2$ SO_4] particles at the deliquescent point (A, about 80% relative humidity [RH]), reversible hygroscopic growth of ammonium sulfate solution droplets at RH greater than 80%, and hysteresis (the droplet remains supersaturated as the RH decreases below 80%) until the crystallization point (B, about 38% RH) is reached (adapted from National Research Council, 1993 and Tang, 1980).

Source: National Research Council (1993) adapted from Tang (1980).

comparable. These problems are addressed in more detail in Section 2.2, Measurement of Particulate Matter.

2.1.3.4 Atmospheric Lifetimes and Removal Processes

The lifetimes of particles vary with size. Nuclei-mode particles rapidly grow into the accumulation mode. However, the accumulation mode does not grow into the coarse mode. Accumulation-mode fine particles are kept suspended by normal air motions and have very low deposition rates to surfaces. They can be transported thousands of km and remain in the atmosphere for a number of days. Coarse particles can settle rapidly from the atmosphere within

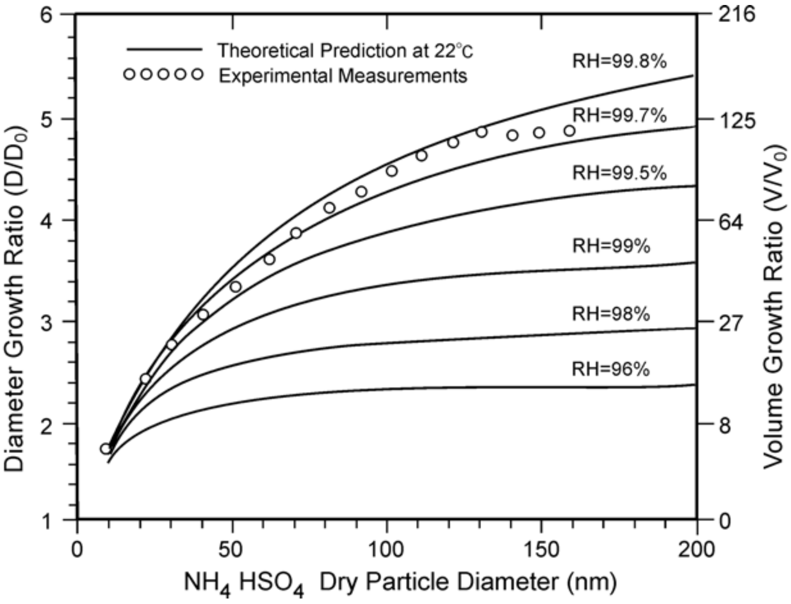

Figure 2-14. Theoretical predictions and experimental measurements of growth of NH_4HSO_4 particles at relative humidity between 95 and 100%.

Source: Li et al. (1992).

hours and normally travel only short distances. However, when mixed high into the atmosphere, as in dust storms, the smaller-sized coarse-mode particles have longer lives and travel greater distances. Dry deposition rates are expressed in terms of a deposition velocity that varies with particle size, reaching a minimum between 0.1 and 1.0 µm aerodynamic diameter (e.g., Lin et al., 1994). Accumulation-mode particles are removed from the atmosphere primarily by cloud processes. Fine particles, especially particles with a hygroscopic component, grow as the relative humidity increases, serve as cloud condensation nuclei, and grow into cloud droplets. If the cloud droplets grow large enough to form rain, the particles are removed in the rain. Falling rain drops impact coarse particles and remove them. Ultrafine or nuclei-mode particles are small enough to diffuse to the falling drop, be captured, and be removed in rain. Falling rain drops, however, are not nearly as effective in removing accumulation-mode particles as the cloud processes mentioned above. A more detailed discussion of particle deposition, including acid deposition, especially as it applies to deposition to vegetation, soil, and water surfaces is given in Chapter 4 (Environmental Effects of Airborne Particulate Matter). Acid deposition and

PM are intimately related, first, because particles contribute to the acidification of rain and, secondly, because the gas-phase species that lead to dry deposition of acidity are also precursors of particles. Therefore, reductions in SO_2 and NO_x emissions will decrease both acidic deposition and PM concentrations.

Sulfate, nitrate, and some partially oxidized organic compounds are hygroscopic and act as nuclei for the formation of cloud droplets. These droplets serve as chemical reactors in which (even slightly) soluble gases can dissolve and react. Thus, SO_2 can dissolve in cloud droplets and be oxidized to sulfuric acid by dissolved ozone or hydrogen peroxide. These reactions take place only in aqueous solution, not in the gas phase. Sulfur dioxide also may be oxidized by dissolved oxygen. This process will be faster if metal catalysts such as iron or manganese are present in solution. If the droplets evaporate, larger particles are left behind. If the droplets grow large enough, they will fall as rain; and the particles will be removed from the atmosphere with potential effects on the materials, plants, or soil on which the rain falls. (Similar considerations apply to dew.) Atmospheric particles that nucleate cloud droplets also may contain other soluble or nonsoluble materials such as metal salts and organic compounds that may add to the toxicity of the rain. Sulfuric acid, ammonium nitrate, ammonium sulfates, and organic particles also are deposited on surfaces by dry deposition. The utilization of ammonium by plants leads to the production of acidity. Therefore, dry deposition of particles can also contribute to the ecological impacts of acid deposition. These effects are discussed in Chapter 4 (Environmental Effects of Airborne Particulate Matter).

2.1.4 Comparison of Fine and Coarse Particles

The physical and chemical properties of fine particles (including ultrafine particles and accumulation-mode particles) and coarse particles are summarized for comparison purposes in Table 2-1. These include important differences in sources, formation mechanisms, composition,, atmospheric residence time, removal processes, and travel distances. Ensuing chapters in this document will also show that fine and coarse particles differ in aspects of concentrations, exposure, dosimetry, toxicology, and epidemiology. Collectively, these differences continue to warrant consideration of fine particles as a separate air pollutant class from coarse particles and the setting of separate standards for fine and coarse particles.

TABLE 2-1. COMPARISON OF AMBIENT PARTICLES, FINE PARTICLES (Ultrafine Plus Accumulation-Mode) AND COARSE PARTICLES

	Fine		
	Ultrafine	Accumulation	Coarse
Formation Processes:	Combustion, high-temperature processes, and atmospheric reactions		Break-up of large solids/droplets
Formed by:	Nucleation Condensation Coagulation	Condensation Coagulation Reactions of gases in or on particles Reactions of gases in or on particles Evaporation of fog and cloud droplets in which gases have dissolved and reacted	Mechanical disruption (crushing, grinding, abrasion of surfaces) Evaporation of sprays Suspension of dusts Reactions of gases in or on particles
Composed of:	Sulfate Elemental Carbon Metal compounds Organic compounds with very low saturation vapor pressure at ambient temperature	Sulfate, Nitrate, Ammonium, and Hydrogen ions Elemental carbon Large variety of organic compounds Metals: compounds of Pb, Cd, V, Ni, Cu, Zn, Mn, Fe, etc. Particle-bound water	Suspended soil or street dust Fly ash from uncontrolled combustion of coal, oil, and wood Nitrates/chlorides from HNO_3/HCl Oxides of crustal elements (Si, Al, Ti, Fe) $CaCO_3$, NaCl, sea salt Pollen, mold, fungal spores Plant and animal fragments Tire, brake pad, and road wear debris
Solubility:	Probably less soluble than accumulation mode	Largely soluble, hygroscopic, and deliquescent	Largely insoluble and nonhygroscopic
Sources:	Combustion Atmospheric transformation of SO_2 and some organic compounds High temperature processes	Combustion of coal, oil, gasoline, diesel fuel, wood Atmospheric transformation products of NO_x, SO_2, and organic compounds, including biogenic organic species (e.g., terpenes) High-temperature processes, smelters, steel mills, etc.	Resuspension of industrial dust and soil tracked onto roads and streets Suspension from disturbed soil (e.g., farming, mining, unpaved roads) Construction and demolition Uncontrolled coal and oil combustion Ocean spray Biological sources
Atmospheric half-life:	Minutes to hours	Days to weeks	Minutes to hours
Removal Processes:	Grows into accumulation mode Diffuses to raindrops	Forms cloud droplets and rains out Dry deposition	Dry deposition by fallout Scavenging by falling rain drops
Travel distance:	<1 to 10s of km	100s to 1000s of km	<1 to 10s of km (100s to 1000s in dust storms)

Source: Adapted from Wilson and Suh (1997).

2.2 MEASUREMENT OF PARTICULATE MATTER

The 1996 PM AQCD (U.S. Environmental Protection Agency, 1996a) summarized sampling and analytical techniques for PM and acid deposition that had appeared in the literature since the earlier 1982 PM AQCD (U.S. Environmental Protection Agency, 1982). Excellent reviews have also been published by Chow (1995) and McMurry (2000). This section discusses problems in measuring PM; new techniques that attempt to alleviate these problems or measure problem species; Federal Reference Methods, speciation monitors, analytical methods for inorganic elements, organic and elemental carbon, and ionic species; and continuous and multiday monitors.

2.2.1 Particle Measurements of Interest

There are many PM components and parameters that are of interest across the various types of uses to which PM measurement data are applied. These uses include analyses of compliance with air quality standards and trends; source category apportionment studies related to the develop of pollution reduction strategies and the validation of air quality models; studies related to health, ecological, and radiative effects; and characterization of current air quality for presentation to the public in the context of EPA's Air Quality Index. PM measurement components and parameters of specific interest for these various purposes are noted below and summarized in Table 2-2.

Particle measurements are needed to determine if a location is in compliance with air quality standards, to determine long-term trends in air quality patterns, and for epidemiologic studies. For these purposes, precision of the measurements by a variety of measurement instruments in use is a critical consideration. Therefore, intercomparisons of various samplers under a variety of atmospheric and air quality conditions are important.

In order to reduce pollution to attain a standard, pollution control agencies and national research organizations need measurements to identify source categories and to develop and validate air quality models. For these purposes, PM parameters other than mass, such as chemical composition and size distribution, must also be measured. Moreover, measurements are needed with shorter time resolution in order to match changes in pollution with diurnal changes in the boundary layer.

TABLE 2-2. PARTICULATE MATTER COMPONENTS/PARAMETERS OF INTEREST FOR HEALTH, ECOLOGICAL, OR RADIATIVE EFFECTS; FOR SOURCE CATEGORY APPORTIONMENT STUDIES; OR FOR AIR QUALITY MODELING EVALUATION STUDIES

- Particle number
- Particle surface area
- Particle size distribution
- PM mass (fine PM mass [$PM_{2.5}$] and coarse thoracic PM mass [$PM_{10-2.5}$]) including both nonvolatile mass as measured by the current Federal Reference method and total mass (including semivolatile components such as ammonium nitrate and semivolatile organic compounds, but not particle-bound water)
- Ions (sulfate, nitrate, and ammonium)
- Strong acidity (H^+)
- Elemental carbon
- Organic carbon (total, nonvolatile, and semivolatile; functional groups and individual species)
- Transition metals (water soluble, bioavailable, oxidant generation)
- Specific toxic elements and organic compounds
- Crustal elements
- Bioaerosols
- Particle refractive index (real and imaginary)
- Particle density
- Particle size change with changes in relative humidity

A number of PM measurements are needed for use in epidemiologic and exposure studies and to determine components of PM to guide planning and interpretation of toxicologic studies. For these purposes, size and chemical composition measurements are important, as is measurement across different time intervals. For epidemiologic studies of acute (i.e., short-term) PM exposures, 1-h or continuous measurements can provide important information beyond that provided by 24-h measurements. However, for epidemiologic studies of chronic PM exposures, measurements that permit integration over longer intervals (e.g., a week to a month) are more relevant. For dosimetric studies and modeling, information will be needed on the particle size distribution and on the behavior of particles as the relative humidity and temperature changes found in the atmosphere are increased to those found in the respiratory system.

For studies of ecological effects and materials damage, measurements of particles and of the chemical components of particulate matter in rain, fog, and dew are needed to understand the contributions of PM to soiling of surfaces and damage to materials and to understand the wet and dry deposition of acidity and toxic substances to surface water, soil, and plants. Some differentiation into particle size is needed to determine dry deposition.

For studies of visibility impairment and radiative effects, information is needed that relates to how particles scatter and absorb light, including refractive index, ratio of scattering to absorption, size distribution, and change in particle size with change in relative humidity.

2.2.2 Issues in Measurement of Particulate Matter

The EPA decision to revise the PM standards by adding daily and yearly standards for $PM_{2.5}$ has led to a renewed interest in the measurement of atmospheric particles and also to a better understanding of the problems in developing precise and accurate measurements of particles. It is very difficult to measure and characterize particles suspended in the atmosphere; however, numerous improvements in PM monitoring are in use and others are in development. EPA's PM standards are based, in part, on epidemiologic relationships between health effects and PM concentrations as measured with existing monitoring methods. As understanding of suspended PM has advanced and new monitoring information has become available, EPA has changed the indicator for the PM NAAQS from TSP to PM_{10}, and added $PM_{2.5}$. During the current PM NAAQS review, consideration will be given to a standard for coarse thoracic PM.

The U.S. Federal Reference Methods (FRM) for $PM_{2.5}$ and PM_{10} provide relatively precise (±10 %) methods for determining the mass of material remaining on a Teflon filter after equilibration. However, numerous uncertainties remain as to the relationship between the mass and composition of material remaining on the filter as determined by the FRM measurement procedure and the mass and composition of material that existed in the atmosphere as suspended PM. As a result, EPA defines accuracy for PM measurements in terms of agreement of a candidate sampler with a reference sampler. Therefore, intercomparison of samplers is very important in determining how well various samplers agree and how various design choices influence what is actually measured.

There are eight general areas where choices are made in the design and use of an aerosol sampler. These include (1) consideration of positive artifacts due to chemical reaction or adsorption; (2) treatment of semivolatile components; (3) selection of particle size cut characteristics for the upper cut point; (4) separation of fine and coarse PM; (5) treatment of pressure, temperature, and relative humidity; (6) time resolution; (7) assessment of the reliability of the measurement technique; and (8) operation and maintenance procedures needed to maintain consistent measurements over time. In many cases, choices have been made without adequate recognition of the consequences. As a result, measurement methods developed by different organizations may give different results when sampling the same atmosphere even though the techniques appear to be similar.

2.2.2.1 Artifacts Due to Chemical Reactions

When TSP was collected on glass fiber filters, the reaction of SO_2 (and other acid gases) with basic sites on the glass fiber or with basic coarse particles on the filter led to the formation of sulfate (or other nonvolatile sales, e.g., nitrate, chloride). These positive artifacts led to overestimation of mass, sulfate (and probably also of nitrate). The metal impurities in the glass fiber caused a high background that led to low precision in the measurement of trace metals. These problems were largely overcome by changing to quartz fiber or Teflon filters and by separate collection of $PM_{2.5}$. However, the possible reaction of acidic gases with basic coarse particles remains a possibility, especially with measurements of PM_{10} and $PM_{10-2.5}$. The reaction of NH_3 with acidic particles, either during sampling or during transportation, storage, and equilibration remains a problem in areas such as the eastern U.S. where PM is frequently acidic. Techniques have been developed that overcome this problem by use of a denuder to remove NH_3 during sampling and to protect the collected PM from NH_3 (Suh et al., 1992, 1994; Brauer et al., 1991; Koutrakis et al., 1988a,b). However, this technique has been applied primarily for measurement of particle strong acidity, not for the measurement of artifact-free ammonium or mass concentrations. In the measurement of particle strong acidity, basic coarse particles must be separated from acidic fine particles (Koutrakis et al., 1992).

2.2.2.2 Treatment of Semivolatile Components of Particulate Matter

Current filtration-based mass measurements can experience significant evaporative losses, during and possibly after collection, of a variety of semivolatile components (i.e., species that exist in the atmosphere in dynamic equilibrium between the condensed phase and gas phase). Important examples include ammonium nitrate, semivolatile organic compounds, and particle-bound water. This problem is illustrated in Figure 2-15.

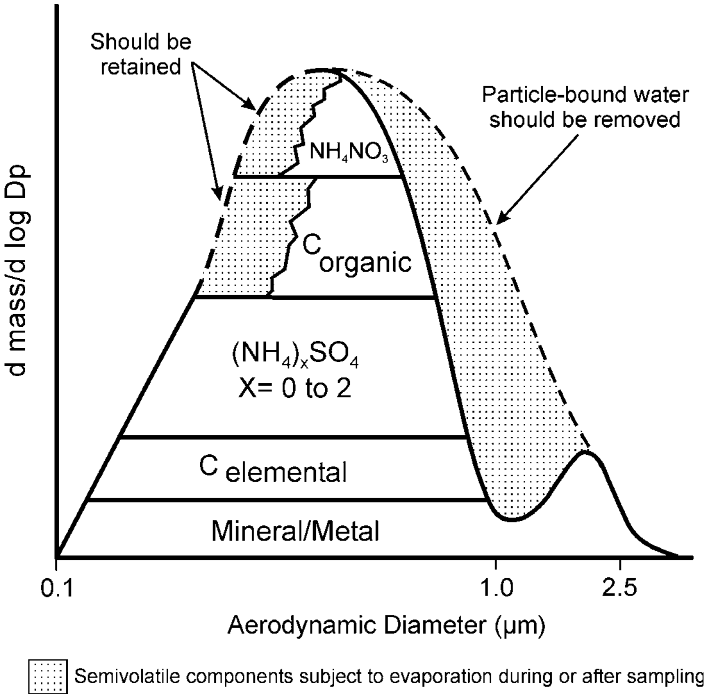

Figure 2-15. Schematic showing major nonvolatile and semivolatile components of $PM_{2.5}$. Semivolatile components are subject to partial to complete loss during equilibration or heating. The optimal technique would be to remove all particle-bound water but no ammonium nitrate or semivolatile organic PM.

Possible approaches that have been used to address the problem of potentially lost semivolatile components include those that follow, which will be discussed in more detail in subsequent sections.

1. Collect/measure all components present in the atmosphere in the condensed phase except particle-bound water. (Examples: Brigham Young absorptive sampler and Harvard pressure drop monitor. Both require preconcentration of the accumulation mode and reduction of ambient humidity.)

2. Stabilize PM at a specified temperature high enough to remove all, or almost all, particle-bound water. This results in loss of much of the semivolatile PM. (Examples: tapered element oscillating microbalance (TEOM) operated at 50 ºC, beta gauge with heated inlet.)

3. Equilibrate collected material at fixed, near-room temperature and moderate relative humidity to reduce particle-bound water. Accept the loss of an unknown but possibly significant fraction of semivolatile PM. (Example: U.S. Federal Reference Method and most filter-weighing techniques.) Equilibration originally was designed to remove adsorbed water vapor from glass fiber filters in order to maintain a stable filter weight. The designated RH (35±5%) was a compromise. If the RH is too low, electrostatic charging becomes a problem. The equilibration process does help provide a stable and reproducible mass. It also reduces the particle-bound water. However, it may not remove all particle-bound water.

2.2.2.3 Upper Cut Point

The upper cut point of the high volume sampler varied with wind speed and direction. Newer PM samplers are usually designed to have an upper cut point and its standard deviation that are independent of wind direction and relatively independent of wind speed. Current PM samplers have upper cut points that are stable under normal operating conditions. However, problems may occur under unusual or adverse conditions. Ono et al. (2000) reported the results of a study in which several PM_{10} samplers were collocated and operated at various sites at Owens Lake, CA, a location with high concentrations of coarse PM. Samplers included the Partisol sampler, the TEOM, a dichotomous sampler, the Wedding high-volume sampler, and the Graseby high-volume sampler. They found that the TEOM and Partisol samplers agreed to within 6% on average. The dichotomous sampler and the Graseby and Wedding high-volume samplers, however, measured significantly lower PM_{10} concentrations than the TEOM (on average 10, 25, and 35% lower, respectively). These lower concentrations were attributed to a decrease in the cut point at higher wind speeds and to a dirty inlet.

The choice of the cut point characteristics depends upon the application for the sampling device. A separation that simulates the removal of particles by the human upper respiratory system might appear to be a good choice for both health risk and regulatory monitoring (i.e., measure what gets into the lungs). The ACGIH-ISO-CEN penetration curve for thoracic particles (particles able to pass the larynx and penetrate into the bronchial and alveolar regions of the lung) has a 50% cut point at 10 μm aerodynamic diameter (D_a). The U.S. PM_{10} separation curve is sharper than the thoracic penetration curve but has the advantage of reducing the problem of maintaining the finite collection efficiency specified by the thoracic penetration curve for particles larger than 10 μm D_a. (See Section 2.1.2.2 and Figure 2-6).

2.2.2.4 Cut Point for Separation of Fine and Coarse Particulate Matter

As shown in Table 2-1, fine and coarse particles differ not only in size but also in formation mechanisms; sources; and chemical, physical, and biological properties. They also differ in concentration-exposure relationships, dosimetry (deposition and retention in the respiratory system), toxicity, and health effects as observed by epidemiologic studies. Thus, it is desirable to measure fine and coarse PM separately in order to properly allocate health effects to either fine or coarse PM and to correctly determine sources by receptor modeling approaches. For example, sulfates in fine particles are associated with hydrogen or ammonium ions while sulfates in coarse particles are associated with basic metal ions. Transition metals in coarse particles are likely to be associated with soil and tend to be less soluble (and presumably less bioavailable) than transition metals in fresh combustion particles found in fine particles.

The 2.5 μm D_a cut point was chosen in the early 1970s as the cut point for a new dichotomous sampler (Loo et al., 1976; Jaklevic et al., 1977) for use in the Regional Air Pollution Study in St. Louis, MO. At that time aerosol scientists were beginning to realize that there was a minimum between 1 and 3 μm in the distribution of particle size by volume (Whitby et al., 1974). The 2.5 μm cut point was subsequently used as an indicator of fine-mode PM in a number of studies including the Harvard Six-City Studies of the relationships between mortality and PM concentrations (Dockery et al., 1993; Schwartz et al., 1996). A 2.5 μm cut point was also used in the Inhalable Particle Network (Suggs and Burton, 1983) which provided data for another major epidemiologic study of PM - mortality relationships using an American Cancer Society cohort (Pope et al., 1995). Therefore, at the time of the last review of the NAAQS for PM (U.S. Environmental Protection Agency, 1996a,b), there were a number of epidemiologic studies demonstrating a statistical relationship between $PM_{2.5}$ concentrations and mortality.

It is now understood that the size range between 1.0 and 2.5 µm, sometimes called the intermodal region may contain either accumulation-mode or coarse-mode material or both, i.e., the two modes may overlap in this region (Kegler et al., 2001). The experimental information on the composition and source of the intermodal mass was discussed extensively in the 1996 PM AQCD (U.S. Environmental Protection Agency, 1996a). Depending on conditions, a significant amount of either accumulation- or coarse-mode material may be found in the intermodal region between 1.0 and 2.5 µm. The analysis demonstrated the important role of relative humidity in influencing the size of particles in both the accumulation and coarse modes.

As the relative humidity increases, hygroscopic accumulation-mode particles will increase in size due to accumulation of particle-bound water. At high relative humidities, some originally submicrometer accumulation-mode PM may be found with a D_a above 1 µm. At a relative humidity of 100%, such as found in fog and clouds, accumulation-mode PM may extend above 2.5 µm D_a. What is not well understood is whether such particles will shrink to diameters below 1 µm as the RH decreases or whether reactions occurring in the wet particles will result in an increase in non-aqueous mass so that even at low RH the diameters would exceed 1 µm. On the other hand, at very low relative humidity, coarse particles may be fragmented into smaller sizes, and small amounts of coarse PM may be found with an D_a below 2.5 µm (Lundgren et al., 1984; Lundgren and Burton, 1995). Thus, a $PM_{2.5}$ sample will contain all of the accumulation-mode PM except during periods of RH near 100 %. However, under conditions of low RH, it may also contain a small fraction of the coarse PM. The selection of a cut point of 2.5 µm as a basis for EPA's 1997 NAAQS for fine particles (Federal Register, 1997) and its continued use in many health effects studies reflect the importance placed on more complete inclusion of accumulation-mode particles while recognizing that intrusion of coarse particles can occur under some conditions with this cut point.

In addition to the influence of relative humidity, in areas where winds cause high concentrations of windblown soil there is evidence that a significant amount of coarse-mode PM may be found below 2.5 µm. An example, taken from data collected during the August 1996 dust storm in Spokane, WA, is shown in Figure 2-16. Note that the PM_{10} scale is 10 times that of the other size fractions. PM_1, although high in the morning, goes down as the wind increases and PM_{10}, $PM_{2.5}$, and $PM_{2.5-1}$ go up. During the peak of the dust storm, around 9 pm, $PM_{2.5-1}$ was 88% of $PM_{2.5}$. For the 24-h period, $PM_{2.5-1}$ was 54% of $PM_{2.5}$. However, PM_1 was not affected by the intrusion of coarse particles. Similar considerations probably apply to short-term intrusions of dust transported from distant sources such as the Sahara and Gobi deserts (Husar et al., 2001).

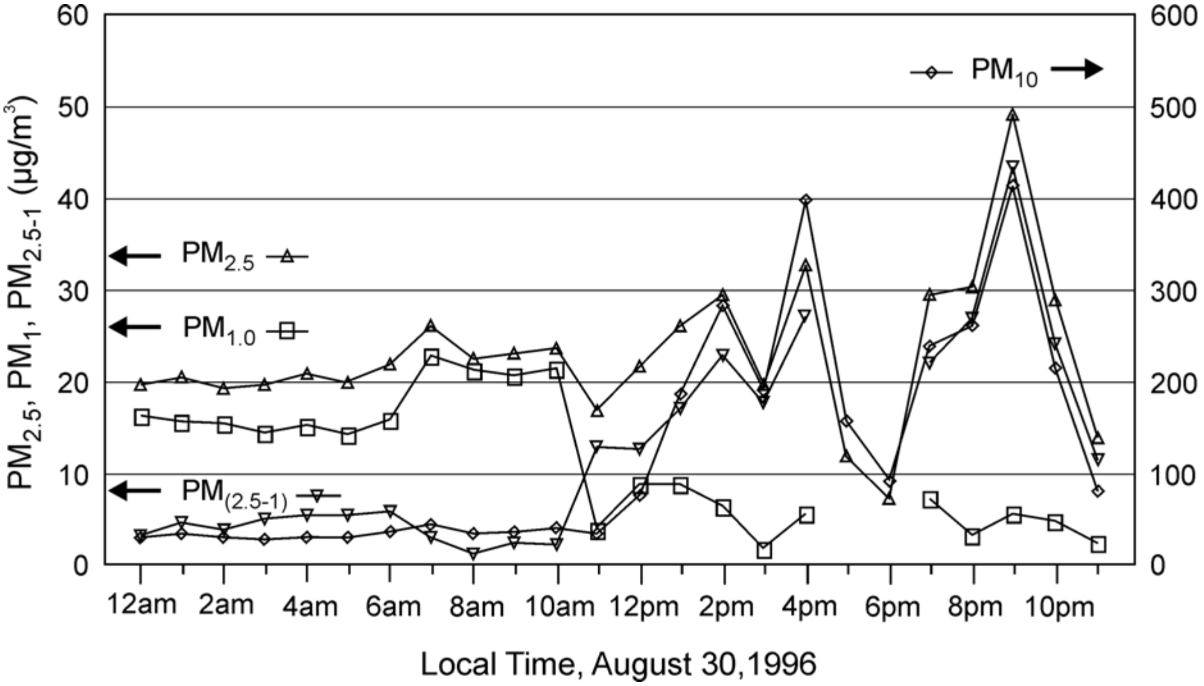

Figure 2-16. Particulate matter concentrations in Spokane, WA, during the August 30, 1996 dust storm.

Source: Claiborn et al. (2000).

A cut point of 1.0 µm could reduce the misclassification of coarse-mode material as fine, especially in areas with high levels of wind blown soil, but under high RH conditions could result in some accumulation-mode material being misclassified as coarse. A reduction in RH, either intentionally or inadvertently, will reduce the mass mean diameter of the accumulation-mode particles. A sufficient reduction in RH should yield a dry accumulation mode with very little material above 1.0 µm. Studies of the changes in particle size with changes in relative humidity suggest that only a small fraction of accumulation-mode particles will be above 1.0 µm in diameter at RH below 60%, but a substantial fraction will grow above 1.0 µm for RH above 80% (Hitzenberger et al., 1997; McMurry and Stolzenburg, 1989; U.S. Environmental Protection Agency, 1996a).

Under high relative humidity circumstances, a monitor using a 1.0 µm D_a cut point can achieve better modal separation if the air stream is dehumidified to some fixed humidity that would remove all or most particle-bound water without evaporating semivolatile components. New techniques which require reduction of RH prior to collection have been developed for measurement of fine particulate matter minus particle-bound water but including semivolatile nitrate and organic compounds. With such techniques, PM_1 measurements in conjunction with concurrent $PM_{2.5}$ measurements would be useful for exposure, epidemiologic, and source apportionment studies especially in areas where intrusion of coarse-mode particles into the intermodal range is likely.

2.2.2.5 Treatment of Pressure, Temperature, and Relative Humidity

There are a variety of techniques for defining (or ignoring) the pressure, temperature, and relative humidity during and after sampling. For example, the sample volume may be based on the mass or volumetric flow corrected to standard temperature and pressure (273 °K and 1 atm.) (current FRM for PM_{10}), or it may be based on the volumetric flow at ambient conditions of temperature and pressure (current FRM for $PM_{2.5}$).

There are also a variety of options for the control of temperature during collection. The particles may be heated enough to remove much of the particle-bound water (i.e., TEOM at 50 °C); the particles may be heated several degrees, just enough to prevent condensation of water in the sampling system; the particles and the sampler may be maintained near ambient temperature (±5 ˚C of ambient temperature is required for EPA FRM samplers); or the particles and sampler may be maintained at constant temperature inside a heated or air conditioned shelter. There are also options for control of temperature after collection: (a) no control (room temperature) or (b) ship and store at cool temperature (4 °C is the current EPA FRM requirement).

Consideration must also be given to relative humidity. Changes in relative humidity cause changes in particle size of hygroscopic or deliquescent particles. Changing relative humidity by adding or removing water vapor affects measurements of particle number, particle surface area, and particle size distribution and the amount of overlap of accumulation-mode and coarse-mode particles. Changing relative humidity by intentional or inadvertent changes in temperature also affects the amount of loss of ammonium nitrate and semivolatile organic compounds. Monitoring personnel should be aware of the various options for treatment of pressure, temperature, and relative humidity; make appropriate selections; and document which options are used.

Studies of relationships between personal/indoor/outdoor measurements present special problems. Indoor environments are typically dryer than outdoors and may be warmer or, if air-conditioned, cooler. These differences may change particle size and the amount of volatilization of semivolatile components. Such changes between indoors and outdoors will complicate the comparison of indoor to outdoor PM concentrations; the modeling of personal exposure to all particles; and apportionment of personal exposure into particles of ambient origin, particles of indoor origin, and particles originating from personal activity.

2.2.2.6 Time Resolution

The classic 24-hour filter collection technique is being supplemented by a variety of continuous monitors for various PM constituents. This process is being accelerated by the lower operational cost of continuous monitors and the availability of new continuous monitors for mass, number, and certain chemical components, as well as refinements of older methods based on beta attenuation or light scattering. Most epidemiologic studies have used 24-hour concentrations as exposure indicators. However, one epidemiologic study of chronic effects uses a filter sampler with a two-week collection period (Gauderman et al., 2000). Another recent study used 1-2 h concentrations (see Peters et al., 2000). Continuous methods are discussed in Section 2.2.5.

2.2.2.7 Accuracy and Precision

Precision is typically determined by comparison of collocated samplers or through replicate analyses; whereas accuracy is determined through the use of traceable calibration standards. Unfortunately, no standard reference calibration material or procedure has been developed for suspended, atmospheric PM. It is possible to determine the accuracy of certain components of the PM measurement system (e.g., flow control, inlet aspiration, $PM_{2.5}$ cut, weighing, etc.). The absolute accuracy for collecting a test aerosol can also be determined by isokinetic sampling in a wind tunnel. However, it is not currently feasible to provide a simulated atmospheric aerosol with naturally occurring semivolatile components. It is particularly challenging to develop an atmospheric aerosol calibration standard suitable for testing samplers in the field. Therefore, it is not possible at the present time to establish the absolute accuracy of a PM monitoring technique. Intercomparison studies may be used to establish the precision of identical monitors and the extent of agreement between different types of monitors. Such studies are important for establishing the reliability of PM measurements. Intercomparison studies have contributed greatly to our understanding of the problems in PM measurement. Such studies will be discussed as they apply to specific measurement problems, monitoring instruments, or analytical techniques.

Some measurement errors of concern in PM_{10} sampling, including those that arise due to uncertainty tolerances in cutpoint, particle bounce and reentrainment, impactor surface overloading, and losses to sampler internal surfaces, were discussed in detail in the 1996 PM AQCD (U.S. Environmental Protection Agency, 1996a). Other measurement errors of concern in $PM_{2.5}$ sampling arise because of our inability to assess accuracy in an absolute sense due to a lack of an atmospheric aerosol calibration standard, the inclusion in $PM_{2.5}$ of a small amount of coarse particles as discussed in Section 2.2.1.3, problems associated with the definition of $PM_{2.5}$ as what remains on a filter after collection and equilibration rather than as the mass of particles as they exist in the air. Still, it is possible to measure PM indicators with high precision. Detailed information on precision and quality assurance may be found on EPA's Technology Transfer Network website (U.S. Environmental Protection Agency, 2002a). See discussion in Section 2.2.4.

Because of the difficulties associated with determining the accuracy of PM measurements, EPA has sought to make FRM measurements equivalent by specifying operating conditions and, in the case of $PM_{2.5}$ samplers, by specifying details of the sampler design. Thus, both the PM_{10} as well as the $PM_{2.5}$ standards are defined with consistency of measurement technique rather than with the accuracy of the true mass concentration measurement in mind (McMurry, 2000). It is acknowledged in the Federal Register (1997) that, "because the size and volatility of the particles making up ambient particulate matter vary over a wide range and the mass concentration of particles varies with particle size, it is difficult to define the accuracy of $PM_{2.5}$ measurements in an absolute sense…." Thus, accuracy is defined as the degree of agreement between a field $PM_{2.5}$ sampler and a collocated $PM_{2.5}$ reference method audit sampler (McMurry, 2000). The Federal Reference Method for $PM_{2.5}$ is discussed in Section 2.2.3.3. As mentioned earlier, volatilization of organic compounds and ammonium nitrate during sampling or post-sampling handling can lead to significant underestimation of the fine particulate mass concentration in some locations. Sources of error in the measurement of mass of $PM_{2.5}$ suspended in the atmosphere also arise because of adsorption or desorption of semivolatile vapors onto or from collected PM, filter media, or other sampler surfaces; neutralization of acid or basic vapors on either filter media or collected PM; and artifacts associated with particle-bound water.

During the past 25 years, there have been advancements in the generation and classification of monodisperse aerosols as well as in the development of electron microscopy and imaging analysis that have contributed to the advancement in aerosol calibration (Chen, 1993). Still, one of the limitations in PM sampling and analysis remains the lack of primary calibration standards for evaluating analytical methods and for intercomparing laboratories. Klouda et al. (1996) examined the possibility of resuspending the National Institute of Science and Technology (NIST) Standard Reference Material 1649 (Urban Dust) in air for collection on up to 320 filters simultaneously using Standard Research International's dust generation and collection system. However, the fine component is not resuspended and the semivolatile component has evaporated. Consequently, this material is not a suitable standard for suspended PM. NIST is continuing work in this area with EPA support.

Methods validation was discussed in the 1996 PM AQCD (U.S. Environmental Protection Agency, 1996a), and the usefulness of intercomparisons and "internal redundancy" was emphasized. For example, a number of internal consistency checks are applied to the IMPROVE network (Malm et al., 1994). These include mass balances, sulfur measurements by both proton-induced X-ray emission (PIXE) and ion chromatography (IC), and comparison of organic matter by combustion and by proton elastic scattering (PESA) of hydrogen. Mass balances compare the gravimetrically determined mass with the mass calculated from the sum of the major chemical components (i.e., crustal elements plus associated oxygen, organic carbon, elemental carbon, sulfate, nitrate, ammonium, and hydrogen ions). Mass balances are useful validation techniques; however, they do not check for, or account for, artifacts associated with the absorption of gases during sampling or the loss of semivolatile material during sampling. The mass balance check may appear reasonable even if such artifacts are present because only the material collected on the filter is included in the balance. Mass balance checks may also suffer from errors due to some particle-bound water remaining in the PM even after equilibration and from the use of an arbitrary factor to account for the amount of oxygen and hydrogen atoms per carbon atom in the organic carbon fractions (Andrews et al., 2000).

2.2.3 Measurement of Semivolatile Particulate Matter

PM suspended in the atmosphere is composed of many chemical species having a wide range of vapor pressures. Substances with vapor pressures below 10^{-9} Torr (mmHg) will typically be nonvolatile; substances with vapor pressures above 10^{-1} Torr will be primarily in the gas phase; substances with vapor pressures between 10^{-1} and 10^{-9} Torr may exist in an equilibrium state with some material in both the gas phase and the condensed (particulate) phase and are known semivolatile material (SVM) (Pankow, 1994a). SVM, originally in the atmosphere in the particulate phase and collected on a filter, may subsequently be lost from the filter. SVM may evaporate during sampling due to a reduction in its concentration in the atmosphere being sampled or due to the pressure drop across the filter. SVM may evaporate after sampling; during intentional equilibration at a low relative humidity; or during transport, handling, and storage if exposed to an atmosphere in which the vapor pressure of one or more semivolatile components is lower than in the atmosphere sampled. Since water is not a pollutant, it is necessary to remove most of the particle-bound water before weighing (Chow, 1995). However, collection and measurement of ammonium nitrate and semivolatile organic compounds in suspended atmospheric PM represents a major analytical challenge (McMurry, 2000).

2.2.3.1 Particle-Bound Water

It is generally desirable to collect and measure ammonium nitrate and semivolatile organic compounds. However, for many measurements of suspended particle mass, it is desirable to remove the particle-bound water before determining the mass. The mass of particle-bound water is strongly dependent on the relative humidity. However, the dependence is not linear since there is significant hysteresis in the water adsorption-desorption pathways (Seinfeld and Pandis, 1998). Water vapor is not a pollutant and cannot be controlled. Particle-bound water is not included in the mass of PM subject to regulation and control. Because the mass of particle-bound water could be equal or greater than that of the other components, a measurement of PM mass including particle-bound water would depend more on relative humidity that pollution. For all these reasons, it is usually desirable to remove most, if not all, particle-bound water before weighing collected PM. However, in some situations it may be important to know how much of the suspended particle's mass or volume results from particle-bound water. Figures 2-13 and 2-14 show the change in diameter of sulfate particles as a function of relative humidity. Figure 2-13 also shows hysteresis resulting from the difference between deliquescence and crystallization points.

Pilinis et al. (1989) calculated the water content of atmospheric particulate matter above and below the deliquescent point. They predicted that aerosol water content is strongly dependent on composition and concluded from their calculations that liquid water could represent a significant mass fraction of aerosol concentration at relative humidities above 60%. Since then, a few researchers have attempted to measure the water content of atmospheric aerosol. Most techniques have focused on tracking the particle mass as the relative humidity is changed and are still in the development phase. There have been only a few demonstrations using actual ambient aerosol to date. Of interest, in particular, is the development of the Tandem Differential Mobility Analyzer (TDMA) and its applications in investigations of the effects of relative humidity on particle growth.

Lee et al. (1997) examined the influence of relative humidity on the size of atmospheric aerosol using a TDMA coupled with a scanning mobility particle sizer (SMPS). They reported that the use of the TDMA/SMPS system allowed for the abrupt size changes of aerosols at the deliquescence point to be observed precisely. They also reported that at relative humidities between 81 and 89% the water content of ammonium sulfate aerosols (by mass) ranged from 47 to 66%.

Andrews and Larson (1993) investigated the interactions of single aerosol particles coated with an organic film within a humid environment. Using an electrodynamic balance, they conducted laboratory experiments in which sodium chloride and carbon black particles were coated with individual organic surfactants (intended to simulate the surface-active, organic films that many atmospheric aerosol particles may exhibit) and their water sorption curves were examined. Their results showed that when ordinarily hydrophobic carbon black particles were coated with an organic surfactant, they sorbed significant amounts of water (20 to 40% of the dry mass of the particle).

Liang and Chan (1997) developed a fast technique using the electrodynamic balance to measure the water activity of atmospheric aerosols. In their technique, the mass of a levitated particle is determined as the particle either evaporates or grows in response to a step change in the relative humidity. Their technique was demonstrated using laboratory experiments with NaCl, $(NH_4)_2SO_4$, $NaNO_3$, and $(NH_4)_2SO_4/NH_4NO_3$ solutions. They concluded that one of the advantages of their fast method is the ability to measure the water activity of aerosols containing volatile solutes such as ammonium chloride and some organics.

McInnes et al. (1996) measured aerosol mass concentration, ionic composition, and associated water mass of marine aerosol over the remote Pacific Ocean. The mass of particle-bound water was determined by taking the difference between the mass obtained at 48% RH and at 19% RH, assuming the aerosol particles were dry at 19% RH. Based on a comparison of the remote Pacific aerosol to aerosol collected at a site at the marine/continental interface of the Washington coast, the amount of water associated with the aerosol was observed to be a function of the ammonium to sulfate ratio. They found that the amount of water associated with the submicrometer aerosol comprised 29% of the total aerosol mass collected at 47% RH and 9% of the total mass at 35% RH.

Ohta et al. (1998) characterized the chemical composition of atmospheric fine particles (50% cut point of 2 μm) in Sapporo, Japan, and as part of their measurements, determined the water content using the Karl Fischer method (Meyer and Boyd, 1959). After exposing a Teflon filter, a portion of the filter was equilibrated at 30% RH for 24 h. Then the filter piece was placed in a water evaporator heated at 150 °C, vaporizing the particle-bound water. The vapor evolved was analyzed for water in an aqua-counter where it was titrated coulometrically in Karl Fischer reagent solution (containing iodine, sulfur, and methanol). The accuracy of the aqua-counter is ±1 mg. Using this technique, they determined that the water content of the particles ranged from 0.4 to 3.2% of the total particulate mass (at RH < 30%). This represents a smaller portion of water compared to their previous reported values (Ohta and Okita, 1990) that were determined by calculation at RH of 50%.

Speer et al. (1997) developed an aerosol liquid water content analyzer (LWCA) in which aerosol samples are collected on PTFE filters and then placed in a closed chamber in which the relative humidity is closely controlled. The aerosol mass is monitored using a beta-gauge, first as the relative humidity is increased from low RH to high RH, and then as the RH is decreased again. They demonstrated the LWCA on laboratory-generated aerosol and on an ambient $PM_{2.5}$ sample collected in Research Triangle Park, NC. The ambient aerosol sample was also analyzed for chemical constituents. It is interesting to note that, although their laboratory-generated $(NH_4)_2SO_4$ aerosol demonstrated a sharp deliquescent point, their atmospheric aerosol, which was essentially $(NH_4)_2SO_4$, did not show a sharp deliquescent point.

Hygroscopic properties of aerosols have been studied from the viewpoint of their ability to act as condensation nuclei. The hygroscopic properties of fresh and aged carbon and diesel soot particles were examined by Weingartner et al. (1997) who found that fresh, submicron-size particles tended to shrink with increasing relative humidity because of a structural change. Lammel and Novakov (1995) found, in laboratory studies, that the hygroscopicity of soot particles could be increased by chemical modification and that the cloud condensation nucleation characteristics of diesel soot were similar to those of wood smoke aerosol.

The results of several of the above studies in which aerosol water content as a function of relative humidity was determined are summarized in Figure 2-17. In this figure, the results of Lee et al. (1997), McInnes et al. (1996), and Ohta et al. (1998) are included. Relative humidity ranged from 9%, at which the aerosol water content was assumed to be zero (McInnes et al., 1996), to 89%, at which the aerosol water content was determined to be 66% by mass (Lee et al., 1997). Koutrakis et al. (1989) and Koutrakis and Kelly (1993) also have reported field measurements of the equilibrium size of atmospheric sulfate particles as a function of relative humidity and acidity.

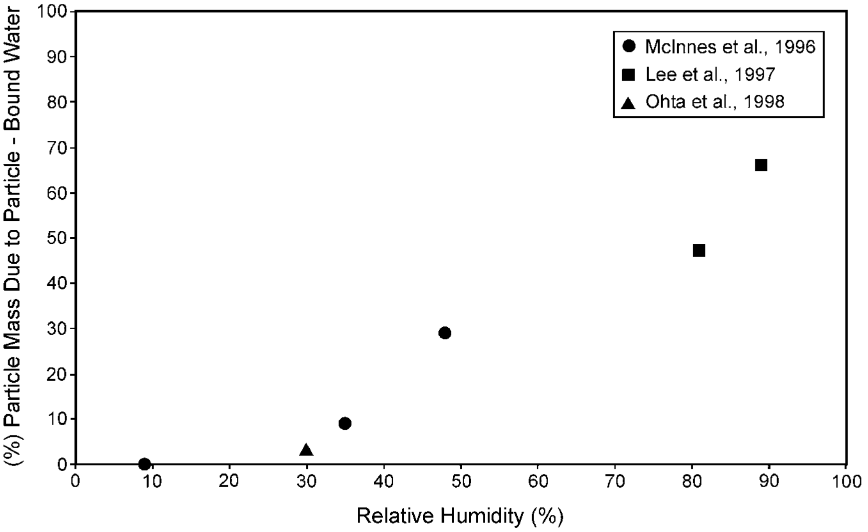

Figure 2-17. Aerosol water content expressed as a mass percentage, as a function of relative humidity.

The effects of relative humidity on particle growth were also examined in several studies. Fang et al. (1991) investigated the effects of flow-induced relative humidity changes on particle cut sizes for aqueous sulfuric acid particles in a multi-nozzle micro-orifice uniform deposit impactor (MOUDI). Laboratory experiments were conducted in which polydisperse sulfuric acid aerosols were generated and the RH was adjusted. The aerosols were analyzed by a differential mobility analyzer. Fang et al. (1991) observed that for inlet RH less than 80%, the cut sizes for the sulfuric acid aerosols were within 5% of that for nonhygroscopic particles except at the stage for which the cut size was 0.047 μm where the cut size was 10.7% larger than the nonhygroscopic particle cut size. They concluded that flow-induced RH changes would have only a modest effect on MOUDI cut sizes at RH < 80%.

Hitzenberger et al. (1997) collected atmospheric aerosol in the size range of 0.06 to 15 μm in Vienna, Austria, using a nine-stage cascade impactor and measured the humidity-dependent water uptake when the individual impaction foils were exposed to high RH. They observed particle growth with varying growth patterns. Calculated extinction coefficients and single scattering albedo increased with humidity.

Hygroscopic properties, along with mixing characteristics, of submicrometer particles sampled in Los Angeles, CA, during the summer of 1987 SCAQS study and at the Grand

Canyon, AZ, during the 1990 Navajo Generating Station Visibility Study were reported by Zhang et al. (1993). They used a tandem differential mobility analyzer (TDMA; McMurry and Stolzenburg, 1989) to measure the hygroscopic properties for particles in the 0.05- to 0.5-μm range. In their experimental technique, monodisperse particles of a known size are selected from the atmospheric aerosol with the first DMA. Then, the relative humidity of the monodisperse aerosol is adjusted, and the new particle size distribution is measured with the second DMA. At both sites, they observed that monodisperse particles could be classified according to "more" hygroscopic and "less" hygroscopic. Aerosol behavior observed at the two sites differed markedly. Within the experimental uncertainty (±2%) the "less" hygroscopic particles sampled in Los Angeles did not grow when the RH was increased to 90%; whereas at the Grand Canyon, the growth of the "less" hygroscopic particles varied from day to day, but ranged from near 0 to 40% when the RH was increased to 90%. The growth of the "more" hygroscopic particles in Los Angeles was dependent on particle size (15% at 0.05 μm to 60% at 0.5 μm); whereas at the Grand Canyon, the "more" hygroscopic particles grew by about 50% with the growth not varying significantly with particle size. By comparison of the TDMA data to impactor data, Zhang et al. (1993) surmised that the more hygroscopic particles contained more sulfates and nitrates while the less hygroscopic particles contained more carbon and crustal components.

Although most of the work to date on the hygroscopic properties of atmospheric aerosols has focused on the inorganic fraction, the determination of the contribution of particle-bound water to atmospheric particulate mass is greatly complicated by the presence of organics. The effect of RH on adsorption of semivolatile organic compounds is discussed elsewhere in this chapter. Saxena et al. (1995) observed that particulate organic compounds also can affect the hygroscopic behavior of atmospheric particles. They idealized the organic component of aerosol as containing a hydrophobic fraction (high-molecular weight alkanes, alkanoic acids, alkenoic acids, aldehydes, and ketones) and a hydrophilic fraction (e.g., lower molecular weight carboxylic acids, dicarboxylic acids, alcohols, aldehydes, etc.) that would be likely to absorb water. They then analyzed data from a tandem differential mobility analyzer in conjunction with particle composition observations from an urban site (Claremont, CA) and from a nonurban site (Grand Canyon) to test the hypothesis that, by adding particulate organics to an inorganic aerosol, the amount of water absorbed would be affected, and the effect could be positive or negative, depending on the nature of the organics added. They further presumed that the particulate organic matter in nonurban areas would be predominantly secondary and thus hydrophilic, compared to the urban aerosol that was presumed to be derived from primary emissions and thus hydrophobic in nature. Their observations were consistent with their hypothesis, in that at the Grand Canyon, the presence of organics tended to increase the water uptake by aerosols; whereas at the Los Angeles site, the presence of organics tended to decrease water uptake.

Peng and Chan (2001) also recently studied the hygroscopic properties of nine water soluble organic salts of atmospheric interest using an electrodynamic balance operated at 25°C. Salts studied included sodium formate, sodium acetate, sodium succinate, sodium pyruvate, sodium methanesulfonate, sodium oxalate, ammonium oxalate, sodium malonate, and sodium maleate. They observed that hygroscopic organic salts have a growth factor of 1.76-2.18 from RH=10-90%, comparable to that of typical hygroscopic inorganic salts such as NaCl and $(NH_4)_2SO_4$.

Nonequilibrium issues may be important for the TDMA, as well as for other methods of measuring water content. Although approach to equilibrium when the RH is increased is expected to be rapid for pure salts, it may be much slower for aerosols containing a complex mix of components (Saxena et al., 1995). For example, if an aerosol contains an organic film or coating, that film may impede the transport of water across the particle surface, thus increasing the time required for equilibrium (Saxena et al., 1995). Insufficient time to achieve equilibrium in the TDMA could result in underestimation of the water content.

2.2.3.2 Nitrate and Organic Species

Particulate Nitrates

It is now well known that volatilization losses of particulate nitrates occur during sampling on Teflon filters (e.g., Zhang and McMurry [1992]; see also Hering and Cass [1999] and Babich et al., [2000]). The effect on the accuracy of atmospheric particulate measurements from these volatilization losses is more significant for $PM_{2.5}$ than for PM_{10}. The FRM for $PM_{2.5}$ will likely suffer loss of nitrates similar to that experienced with other simple filter collection systems. Sampling artifacts resulting from the loss of particulate nitrates represents a significant problem in areas such as southern California that experience high amounts of nitrates. Hering and Cass (1999) reported on errors in $PM_{2.5}$ mass measurements due to volatilization of particulate nitrate

(Figure 2-18). They examined data from two field measurement campaigns conducted in southern California: (1) the Southern California Air Quality Study (SCAQS) (Lawson, 1990) and (2) the 1986 CalTech study (Solomon et al., 1992). In both these studies, side-by-side sampling of $PM_{2.5}$ was conducted. One sampler collected particles directly onto a Teflon filter. The second sampler consisted of a denuder to remove gaseous nitric acid followed by a nylon filter that absorbs the HNO_3 which evaporates from ammonium nitrate. In both studies, the denuder consisted of MgO-coated glass tubes (Appel et al., 1981). Fine particulate nitrate collected on the Teflon filter was compared to fine particulate nitrate collected on the denuded nylon filter. In both studies, the $PM_{2.5}$ mass lost because of volatilization of ammonium nitrate represented a significant fraction of the total $PM_{2.5}$ mass. The fraction of mass lost was higher during summer than during fall (17% versus 9% during the SCAQS study and 21% versus 13% during the CalTech study; Figure 2-18). In regard to percentage loss of nitrate, as opposed to percentage loss of mass discussed above, Hering and Cass (1999) found that nitrate remaining on the Teflon filter samples was on average 28% lower than that on the denuded nylon filters.

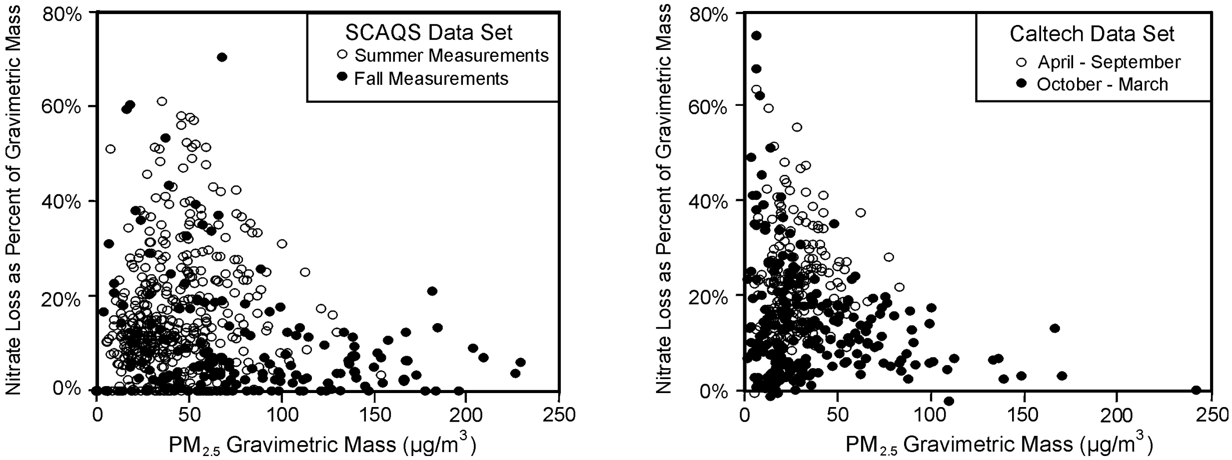

Figure 2-18. Amount of ammonium nitrate volatilized from Teflon filters, expressed as a percentage of the measured $PM_{2.5}$ mass, for the SCAQS and CalTech studies, for spring and fall sampling periods.

Source: Hering and Cass (1999).

Hering and Cass (1999) also analyzed these data by extending the evaporative model developed by Zhang and McMurry (1987). The extended model utilized by Hering and Cass (1999) takes into account dissociation of collected particulate ammonium nitrate on Teflon filters into nitric acid and ammonia via three mechanisms: (1) scrubbing of nitric acid and ammonia in the sampler inlet (John et al., 1988 showed that clean PM_{10} inlet surfaces serve as an effective denuder for nitric acid), (2) heating of the filter substrate above ambient temperature by sampling, and (3) pressure drop across the Teflon filter. For the sampling systems modeled, the flow-induced pressure drop was measured to be less than 0.02 atm, and the corresponding change in vapor pressure was 2%, so losses driven by pressure drop were not considered to be significant in this work. Losses from Teflon filters were found to be higher during the summer compared to the winter, higher during the day compared to night, and reasonably consistent with modeled predictions.

Finally, during the SCAQS study, particulate samples also were collected using a Berner impactor and greased Tedlar substrates in size ranges from 0.05 to 10 μm in aerodynamic diameter. The Berner impactor $PM_{2.5}$ nitrate values were much closer to those from the denuded nylon filter than those from the Teflon filter with the impactor nitrate being approximately 2% lower than the nylon filter nitrate for the fall measurements and approximately 7% lower during the summer measurements. When the impactor collection was compared to the Teflon filter collection for a nonvolatile species (sulfate), the results were in agreement.

It should be noted that filters or collection surfaces were removed immediately after sampling and placed into vials containing a basic extraction solution during these intercomparison studies. Therefore, losses that might occur during handling, storage, and equilibration of filters or impaction surfaces were avoided. The loss of nitrate observed from Teflon filters and impaction surfaces in this study, therefore, is a lower limit compared to losses that might occur during the normal processes involved in equilibration and weighing of filters and impaction surfaces. Brook and Dann (1999) observed much higher nitrate losses during a study in which they measured particulate nitrate in Windsor and Hamilton, Ontario, Canada, by three techniques: (1) a single Teflon filter in a dichotomous sampler, (2) the Teflon filter in an annular denuder system (ADS), and (3) total nitrate including both the Teflon filter and the nylon back-up filter from the ADS. The Teflon filter from the dichotomous sampler averaged only 13% of the total nitrate. The Teflon filter from the ADS averaged 46% of the total nitrate.

The authors concluded that considerable nitrate was lost from the dichotomous sampler filters during handling, which included weighing and x-ray fluorescence (XRF) measurement in a vacuum.

Kim et al. (1999) also examined nitrate sampling artifacts by comparing denuded and undenuded quartz and nylon filters, during the PM_{10} Technical Enhancement Program (PTEP) in the South Coast Air Basin of California. They observed negative nitrate artifacts (losses) for most measurements; however, for a significant number of measurements they observed positive nitrate artifacts. Kim et al. (1999) pointed out that random measurement errors make it difficult to measure true amounts of nitrate loss.

Diffusion denuder samplers, developed primarily to measure particle strong acidity (Koutrakis et al., 1988a,b, 1992), also can be used to study nitrate volatilization. Such techniques were used to measure loss of particulate nitrate from Teflon filters in seven U.S. cities (Babich et al., 2000). Measurements were made with two versions of the Harvard-EPA Annular Denuder System (HEADS). Nitric acid vapor was removed by a Na_2CO_3-coated denuder. Particulate nitrate was the sum of nonvolatile nitrate collected on a Teflon filter and volatized nitrate collected on a Na_2CO_3-coated denuder downstream of the Teflon filter (full HEADS) or on a Nylon filter downstream of the Teflon filter (Nylon HEADS). It was found that full HEADS (using a Na_2CO_3 denuder) consistently underestimated the total particulate nitrate by approximately 20% compared to the nylon HEADS. Nonvolatilized nitrate was also measured on a Teflon filter from collocated Harvard Impactors (HI). The $PM_{2.5}$ HI sampler, like the $PM_{2.5}$ FRM, use impactors with a 50% cut at 2.5 µm. The HI uses a 37 mm filter and a flow rate of 10 L/min (0.465 $L/min/cm^2$) which the FRM uses a 47 mm filter and a flow rate of 16.7 L/min (0.481 $L/min/cm^2$). Therefore, the flow rate and pressure drop across the filters are similar and the loss of nitrate should be similar in both types of samples. Babich et al. (2000) found significant nitrate losses in Riverside, CA; Philadelphia, PA; and Boston, MA but not in Bakersfield, CA; Chicago, IL; Dallas, TX; or Phoenix, AZ where measurements were made only during winter.

Eatough et al. (1999a) developed a high-volume diffusion denuder system in which diffusion denuder and particle concentrator techniques were combined (see Section 2.2.3.2). The particle concentrator reduces the flow through the denuder so that the denuder can be operated for weeks without a loss of collection efficiency, making the sampler suitable for routine field sampling. The system was evaluated for the collection of fine particulate sulfate and nitrate in Riverside, CA (Eatough et al., 1999b). Concentrations of $PM_{2.5}$ nitrate obtained from the PC-BOSS agreed with those obtained using the Harvard-EPA Annular Denuder Sampler, HEADS (Koutrakis et al., 1988b).

Particulate Organic Compounds

Many semivolatile organic compounds (SVOC) are of interest because of their possible health effects. SVOC include products of incomplete combustion such as polycyclic aromatic hydrocarbons (PAHs) and polycyclic organic matter, which has been identified as a hazardous air pollutant. PAHs also have been suggested as alternative particulate tracers for automobile emissions because the phase-out of organo-lead additives to gasoline means that lead is no longer a good tracer for automobiles (Venkataraman et al., 1994). PAHs also are emitted during biomass burning, including burning of cereal crop residues and wood fuels (Jenkins et al., 1996; Roberts and Corkill, 1998).

A number of studies have used absorbing material following quartz filters to determine phase equilibria of specific organic compounds (Liang et al., 1997; Gundel et al., 1995; Kamens et al., 1995). Much work has also gone into the development of a theory to help understand the phase relationships (Yamasaki et al., 1982; Rounds and Pankow, 1990; Pankow, 1987, 1994a,b; Pankow et al., 1993; Rounds et al., 1993; Odum et al., 1994). The theory describing phase equilibria of semivolative organic compounds (SVOC) and the gas/particle partitioning of SVOC on inorganic, organic, and ambient smog aerosols continues to be developed (Liang et al., 1997; Jang et al., 1997, 1999; Strommen and Kamens, 1997; Jang and Kamens, 1998, 1999, 2001; Leach et al., 1999; Kamens et al., 1999, 2001).

The mass of organic and elemental carbon is usually determined by analysis of PM collected on a quartz filter. However, quartz fiber filters have a large specific surface area on which adsorption of gases can occur. Possible artifacts associated with adsorption of organic gases onto quartz filters have been examined in experiments in which two quartz fiber filters were deployed in series. The second quartz filter may indicate gaseous volatile organic compounds (VOC) adsorbed on both filters (positive artifact), SVOC evaporated from particles on the first filter and subsequently adsorbed on the second filter (negative artifact), or a combination of both effects. Unless the individual compounds are identified, the investigator does not know what to do with the loading value on the second filter (i.e., to add or subtract from the first filter loading value). Moreover, even if the individual compounds were identified on the back-up filter, the decision concerning adding or subtracting the back-up filter loading would not be straightforward.

The positive quartz filter artifact has been discussed by Gundel et al. (1995) and Turpin et al. (2000). It is also possible that some SVOC may desorb from the filter resulting in a negative artifact (Eatough et al., 1993; Tang et al., 1994; Eatough et al., 1995; Gundel et al., 1995; Cui et al., 1998; Pang et al., 2001; Finn et al., 2001). Semivolatile organic compounds can similarly be lost from Teflon filters because of volatilization, causing the $PM_{2.5}$ mass to be significantly underestimated (negative artifact). Like particulate nitrates, the FRM for $PM_{2.5}$ will suffer loss of SVOC, similar to the losses experienced with other simple filter collection systems. Most studies that have focused on the positive and negative sampling artifacts associated with SVOC compounds have utilized either diffusion denuder technology (Eatough et al., 1995; Mader et al., 2001) or placed an adsorbent media, such as a back-up quartz filter or a polyurethane foam adsorbent behind the main filter (Wallace and Hites, 1995). Further information on denuder techniques are given in Appendix 2A.

Using their multichannel diffusion denuder sampling system (BOSS), Eatough et al. (1995) reported that, for samples collected at the South Coast Air Quality Management District sampling site at Azusa, CA, changes in the phase distribution of SVOC could result in a loss on average of 35% of the particulate organic material. Cui et al. (1998) found that losses of SVOC from particles in the Los Angeles Basin during the summer were greater during the night (average = 62%) than during the day (average = 42%).

The percent SVOC lost from the front filter in a filter-denuder system may be greater than that lost in a filter-only system such as the FRM. In a filter-denuder system, the gas-phase component of the SVOC is removed. The absence of the gas-phase causes the gas-particle equilibrium to shift so the SVOC collected on the filter may evaporate more rapidly in a filter-denuder system than in a filter-only collection system. To determine the fraction of SVOC lost from a Teflon filter in a filter-only system, it is necessary to compare the amount measured by a nondenuder system with that measured by a denuder system. At present, little information is available on the volatilization losses of SVOC. However, in one study (Pang et al., 2001), the total mass on denuded and undenuded filters were compared and found to be identical within error limits ($R^2 = 0.816$, slope = 0.961 ± 0.027 for total mass compared to $R^2 = 0.940$, slope = 0.986 ± 0.020 for sulfate). Pang et al. interpreted this result as suggesting that the major cause of loss of SVOC is the pressure drop across the filter.

Positive artifacts may occur during sample collection because of the adsorption of gases onto the filter materials (e.g., Gundel et al., 1995). Using a quartz filter behind a Teflon filter, Kim et al. (2001a) estimated that on an annual average basis 30% of the $PM_{2.5}$ organic carbon concentration resulted from positive artifacts. There is a larger positive artifact because of greater adsorption of organic vapor onto quartz fiber filters than onto Teflon filters (Turpin et al., 1994; Chow et al., 1994a,b, 1996; Eatough et al., 1996; Finn et al., 2001; Kirchstetter et al., 2001).

Kirchstetter et al. (2001) report that adsorptive properties of quartz fiber filters vary with lot number; therefore, front and back-up filters should be taken from the same lot. The literature suggests that a Teflon filter followed by a quartz back-up filter appears to provide a better estimate of the adsorption of gases on a quartz fiber front filter than does a quartz filter followed by a quartz backup and that the difference between these two adsorption estimates can be substantial for short durations (Novakov et al., 1997; Kirchstetter et al., 2001; Turpin et al., 2000). The typically lower organic carbon loadings on concurrently collected quartz followed by quartz filters relative to Teflon followed by quartz filters are believed to occur because adsorption on the quartz front filter acts to reduce the gas-phase concentration downstream until adsorption equilibrium has been achieved in the vicinity of the front quartz filter surface. Because Teflon filters have little affinity for organic vapors, this equilibrium occurs almost instantaneously for Teflon filters, and the Teflon-quartz back-up filter is exposed to the ambient concentration of organic vapors from the beginning of the sampling period. It might be expected that the quantity of organic vapor adsorbed on quartz filters would depend on the organic composition and would vary by season and location. However, it is also possible that the quartz possesses a limited number of adsorption sites which are rapidly occupied so that the quantity of OC on the back up filter would be relatively constant and depend on the pretreatment of the quartz.

Combined Measurement of Semivolatile Nitrate and OC and Nonvolatile Species (OC, EC, Nitrate, and Sulfate)

Fine particles in urban atmospheres contain substantial quantities of semivolatile material (e.g., NH_4NO_3 and semivolatile organic compounds [SVOC]) that are lost from particles during collection on a filter. Several diffusion denuder samplers have been developed for the determination of both NO_3^- and organic semivolatile fine particulate components as well as nonvolatile nitrate and organic compounds and nonvolatile sulfate (Pang et al., 2001; Eatough et al., 1993). The combination of technology used in the BOSS diffusion denuder sampler and the Harvard particle concentrator has resulted in the Particle Concentrator-Brigham Young University Organic Sampling System (PC-BOSS) for the 24-hr integrated collection of $PM_{2.5}$, including NH_4NO_3 and semivolatile organic material. Modifications of the BOSS sampler allow for the determination of these same species on a time scale from a few hours to weekly (Ding et al., 2002; Eatough et al., 1999a,b; 2001). Episodic studies have been conducted in Riverside, CA and Bakersfield, CA (Obeidi et al., 2002) and Provo, UT (Obeidi and Eatough, 2002). The average concentration of semivolatile and nonvolatile components in the three cities, during the study periods, are shown in Figure 2-19.

2.2.3.3 Continuous Measurement of Semivolatile and Nonvolatile Mass

Techniques for the continuous measurement of PM mass is needed both to provide real-time information on pollution levels (Long et al., 2002) and to reduce the costs involved in visiting sites to change filters and in the equilibration and weighing of filters. Two techniques are currently in use for the continuous measurement of PM mass. The TEOM is normally operated at 50° C in order to remove particle-bound water. However, at 50° C most semivolatile material is also evaporated. Therefore, the TEOM, operated at 50° C, may be considered to measure the mass of nonvolatile PM. The beta gauge mass monitor changes the filter more frequently than the TEOM and is less sensitive to changes in mass caused by changes in relative humidity. It does not control the temperature at the filter. However, most beta gauge monitors heat the inlet. This heating causes evaporation of a substantial fraction of the particle-bound water and an unknown fraction of the semivolatile PM. Thus, the beta gauge may be considered to measure the nonvolatile PM plus a small fraction of the particle-bound water and an unknown fraction of the semivolatile PM. Three new techniques have been developed to address the issue of lost semivolatile PM mass.

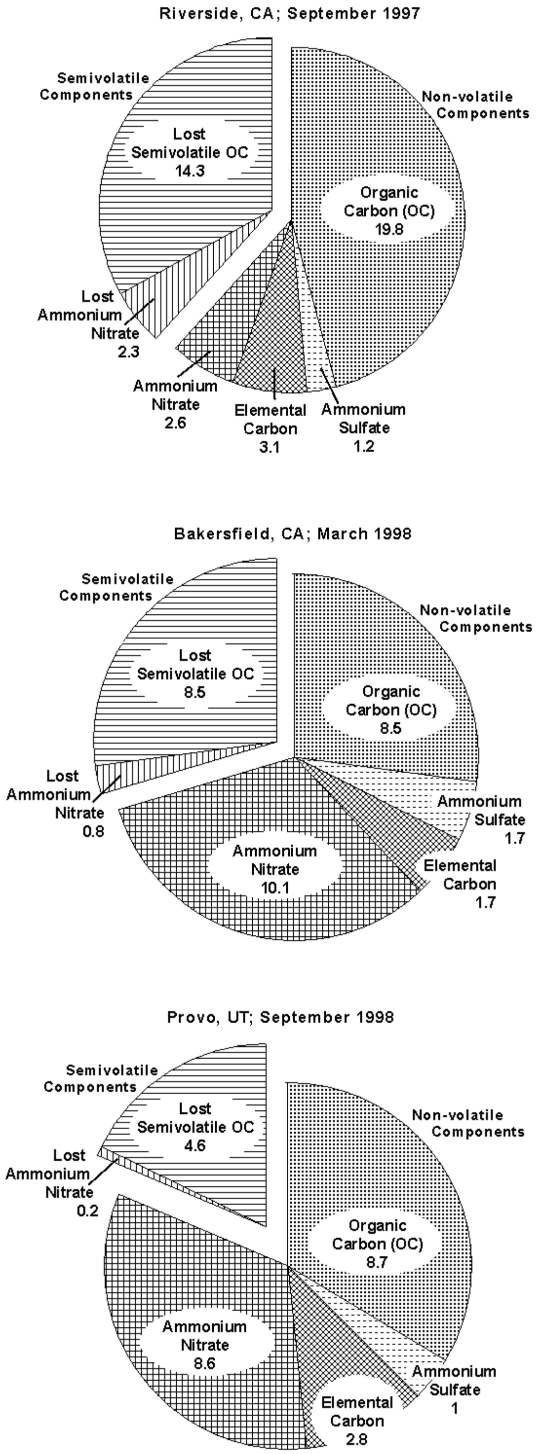

Figure 2-19. Average concentration of nonvolatile and semivolatile PM components in three cities (µg/m^3).

Source: Obeidi and Eatough (2002); Obeidi et al. (2002).

Real-Time Total Ambient Mass Sampler (RAMS)

The RAMS, a monitor based on diffusion denuder and TEOM monitor technology, has been developed, validated, and field tested for the real-time determination of total fine PM mass, including semivolatile PM (Eatough et al., 1999a; Obeidi and Eatough, 2002; Obedi et al., 2002; Pang et al., 2001). The RAMS measures the total mass of collected particles including semivolatile species with a TEOM monitor using a "sandwich filter." The sandwich contains a Teflon coated particle collection filter followed by a charcoal-impregnated filter (CIF) to collect any semivolatile species lost from the particles during sampling. Because the instrument measures total mass collected by the sandwich filter, all gas phase compounds that can be adsorbed by a CIF must be removed from the sampling stream prior to the TEOM monitor. Laboratory and field validation data indicate that the precision of fine PM mass determination is better than 10%. The RAMS uses a Nafion dryer to remove particle-bound water from the suspended particles and a particle concentrator to reduce the amount of gas phase organics that must be removed by the denuder. An example of data from the RAMS, the TEOM, and the PC-BOSS is shown in Figure 2-20. This figure also shows the $PM_{2.5}$ mass from the TEOM as being negative for the hours of 16 to 19. This likely results from the loss of volatile materials from the heated filter.

Differential TEOM

Patashnick et al. (2001) developed a differential TEOM system that is based on a pair of TEOM sensors, each of which is preceded by its own electrostatic precipitator (ESP) and downstream from a common size selective inlet. By alternately switching the ESPs on and off and out of phase with each other, the two sensors measure "effective mass" that includes both the nonvolatile component and the volatile component sampled by the TEOM, less the volatile component that vaporized during the sampling interval. On the sensor side with the ESP turned on, there is no particle collection on that filter so that only volatilization of previously collected particles continues. This allows a correction for the effective mass as measured by the first sensor by subtracting out the volatilization artifact and leaving the nonvolatile and volatile components of the particulate matter. This system has yet to be well characterized for other biases or interferences such as reactions on the filters, particle collection efficiency of the ESPs, and particle and semivolatile material losses.

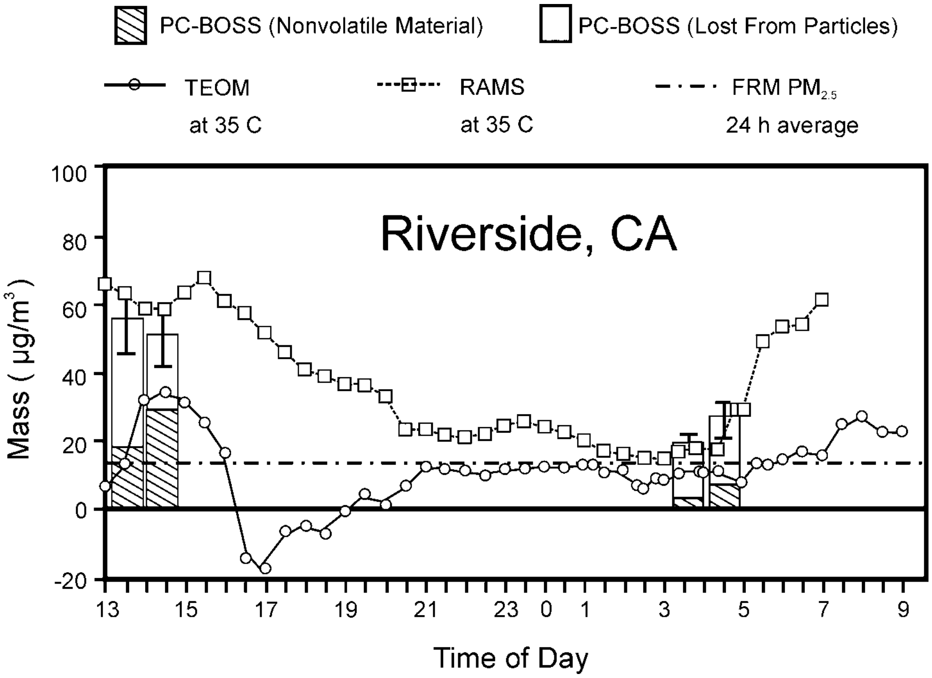

Figure 2-20. Comparison of mass measurements with collocated RAMS (real-time data), PC-BOSS (1-h data), FRM $PM_{2.5}$ sampler (average of 24-h data), and a conventional TEOM monitor (real-time data). The semivolatile fine particulate matter is sampled with the RAMS and PC-BOSS, but not with the TEOM monitor or the FRM $PM_{2.5}$ single filter sampler. The PC-BOSS provides information on both the nonvolatile component (NV) and the semivolatile organic component (SVOC).

Source: Eatough et al. (1999a).

Continuous Ambient Mass Monitor (CAMM)

Koutrakis and colleagues (Koutrakis et al., 1996; Wang, 1997) have developed CAMM, a technique for the continuous measurement of ambient particulate matter mass concentration based on the measurement of pressure drop increase with particle loading across a membrane filter. Recently, Sioutas et al. (1999) examined the increase in pressure drop with increasing particle loading on Nuclepore filters. They tested filters with two pore diameters (2 and 5 µm) and filter face velocities ranging from 4 to 52 cm s^{-1} and examined the effects of relative humidity in the range of 10 to 50%. They found that, for hygroscopic ammonium sulfate particles, the change in pressure drop per unit time and concentration was a strong function of relative humidity, decreasing with increasing relative humidity. These results suggest that particulate concentration measurements, similar to the method of Koutrakis et al. (1996) that uses the pressure drop method, may be subject to additional uncertainties if used in an environment where the ambient relative humidity is quite variable and the relative humidity where the particles are measured cannot be controlled accurately. The current version of the CAMM (Wang, 1997) uses a particle concentrator, a Nafion dryer, and frequently moves the filter tape to avoid artifacts due to evaporation of semivolatile components from the active portion of the filter tape which would occur if the atmospheric concentration of the semivolatile components decreased.

The CAMM was recently operated alongside a gravimetric PM method (the Harvard Impactor, or HI) in seven U.S. cities selected for their distinctly different ambient particulate compositions and densities. The correlation between the two methods was high, with an overall r^2 of 0.90 and average CAMM/HI ratio of 1.07 (Babich et al., 2000).

2.2.4 U. S. Environmental Protection Agency Monitoring Methods

2.2.4.1 The Federal Reference Methods for Measurement of Equilibrated Mass for PM_{10}, $PM_{2.5}$, and $PM_{10-2.5}$

In 1997, EPA promulgated new standards for $PM_{2.5}$ to address fine-fraction thoracic particles and retained with minor revisions the 1987 PM_{10} standards to continue to address coarse-fraction thoracic particles (Federal Register, 1997). In partial response to numerous challenges to these standards, the U.S. Court of Appeals for the District of Columbia Circuit in *American Trucking Association v. EPA*, 175 F. 3d 1027 (U.S. Court of Appeals, D.C. Cir. 1999) found “ample support” for regulating coarse-fraction particles but revoked the revised PM_{10} standards (leaving in effect the 1987 PM_{10} standards) on the basis of PM_{10} being a “poorly matched indicator for coarse particulate pollution” because PM_{10} includes fine particles. Consistent with this specific aspect of the Court’s ruling, which EPA did not appeal, EPA is now considering use of $PM_{10-2.5}$ as the indicator for coarse-fraction thoracic particles, in conjunction with $PM_{2.5}$ standards that address fine-fraction thoracic particles. Thus, EPA is now developing a Federal Reference Method for the measurement of $PM_{10-2.5}$.

2.2.4.1.1 PM_{10}

The FRM specified for measuring PM_{10} (Code of Federal Regulations, 2001a,b) has been discussed in previous PM AQCD's and will only be mentioned briefly. The PM_{10} FRM defines performance specifications for samplers in which particles are inertially separated with a penetration efficiency of 50% at an aerodynamic diameter (D_a) of 10 ± 0.5 µm. The collection efficiency increases to ≈100% for smaller particles and drops to ≈ 0% for larger particles. Particles are collected on filters and mass concentrations are determined gravimetrically. Instrument manufacturers are required to demonstrate through field tests a measurement precision for 24-h samples of ± 5 $\mu g/m^3$ for PM_{10} concentrations below 80 $\mu g/m^3$ and 7% above this value. A number of samplers have been designated as PM_{10} reference samplers. The TEOM and several beta gauge samplers with 1-h time resolution have been designated as automated equivalent methods (U.S. Environmental Protection Agency, 2001).

2.2.4.1.2 $PM_{2.5}$

In contrast to the performance-based FRM standard for PM_{10}, the FRM for $PM_{2.5}$ (Code of Federal Regulations, 2001a) specifies certain details of the sampler design, as well as of sample handling and analysis, whereas other aspects have performance specifications (Noble et al., 2001). The $PM_{2.5}$ FRM sampler consists of a PM_{10} inlet/impactor, a $PM_{2.5}$ impactor with an oil-soaked impaction substrate to remove particles larger than 2.5 µm D_a, and a 47-mm PTFE filter with a particle collection efficiency greater than 99.7%. The sample duration is 24 h, during which time the sample temperature is not to exceed ambient temperatures by more than 5 °C. A schematic diagram of the $PM_{2.5}$ FRM sample collection system is shown in Figure 2-21. After collection, samples are equilibrated for 24 h at temperatures in the range of 20 to 23 °C (± 2 °C) and at relative humidities in the range of 30 to 40% (± 5%). The equilibration tends to reduce particle-bound water and stabilizes the filter plus sample weight. Filters are weighed before and after sampling under the same temperature and relative humidity conditions. For sampling conducted at ambient relative humidity less than 30%, mass measurements at relative humidities down to 20% are permissible (Code of Federal Regulations, 2001a).

The PM_{10} inlet specified for the $PM_{2.5}$ FRM is modified from a previous low flow-rate PM_{10} inlet that was acceptable in both EPA-designated reference and equivalent PM_{10} methods. The modification corrects a flaw that was reported for the previous sampler, in that under some

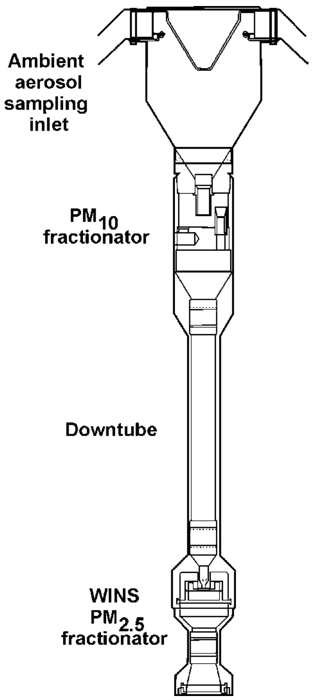

Figure 2-21. Schematic diagram of the sample collection portion of the $PM_{2.5}$ FRM sampler.

Source: Noble et al. (2001).

meteorological conditions, the inlet may allow precipitation to penetrate the inlet. The modification includes a larger drain hole, a one-piece top plate, and louvers. Tolocka et al. (2001a) evaluated the performance of this modified inlet in a series of wind tunnel experiments. The modified inlet was found to provide a size cut comparable to the original inlet, for both $PM_{2.5}$ and PM_{10} sampling. Since the modification did not change the characteristics of the size cut, the modified inlet may be substituted for the original inlet as part of a reference or equivalent method for PM_{10} and $PM_{2.5}$ (Tolocka et al., 2001a).

WINS Impactor. Design and calibration of the EPA $PM_{2.5}$ Well Impactor Ninety-Six (WINS) is given by Peters et al. (2001a). The WINS impactor was designed to be deployed downstream of the Graseby-Andersen 246B PM_{10} inlet as part of a sampler operating at a flow rate of 16.7 L/m. The WINS is pictured in Figure 2-22. The $PM_{2.5}$ inlet consists of a single jet, directed toward a round hole, with a jet exit impaction surface comprised of a 37 mm diameter

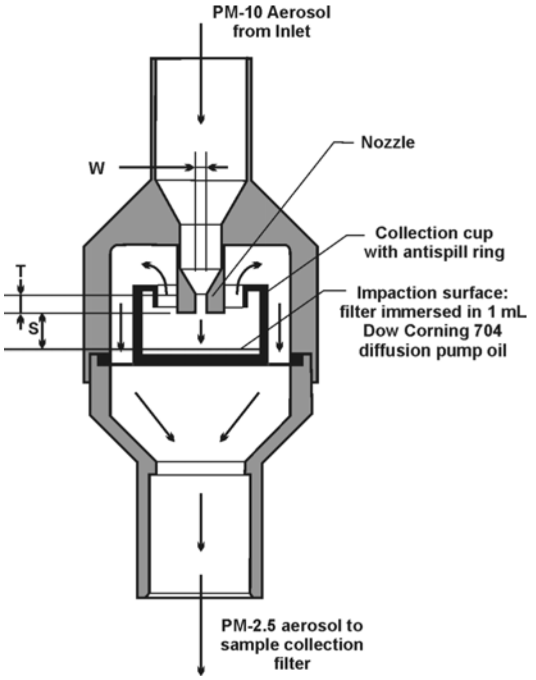

Figure 2-22. Schematic view of the final design of the WINS.

Source: Peters et al. (2001a).

glass fiber filter immersed in 1 ml of low volatility diffusion pump oil (i.e., the well). Particles not having enough inertia to be removed by the impactor are captured downstream on the sample collection filter. This design was selected to minimize impactor overloading that would otherwise result in particle bounce. The oil wicks through the particulate deposit on the impactor to provide a continuously wetted surface for impaction. The penetration curve indicated a 50% cutpoint of 2.48 µm D_a with a geometric standard deviation of 1.18 (Figure 2-23).

The WINS separator was evaluated for its loading characteristics (Vanderpool et al., 2001) by monitoring the performance after repeated operation in an artificially generated, high concentration, coarse-mode aerosol composed of Arizona Test Dust, as well as in the field in Rubidoux, Phoenix, Philadelphia, Research Triangle Park, and Atlanta. In the wind tunnel experiments, the WINS performance was found to be a monotonic function of loading. A minus 5% bias in the $PM_{2.5}$ measurement resulted from a coarse particulate loading of approximately 16 mg. This negative bias was due to a slight reduction in the separator cutpoint. It was also

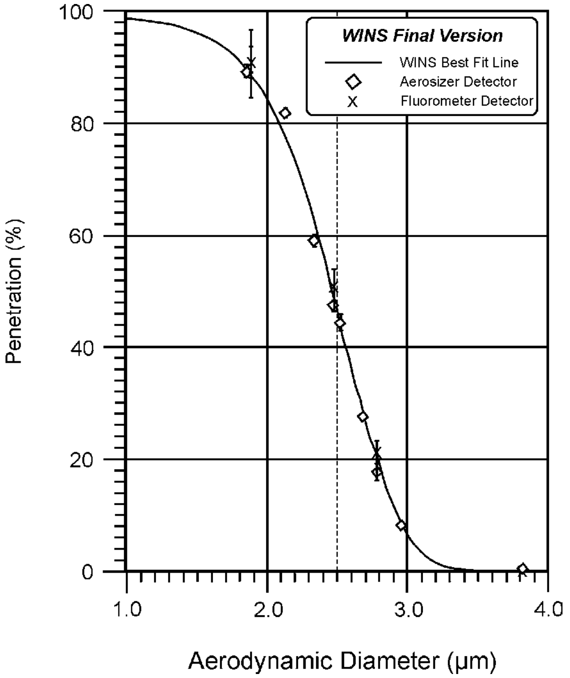

Figure 2-23. Evaluation of the final version of the WINS.

Source: Peters et al. (2001a).

found that the predictable results from the controlled laboratory experiments could not be extrapolated to field settings and that the WINS performance was more sensitive to the impactor loading in the field than it was in experiments with the single component aerosol. Significant particle bounce was not observed in either the laboratory or the field experiments. Vanderpool et al. (2001) concluded that their study supports the recommendation that the FRM WINS wells should be replaced after every 5 days of 24-h operation (U.S. Environmental Protection Agency, 1998).

A detailed sensitivity study of the WINS impactor was conducted (Vanderpool et al., 2001) in which the effects on the impactor performance of a number of parameters were examined. The results of this study are summarized in Table 2-3.

The regulations also allow for Class I, II, and III equivalent methods for $PM_{2.5}$ (Code of Federal Regulations, 2001c). Class I equivalent methods use samplers with relatively small deviations from the sampler described in the FRM. Class II equivalent methods include “all other $PM_{2.5}$ methods that are based upon 24-h integrated filter samplers that are subjected to

TABLE 2-3. SUMMARY OF SENSITIVITY STUDIES OF WINS IMPACTOR PERFORMANCE

Parameter	Amount of variance	Cutpoint variation	$PM_{2.5}$ mass concentration bias
Manufacturing tolerances on WINS components	Specified tolerances	0.05 micrometers	<1%
Flow control biases	4%	0.05 micrometers	Cutpoint shift partially offset volume bias
T and P measurement	Allowable ambient	± 0.02 micrometers	± 0.4%
Diffusion oil volume	0.75 ml to 3 ml	No effect	
Impactor loading	After 5 24 h events	−0.07 micrometers	<1.5%
Ambient P variations		Negligible	Negligible
Air Properties	0 C	2.40 micrometers	NA
Impactor oil crystallization		No effect	No effect
Impactor oil viscosity	−20 C	No effect	No effect
	−35 C	Need to change WINS more frequently than every 5 days	

Source: Vanderpool et al. (2001).

subsequent moisture equilibration and gravimetric mass analysis." Class III equivalent methods include non-filter-based methods such as beta attenuation, harmonic oscillating elements, or nephelometry (McMurry, 2000). As of July 2001, 11 $PM_{2.5}$ samplers (listed in Table 2-4) had been tested and led to the conclusion that the PM_{10} sampling systems can be designed such that concentration measurements are precise to ± 10%. For $PM_{2.5}$, cutpoint tolerances are not expected to affect the mass concentration as much as for PM_{10}, because the 2.5 μm D_a cutpoint generally occurs near a minimum in the mass distribution (e.g., Figure 2-5).

The $PM_{2.5}$ mass concentration will be affected, on the other hand, by other sampling issues mentioned but not discussed extensively in the previous 1996 PM AQCD (U.S. Environmental Protection Agency, 1996a). These issues have been discussed earlier in this chapter and include gas/particle, particle/particle, and particle/substrate interactions for sulfates and nitrates (e.g., Appel et al., 1984), volatilization losses of nitrates (Zhang and McMurry, 1992), semivolatile organic compound artifacts (e.g., Eatough et al., 1993), and relative humidity effects (e.g., Keeler et al., 1988).

TABLE 2-4. $PM_{2.5}$ SAMPLERS CURRENTLY DESIGNATED AS FRMs FOR $PM_{2.5}$ MASS CONCENTRATIONS

Sampler	Manufacturer	Description	Federal Register Reference
RAAS2.5-100	Andersen Instruments	FRM single	Vol. 63, p. 31991, 6/11/98
RAAS2.5-300	Andersen Instruments	FRM sequential	Vol. 63, p. 31991, 6/11/98
RAAS2.5-200	Andersen Instruments	FRM audit	Vol. 64, p. 12167, 3/11/99
Partisol 2000	Rupprecht & Patashnick	FRM single	Vol. 63, p. 18911, 4/16/98
Partisol-Plus 2025	Rupprecht & Patashnick	FRM sequential	Vol. 63, p. 18911, 4/16/98
Partisol 2000 audit	Rupprecht & Patashnick	FRM audit	Vol. 64, p. 19153, 4/19/99
PQ 200	BGI, Inc.	FRM single	Vol. 63, p. 18911, 4/16/98
PQ 200A	BGI, Inc.	FRM audit	Vol. 63, p. 18911, 4/16/98
605 CAPS	ThermoEnvironmental Instruments	FRM single	Vol. 63, p. 58036, 10/29/98
MASS 100	URC	FRM single	Vol. 65, p. 26603, 05/08/00
MASS 300	URC	FRM sequential	Vol. 65, p. 26603, 05/08/00

Source: Peters et al. (2001b); U.S. Environmental Protection Agency (2001).

Several studies now have been reported in which the FRM was collocated with other $PM_{2.5}$ samplers in intercomparison studies. During the Aerosol Research and Inhalation Epidemiology Study (ARIES), several $PM_{2.5}$ samplers were collocated at a mixed industrial-residential site near Atlanta, GA (Van Loy et al., 2000). These samplers included a standard $PM_{2.5}$ FRM, a TEOM with Nafion drier, a particulate composition monitor (PCM; Atmospheric Research and Analysis, Cary, NC), a medium-volume (113 L/min flow rate) fine particle ($PM_{2.5}$) and semivolatile organic compound (i.e., a filter followed by a solid adsorbent) sampler, operated by the Desert Research Institute, a HEADS sampler, and a dichotomous sampler for coarse PM. The PCM sampler has three channels, all of which have PM_{10} cyclone inlets. The first two channels both have two denuders preceding a 2.5-µm WINS impactor and filter packs. The first denuder is coated with sodium carbonate to remove acid gases, and the second is coated with citric acid to remove ammonia. The third channel has a carbon coated parallel-plate denuder preceding the WINS impactor. Measurements of 24-h mass from the FRM, PCM, and TEOM samplers, as well as reconstructed $PM_{2.5}$ mass (RPM), were compared for a 12-mo period. The slopes for the TEOM-FRM, PCM-FRM, and RPM-FRM correlations were 1.01, 0.94, and 0.91, respectively; whereas the y-intercepts for each were 0.68, 0.04, and 0.98. Particulate sulfate measurements on the FRM Teflon filter, the PCM Teflon filter, and PCM Nylon filter were nearly identical. Nitrate results from the three filters were much less consistent, with the FRM collecting substantially less nitrate than that collected on either the denuded nylon filter or a denuder followed by a Teflon-nylon filter sandwich. Particulate ammonia measurements were also compared and showed more scatter than the sulfate measurements but less than the nitrate measurements.

An intercomparison of both PM_{10} and $PM_{2.5}$ mass measurements was conducted during the 1998 Baltimore PM Study (Williams et al., 2000). PM monitors were collocated at a residential indoor, residential outdoor, and ambient monitoring site within Baltimore County, MD. PM samplers included TEOMs, $PM_{2.5}$ FRMs, cyclone-based inlets manufactured by University Research Glassware (URG), and Versatile Air Pollution Samplers (VAPS). The VAPS sampler is a dichotomous sampler operating at 33 L/min (one coarse particle channel at 3 L/min, and two fine particle channels at 15 L/min, each). In the configuration employed during this study, one fine particle channel was operated with a Teflon filter backed by a nylon filter and preceded by a sodium carbonate coated annular denuder; the second fine particle channel had a quartz filter preceded by a citric acid-coated annular denuder; and the coarse particle channel had a polycarbonate filter followed by a Zefluor filter for flow distribution. Differences in $PM_{2.5}$ mass concentrations between the samplers, although not large, were attributed to potential particle nitrate losses, denuder losses, and losses of SVOC for some samplers. Differences between coarse particulate mass concentrations, on the other hand, varied widely between the instruments.

In another intercomparison study, Tolocka et al. (2001b) examined the magnitude of potential sampling artifacts associated with the use of the FRM by collocating FRMs alongside other chemical speciation samplers at four U.S. cities. The locations included a high nitrate and carbon, low sulfate site (Rubidoux, CA); high crustal, moderate carbon and nitrate site (Phoenix); high sulfate, moderate carbon, and low nitrate (Philadelphia); and low $PM_{2.5}$ mass (Research Triangle Park, NC). The use of Teflon and heat-treated quartz filters was also examined in this study. The Teflon filters collected less nitrate than the heat-treated quartz filters. Filters in samplers using denuders to remove organic gases collected less organic PM than filters in samplers without denuders.

Peters et al. (2001b) compiled the results of several field studies in which a number of FRM and other $PM_{2.5}$ samplers were intercompared. In addition to the FRM samplers listed in Table 2-3, other $PM_{2.5}$ samplers included the Sierra Instruments dichotomous sampler, the Harvard impactor, the IMPROVE sampler, and the Air Metrics saturation monitor. Results were compiled from $PM_{2.5}$ field studies conducted in Birmingham, Denver, Bakersfield, Phoenix, Research Triangle Park, Atlanta, and Rubidoux. Limited studies on precision for the non-FRM samplers suggest that the Harvard Impactor and dichotomous samplers had the lowest coefficient of variations (CV), with both under 10%. The CV for this study was calculated by dividing the sample standard deviation by the average concentration. The IMPROVE samplers had CVs between 10 and 12%, and the Air Metrics samplers had the highest observed CVs, over 15%. In intercomparisons with FRM samplers, the non-FRM samplers showed strong linear relationships in comparison to the FRM sampler; however, none of the comparisons passed the current EPA Subpart C equivalent method criteria, which EPA is in the process of revising.

Detailed information on precision of PM samplers used in monitoring networks may be found in EPA's Technology Transfer Network website (U.S. Environmental Protection Agency, 2002a).

2.2.4.1.3 $PM_{10\text{-}2.5}$

Measurement techniques for $PM_{10\text{-}2.5}$ are somewhat more complex than those for $PM_{2.5}$ or PM_{10} because, for $PM_{10\text{-}2.5}$, it is necessary to isolate a size fraction between an upper 50% cut point of 10 μm D_a and a lower 50% cut point of 2.5 μm D_a. EPA is currently developing an FRM for $PM_{10\text{-}2.5}$. Several candidate techniques are discussed below.

The Difference Method. One approach to measurement of $PM_{10\text{-}2.5}$ is to make separate measurements of PM_{10} and $PM_{2.5}$ and take the difference of the resulting equilibrated masses. One problem is that, if either the $PM_{2.5}$ or the PM_{10} sampler fails, no $PM_{10\text{-}2.5}$ measurement can be obtained. In addition, errors in cut-point, flow rate, and filter weights (both before use and after collection and equilibration of particles) and uncertainties due to loss of semivolatile components of PM may occur for each size cut. Careful control of flow rate and equivalent treatment of PM_{10} and $PM_{2.5}$ filters in terms of pressure drop across the filter and temperature of the filter during and after collection can improve precision and accuracy. Allen et al. (1999a) summarized several sampling issues to consider in measuring coarse particulate mass by difference, including the use of identical instrumentation (except cutpoints), filter media, filter face velocity, and ambient-filter temperature differences; common flow measurement devices; use of higher sampler flow rates (10 L/min minimum for 24-h sample is recommended); and avoiding excessive filter loading. The concern, expressed by Allen et al. (1999a), that the "pie-plate" inlet required by the final version of the $PM_{2.5}$ FRM might have a different cut point than the "flat-top" inlet of the PM_{10} FRM, has been addressed by a wind tunnel study which found both to have an appropriate PM_{10} cut point (Tolocka et al., 2001a).

Since the difference method requires weighing two filters, the key to obtaining high precision in the coarse mass measurement is precise measurements of filter weights. Allen et al. (1999a) discuss techniques for increasing the precision of the difference method by reducing errors in filter weights. These include proper temperature and humidity controls, use of a high quality microbalance, 100% replicate weighings, control of static charge, aging of new filters, weighing of a sufficient number of laboratory blank filters, and accounting for buoyancy errors caused by variability in barometric pressure. Allen et al. (1999a) emphasize the necessity of replicate weighing of filters and a third weighing if the difference between the first two weights exceeds a specified minimum. Lawless et al. (2001) investigated the magnitude of uncertainties attributed to fluctuations in some of these parameters (humidity, temperature, drafts, vibration, and electrostatic charges) and recommended methods for improving their control. Koistinen et al. (1999) and Hänninen et al. (2002) give a excellent discussion of the procedures developed to overcome problems associated with gravimetric measurements of $PM_{2.5}$ mass in the EXPOLIS (The Air Pollution Exposure Distributions Within Adult Urban Populations in Europe) Study. They discuss factors such as corrections for buoyancy, elimination of static charge, and increases in the mass of blank filters with time. The establishment of a temperature and humidity controlled room required for the equilibration and weighing of filters for the FRM is expensive. Allen et al. (2001) describe a more cost-effective technique that uses a chamber with relative humidity controlled at 34% relative humidity by a saturated aqueous solution of $MgCl_2$.

Allen et al. (1999a) recommend that, in reporting precision from collocated samplers both the (CV) and the square of the correlation coefficient (r^2) be reported. For a study in Boston with 27 pairs of mass data from collocated PM_{10} and $PM_{2.5}$ using standard weighing methods, they obtained a CV of 4.7% and an r^2 of 0.991 for $PM_{2.5}$, a CV of 4.4% and an r^2 of 0.994 for PM_{10}, and a CV of 15% and an r^2 of 0.88 for $PM_{10-2.5}$. By using duplicate weighings and other techniques suggested for improving precision, they obtained a CV of 1.3% and an r^2 of 0.998 for $PM_{2.5}$ in a study in Chicago with 38 collocated measurements. On the basis of the improvement in the CV for $PM_{2.5}$, they estimate that use of the recommended techniques for $PM_{10-2.5}$ by difference would have yielded a CV of 3.8% and an r^2 of 0.98 if they had been applied in the Chicago study.

Multistage Impaction. A second technique involves the use of impaction to isolate the size fraction between 2.5 and 10 μm D_a. In the impaction process, the air stream is first accelerated through a small hole (nozzle) or slit. The air stream is directed so that it "impacts" on a surface. Depending on the velocity and pressure of the air stream, particles smaller than a certain size will follow the air stream around the impactor surface. Larger particles will impact on the surface. In practice, impactors have 50% cut points similar to those for the rejection of larger particles in $PM_{2.5}$ and PM_{10} samples (see Figure 2-6).

Multistage impactors are used to separate particles into several size fractions for the determination of mass and chemical composition as a function of size (Wang and John, 1988; Marple et al., 1991). The major problem with the use of impactors to separate the 10-2.5 μm D_a fraction of coarse particles (thoracic coarse PM) is bounce. Coarse particles tend to be dry, solid particles. When they hit a hard surface, they can bounce and be carried away with the air stream (e.g., Dzubay et al., 1976; Wesolowski et al., 1977; Rao and Whitby, 1978; Cheng and Yeh, 1979; Wang and John, 1987; John and Sethi, 1993). Various techniques have been used to reduce bounce. One technique is to use a porous substance such as a glass or quartz fiber filter (Chang et al., 1999) material or a polyurethane foam (Breum, 2000; Kavouras and Koutrakis, 2001). These techniques may result in less precise separation and yield a sample that must be extracted before chemical analyses can be performed. Another technique is to coat the impactor with a soft wax or grease (Rao and Whitby, 1977; Turner and Hering, 1987; Pak et al., 1992). This can cause problems with weighing and chemical analyses. In addition, as the deposit of particles builds up, incoming particles may not hit the soft surface, but instead hit a previously collected hard particle and bounce off of it. The WINS impactor discussed earlier uses a filter in a well of low volatility oil to ensure a wetted surface at all times. However, such a technique, while appropriate for removing unwanted particles, would not yield a particle sample suitable for weighing or for chemical analyses.

Virtual Impaction. The problems of bounce and blow off of particles from impactors, especially for the collection of large quantities of particles, was addressed by aerosol scientists in the mid-1960s by the development of what is now known as "virtual" impaction (Hounam and Sherwood, 1965; Conner, 1966).

In a virtual impactor, a hole is placed in the impaction plate just below the accelerating jet. Two controlled flows allow a fraction, e.g., 10% (or another predetermined fraction, typically 5 - 20%), of the air containing the coarse particles to go through the hole and through a filter (minor flow). A 10% minor flow gives a coarse channel enrichment factor of 10. The remaining fraction (e.g., 90% of the airflow) containing the fine particles follows a different path and goes through a second filter (major flow). The upper cutpoint is usually set by the inlet (e.g., 10 μm D_a). The flow rates, pressures, and distance from the nozzle to the virtual impactor surface can be varied to direct particles with an D_a greater than the lower cutpoint (i.e., > 2.5 μm) to go through the hole and be collected on the first filter and to direct smaller particles (i.e., < 2.5 μm) to flow around the impactor be collected on the second filter. Large particles "impact" into the hole with a small amount of the air flow. The smaller particles follow the major air flow around the impactor plate. This technique overcomes the problem of bounce. An example of the separation into fine and coarse particles is shown in Figure 2-24.

The usefulness of this technique for collecting samples of fine and coarse particles for chemical analysis was recognized by EPA in the mid-1970s. A development program was undertaken leading to the development of the now well known "dichotomous sampler" (a virtual impactor that separates particles into two size fractions) and an associated XRF analyzer (Dzubay and Stevens, 1975; Loo et al., 1976; Jaklevic et al., 1977; Dzubay et al., 1977). The dichotomous sampler was originally developed for use in the Regional Air Monitoring Study (RAMS), part of the Regional Air Pollution Study (RAPS), conducted in St. Louis, Missouri in the mid-1970s. Dichotomous samplers were operated at 10 RAMS sites from March 1975 to March 1977; and 33,695 filters were collected and analyzed by XRF with an overall sampling efficiency of 97.25% (Strothmann and Schiermeier, 1979; Loo et al., 1976; Loo et al., 1978; Dzubay, 1980; Lewis and Macias, 1980). Dichotomous samplers were a novel concept at that

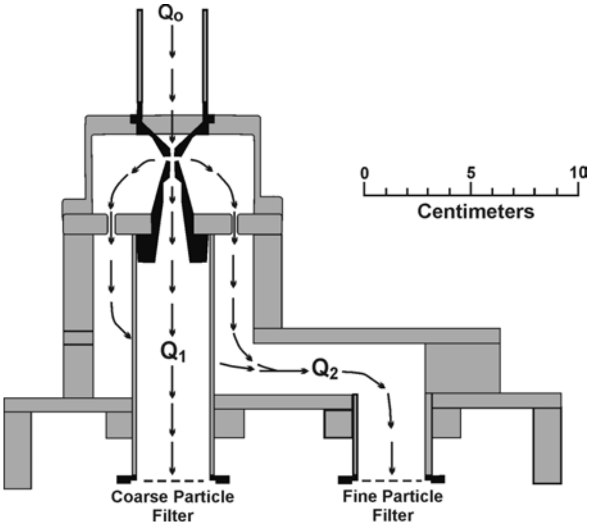

Figure 2-24. Schematic diagram showing the principle of virtual impaction. The initial flow, Q_0, is split into a minor flow, Q_1, which carries the larger particles, which impact into the hole, to the coarse particle filter and a major flow, Q_2, which carries the smaller particles, which can follow the airflow, to the fine particle filter.

Source: Loo et al. (1976).

time. Concern over particle losses and other problems at cut point sizes smaller than 2.5 µm D_a influenced the decision to choose 2.5 instead of 1.0 as the cut point diameter.

Subsequent to the use of the dichotomous sampler in RAPS, considerable progress has been made in the theory and practice of designing virtual impactors, especially in how to reduce losses and provide a sharp cut (Masuda et al., 1979; Marple and Chien, 1980; Chen at al., 1985, 1986; Loo and Cork, 1988). Now virtual impactors, with rectangular slits or round holes, are used (a) to provide cut point sizes as low as 0.15 µm D_a and (b) to concentrate coarse, accumulation, and ultrafine mode particles for use in health studies (Solomon et al., 1983; Marple et al., 1990; Sioutas et al., 1994a,b,c). Dichotomous samplers were also used in a national network to measure $PM_{2.5}$ and $PM_{10-2.5}$ in the Harvard Six City Study (Spengler and Thurston, 1983; Dockery et al., 1993) and the Inhalable Particulate Network (Suggs and Burton, 1983). A trichotomous high volume sampler has also been developed that provides samples of particles less than 1.0 µm, 1.0 µm – 2.5 µm, and 2.5 µm (Marple and Olsen, 1995). This sampler was intended for study of the composition of the intermodal mass between 1.0 and 2.5 µm D_a.

More recently, two dichotomous sequential PM air samplers were collocated with a manual Federal Reference Method (FRM) air sampler and operated for over one year at a waterfront site on Tampa Bay (Poor et al., 2002). The FRM sampler was alternately configured as a $PM_{2.5}$, then as a PM_{10} sampler. For the dichotomous sampler measurements, daily 24-h integrated $PM_{2.5}$ and $PM_{10\text{-}2.5}$ ambient air samples were collected at a total flow rate of 16.71 min^{-1}. As was the case in earlier versions of the dichotomous sampler, a virtual impactor split the air into flow rates of 1.67 and 15.01 min^{-1} and collected $PM_{10\text{-}2.5}$ and $PM_{2.5}$ on 47-mm diameter PTFE® filters. Between the two dichotomous air samplers, the average concentration, relative bias and relative precision for $PM_{2.5}$ were 13.3 µg m^{-3}, 0.02% and 5.2% concentrations (n = 282), and for $PM_{10\text{-}2.5}$ were 12.3 µg m^{-3}, 3.9% and 7.7% (n = 282). FRM measurements were alternate day 24-h integrated $PM_{2.5}$ or PM_{10} ambient air samples collected onto 47-mm diameter PTFE® filters at a flow rate of 16.71 min^{-1}. Between a dichotomous and a $PM_{2.5}$ FRM air sampler, the average concentration, relative bias and relative precision were 12.4 µg m^{-3}, -5.6% and 8.2% (n = 43); and between a dichotomous and a PM_{10} FRM air sampler, the average concentration, relative bias and relative precision were 25.7 µg m^{-3}, -4.0% and 5.8% (n = 102). The $PM_{2.5}$ concentration measurement standard errors for two dichotomous and one FRM samplers were 0.95, 0.79 and 1.02 µg m^{-3}; and for PM_{10}, the standard errors were 1.06, 1.59, and 1.70 µg m^{-3}. The authors (Poor et al., 2002) concluded that their results indicate that “the dichotomous samplers have superior technical merit” and demonstrate “the potential for the dichotomous sequential air sampler to replace the combination of the $PM_{2.5}$ and PM_{10} FRM air samplers, offering the capability of making simultaneous, self-consistent determinations of these particulate matter fractions in a routine ambient monitoring mode.”

The dichotomous sampler provides two separate samples. However, a fraction of the smaller particles, equal to the minor flow, will go through the virtual impaction opening with the air stream and be collected on the coarse particle filter. In the dichotomous sampler used in the RAPS program, 10% of the fine particles were collected with the coarse particles. Thus, in order to determine the mass or composition of the coarse particles, it is necessary to determine the mass and composition of the fine particles and subtract the appropriate fraction from the mass or composition of the particles collected on the coarse particle filter. Allen et al. (1999b) discuss potential errors in the dichotomous sampler caused by uncertainties in the coarse mass channel enrichment factor. Virtual impactors have also been designed with a clean air jet in the center of the round nozzle. This makes possible lower contamination of coarse particles by fine particles but maintains low losses and sharp cuts (Chen and Yeh, 1986; Chien and Lundgren, 1993). The fine particle intrusion into the coarse particle sample can also be reduced by operating two virtual impactors in series (Dzubay and Stevens, 1975).

Aerosol physicists have also conducted theoretical and experimental investigations of virtual impaction using slits instead of round holes (Forney et al., 1978, 1982; Ravenhall et al., 1978; Masuda and Nakasita, 1988; Sioutas et al., 1994b, c, d; Ding and Koutrakis, 2000). The slit virtual impactor permits much higher flow rate than round hole virtual impactors and resolves problems that occur with multihole virtual impactors (Marple et al., 1990; Fang et al., 1991). The slit technique has been used to develop virtual impaction systems for concentrating particles in the size range 0.1 to 2.5 μm D_a for exposure studies using animals and people (Sioutas et al., 1995a, b). The slit impactor can also be used to concentrate coarse particles for measurement (Misra et al., 2001) or exposure studies (Chang et al., 2002). It has also been possible to concentrate ultrafine particles (> 0.1 μm) by first separating ultrafine particles from larger particles, adding water vapor to saturate the air containing the ultrafine particles, cooling the air to cause supersaturation and growth of the ultrafine particles into the 1.0 – 4.0 μm size range, concentrating these particles with a slit virtual impactor, and heating the air to return the particles to their original size (Sioutas and Koutrakis, 1996; Sioutas et al., 1999; Sioutas et al., 2000; Kim et al., 2001b,c; Geller et al., 2002).

2.2.5 Speciation Monitoring

Speciation Network and Monitoring

In addition to FRM sampling to determine compliance with PM standards, EPA requires states to conduct chemical speciation sampling primarily to determine source categories and trends (Code of Federal Regulations, 2001b). Source category apportionment calculations are discussed in Chapter 3. A $PM_{2.5}$ chemical Speciation Trends Network (STN) has been deployed that consists of 54 core National Ambient Monitoring Stations (NAMS) and approximately 250 State and Local Air Monitoring Stations (SLAMS). In addition, over 100 IMPROVE (Interagency Monitoring of Protected Visual Environments) samplers located at regional background and transport sites can be used to fulfill SLAMS requirements. The overall goal of the speciation program is “to provide ambient data that support the Nation’s air quality program objectives” (U.S. Environmental Protection Agency, 1999). Information and reports on EPA’s speciation monitoring program may be found on EPA’s Technology Transfer Network at http://www.epa.gov/ttn/amtic/pmspec.html. The NAMS speciation sites will provide routine chemical speciation data that will be used to develop annual and seasonal aerosol characterization, air quality trends analysis, and emission control strategies. The SLAMS speciation sites will further support the NAMS network and provide information for development of State Implementation Plans (SIPs).

At both NAMs and SLAMs sites, aerosol samples will be collected for analysis of trace elements, ions (sulfate, nitrate, ammonium, sodium, and potassium), and total carbon. The NAMS speciation sites will operate on a 1 in 3 day schedule, with 10 of these sites augmented with continuous speciation analyses for everyday operation. The SLAMS speciation sites will generally operate on a 1 in 6 day basis; however, many sites may be operated on a 1 in 3 day basis in locations where increased data collection is needed. There are several samplers that are suitable for use in the NAMS/SLAMS network. These samplers include an inlet cutpoint with size cut characteristics comparable to the WINS FRM; proven denuder technology for nitrate; and sampler face velocity and sample volume similar to that of the FRM. The current samplers include three filters: (1) Teflon for equilibrated mass and elemental analysis by energy dispersive x-ray fluorescence (EDXRF), (2) a nitric acid denuded Nylon filter for ion analysis (ion chromatography), (3) a quartz fiber filter for elemental and organic carbon. EC and OC are determined by thermal optical analysis via a modification of the NIOSH (National Institute for Occupational Safety and Health) method 5040 (Thermal Optical Transmission) [TOT]). However, no corrections are made for positive artifacts caused by adsorption on organic gases or the quartz filters or negative artifacts due to evaporation of semivolatile organic compounds from the collected particles.

Since 1987, the IMPROVE network has provided measurements of ambient PM and associated light extinction in order to quantify PM chemical components that affect visibility at Federal Class 1 areas that include designated national parks, national monuments, and wilderness areas. Management of this network is a cooperative effort between U.S. EPA, federal land management agencies, and state governments. The IMPROVE program has established protocols for analysis of aerosol measurements that provide ambient concentrations for PM_{10}, $PM_{2.5}$, sulfates, nitrates, organic and elemental carbon, crustal material, and a number of other elements. Information on the IMPROVE program may be found at http://vista.cira.colostate.edu/ improve.

IMPROVE aerosol monitoring consists of a combination of particle sampling and sample analysis. The IMPROVE sampler, which collects two 24-hour duration samples per week, simultaneously collects one sample of PM_{10} on a Teflon filter, and three samples of $PM_{2.5}$ on Teflon, nylon, and quartz filters. PM_{10} mass concentrations are determined gravimetrically from the PM_{10} filter sample, while $PM_{2.5}$ mass concentrations are determined gravimetrically from the $PM_{2.5}$ Teflon filter sample. The $PM_{2.5}$ Teflon filter sample is also used to determine concentrations of selected elements using particle-induced x-ray emission (PIXE), x-ray fluorescence (XRF), and Proton Elastic Scattering Analysis (PESA). The $PM_{2.5}$ nylon filter sample, which is preceded by a denuder to remove acidic gases, is analyzed to determine nitrate and sulfate aerosol concentrations using Ion Chromatography (IC). Finally, the $PM_{2.5}$ quartz filter sample is analyzed for organic and elemental carbon using the Thermal Optical Reflectance (TOR) method. Corrections are made for positive artifacts but not for negative artifacts.

The STN and the IMPROVE networks represent a major advance in the measurement of nitrate since the combination of a denuder to remove nictric acid vapor and a Nylon filter to adsorb nitric acid vapor that volatilizes from the collected ammonium nitrate particles overcomes the loss of nitrate from Teflon filters. However, the different techniques used for the measurement of OC and EC lead to significant differences between OC and EC measurements when the two techniques are intercompared (Chow et al., 2001). IMPROVE yields higher EC and lower OC although there is good agreement for TC. Another difference arises from the treatment of the positive artifact due to the absorption of organic gases by the quartz filters used in IMPROVE and STN samplers. More information on these differences is given in Section 2.2.7 and details are discussed in Appendix 2B.

Several of the $PM_{2.5}$ size selectors developed for use in the EPA National $PM_{2.5}$ STN were recently evaluated by comparing their penetration curves under clean room experiments with that of the WINS impactor (Peters et al., 2001c). The corresponding speciation monitors were then compared to the FRM in four cities. The $PM_{2.5}$ inlets tested were the SCC 2.141 cyclone (6.7 L/min) that is in the Met One Instruments SASS sampler; the SCC 1.829 cyclone

(5.0 L/min) that is proposed for use in the Rupprecht and Patashnik real-time sulfate/nitrate monitor; the AN 3.68 cyclone (24.0 L/min) that is in the Andersen RAAS; and the spiral separator (7.0 L/min) that was previously in the Met One SASS. The cutpoints of the SCC cyclones compared reasonably well with the WINS (2.52 and 2.44 micrometers for the SCC 2.141 and SCC 1.829, respectively, at their design flowrates), but both demonstrated a tail extending into the coarse particle mode. The AN inlet had the sharpest cutpoint curve, but the 50% cutpoint diameter was 2.7 μm D_a at its design flowrate. The spiral inlet had the shallowest cutpoint curve, and the 50% cut point was 2.69 and 2.67 μm D_a for an ungreased and greased inlet, respectively. The speciation samplers were also compared to the FRM sampler with WINS inlet under ambient conditions in four cities. The Andersen RAAS equipped with the AN 3.68 cyclone compared well to the FRM in all four cities, when compared on the basis of $PM_{2.5}$ mass, sulfate, and crustal concentrations. Greasing the spiral inlet in the Met One sampler improved the performance of that sampler, which tended to give much higher $PM_{2.5}$ concentrations than the FRM in cities with high crustal particulate matter.

2.2.6 Inorganic Elemental Analyses

In addition to the lighter elements, hydrogen, carbon, oxygen and nitrogen, the following 40 heavier elements are commonly found in ambient air samples: sodium, magnesium, aluminum, silicon, phosphorus, sulfur, chlorine, potassium, calcium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, gallium, arsenic, selenium, bromine, rubidium, strontium, yttrium, zirconium, molybdenum, palladium, silver, cadmium, indium, tin, antimony, barium, lanthanum, gold, mercury, thallium, lead, and uranium. These often indicate air pollution sources and several of them are considered to be toxic (transition metals, water-soluble metals, and metals in certain valence states [e.g., Fe(II), Fe(III), Cr(III), Cr(VI), As(III), As(V)]). Measurement methods for inorganic elements are listed in Table 2-5. These methods differ with respect to detection limits, sample preparation, and cost (Chow, 1995). EDXRF and PIXE are the most commonly applied methods because they quantify more than 40 detectable elements, they are non-destructive, and they are relatively inexpensive. Both were discussed in the previous 1996 PM AQCD. TRXRF and S-XRF are newer techniques with lower detection limits. AAS, ICP-AES, and ICP-MS are also appropriate for ionic measurements of elements that can be dissolved. PESA provides a means for measuring

TABLE 2-5. MEASUREMENT METHODS FOR INORGANIC ELEMENTS

#	Acronym	Full Name	Comments
1.	EDXRF	energy dispersive x-ray fluorescence	heavier elements
2.	S-XRF	synchrotron induced X-ray emission	heavier elements; lower detection limits than EDXRF
3.	PIXE	proton induced x-ray emission	heavier elements; lower detection limits than EDXRF
4.	PESA	proton (or particle) elastic scattering analysis	lighter elements
5.	TRXRF	total reflection X-ray fluorescence	heavier elements; lower detection limits than EDXRF
6.	INAA	instrumental neutron activation analysis	many elements; sensitivity different than EDXRF
7.	AAS	atomic absorption spectrophotometry	many elements that can be dissolved
8.	ICP-AES	inductively coupled plasma with atomic emission spectroscopy	many elements that can be dissolved
9.	ICP-MS	inductively coupled plasma with mass spectroscopy	many elements that can be dissolved
10.	SEM	scanning electron microscopy	heavier elements

elements with lower atomic numbers from hydrogen to carbon. More detailed information on each technique is given in Appendix 2B.1.

2.2.7 Elemental and Organic Carbon in Particulate Matter

Ambient particles from combustion sources contain carbon in several chemically and optically distinct forms. Health- and visibility-related studies of these particles require information about the relative contributions to total particle mass by these different forms of carbon. With the exception of carbonate-based carbon, however, a clear classification scheme has not yet been established to distinguish organic carbon, light-absorbing carbon, black carbon, soot and elemental carbon. The absence of clear, physically-based definitions results in confusion in the interpretation of speciation data. For example, depending on the radiation wavelength specified, “light absorbing” carbon can include compounds that volatilize without oxidation. “Black” carbon includes various mixtures containing “elemental” (graphitic) carbon;

partially degraded, oxidized graphitic fragments; and partially-oxidized amorphous aromatic carbon. For studying visibility reduction, a measurement of light-absorbing carbon may be more useful than one of elemental carbon. For source apportionment by receptor models, several consistent but distinct fractions of carbon in both source and receptor samples are desired, regardless of their light-absorbing or chemical properties. Differences in ratios of the carbon concentrations in these fractions form part of the source profiles that distinguish the contribution of one source from the contributions of other sources (Watson et al., 1994a,b).

Three method-dependent operational classes of carbon are commonly measured in ambient aerosol samples collected on quartz-fiber filters: (1) semi-volatile organic or non-visible light-absorbing carbon, termed “organic carbon (OC)”; (2) elemental carbon, soot, black carbon, or light-absorbing carbon, termed “elemental carbon (EC)”; and (3) carbon present as K_2CO_3, Na_2CO_3, $MgCO_3$, $CaCO_3$, termed “carbonate carbon (CC).” The sum of OC, EC, and CC in PM gives the total carbon (TC).

The thermal/optical reflectance (TOR), thermal/optical transmission (TOT), and thermal manganese oxidation (TMO) methods are most commonly used for the analysis of organic and elemental carbon in atmospheric PM. In thermal separation methods, OC is vaporized and the EC remaining on the filter is then oxidized to CO_2 and quantified by nondispersive infrared detection, by electrochemical techniques or by reducing the CO_2 to CH_4 and quantifying CH_4 via flame ionization detection (FID). OC that does not vaporize below 550 C can pyrolyze at higher temperatures to form additional black carbon. Thermal/optical methods must correct for this effect in order to correctly distinguish OC from EC. The various methods give similar results for TC, but not for EC or OC, due to differing assumptions regarding the thermal behavior of ambient aerosol carbon. These methods are discussed in detail in Appendix 2B.2.

Carbonate carbon (i.e., K_2CO_3, Na_2CO_3, $MgCO_3$, $CaCO_3$) can be determined thermally, or on a separate filter section by measurement of the carbon dioxide (CO_2) evolved upon acidification (Johnson et al., 1980). It is usually on the order of 5% or less of TC for ambient particulate samples collected in urban areas (Appel, 1993).

The forms of carbon present in natural materials that may be burnt to generate atmospheric aerosol tend to be poorly defined. Thus, the pyrolysis products of these materials during thermal/optical analysis cannot be predicted. The Geochemical Society convened an international steering committee in 1999 to define a set of representative black carbon and black carbon-containing benchmark materials to be used to support ambient aerosol sample analysis. These standard materials may be used to provide thermal/optical "fingerprints" for deducing primary aerosol sources, and to establish characteristic analytic interferences or artifacts associated with such sources. The materials recommended to date include n-hexane soot, lignocellulosic chars, soils, marine sediments, and the NIST urban dust standard reference material (SRM 1649a). The committee has also recommended a set of standard materials that may potentially interfere with black carbon analyses: shale, natural organic matter, melanoidin (an amino acid-based material) and coals. These recommendations are discussed on the steering committee website: http://www.du.edu/~dwismith/bcsteer.html.

2.2.8 Ionic Species

Ion chromatography (IC) is widely used for analyzing ionic species in the water-soluble portion of suspended PM. IC is the method of choice for the measurement of sulfate, nitrate, ammonium, sodium, and potassium ions for the NAMS program. Aerosol strong acidity, H^+, is determined by titration of a water solution of PM collected following a series of annular denuders to remove acid and basic gases with back-up filters to collect NH_3 and HNO_3 that volatilize from the PM during collection. The 1996 PM AQCD (U.S. Environmental Protection Agency, 1996a) discussed measurement of ions by IC (Section 4.3.3.1) and of strong acidity (Sections 3.3.1.1 and 4.3.3.1); so, no further details will be discussed here.

2.2.9 Continuous Monitoring

The EPA expects that many local environmental agencies will operate continuous PM monitors. All currently available continuous measurements of suspended particle mass share the problem of dealing with semivolatile PM components. So as not to include particle-bound water as part of the mass, the particle-bound water must be removed by heating or dehumidification. However, heating also causes loss of ammonium nitrate and semivolatile organic components. A variety of potential candidates for continuous measurement of particle mass and related properties are listed in Table 2-6. These techniques are discussed in more detail in Appendix 2B.3.

TABLE 2-6. METHODS FOR CONTINUOUS MEASUREMENT OF PM MASS, COMPONENTS, ETC.

#	Acronym	Name	Comments
1.	TEOM	Tapered Element Oscillating Microbalance	Measures only nonvolatile components of PM.
2.	TEOM with SES	TEOM with Sample Equilibration System	By using dehumidification instead of heat for drying and a lower temperature for stabilization, includes some of the semivolatile components of PM.
3.	—	Differential TEOM	Research instrument designed to measure both the nonvolatile and semivolatile components of PM.
4.	FDMS	Filter Dynamics Measurement System	Commercial version of the differential TEOM.
5.	RAMS	Real-Time Total Ambient Mass Sampler	Research instrument designed to measure total PM using denuders and an adsorptive filter.
6.	CAMM	Continuous Ambient Mass Monitor	Measures total PM by pressure drop across a frequently changed filter.
7.	—	Beta gauge	Measures PM mass by beta attenuation. Unless dried by heat or dehumidification will also measure particle-bound water.
8.	—	Piezoelectric microbalance	Measures mass by change in resonance frequency when particles are deported on a crystal.
9.	CCPM	Continuous Coarse Particle Monitor	Virtual impaction is used to concentrate $PM_{10-2.5}$ which is then measured by a TEOM.
10.	—	Semi-continuous EC/OC	Several commercially available instruments automate the thermal technique for EC/OC and provide hourly measurements.
11.	—	Semi-continuous nitrate	Collection of PM followed by flash vaporization and determination of NO_x provides 10 minute measurements of particulate nitrate.
12.	—	Semi-continuous sulfate	Several techniques are available in which particulate sulfate is measured using flame ionization detection.
13.	—	Continuous ion chromatography of water-soluble ions	Particles are grown by mixing with water vapor, collected in water, and injected into an automatic ion chromatography.
14.	—	Mass spectroscopy of individual particles	Single particles are evaporated, ionized and the components analyzed by mass spectroscopy. Several different systems are in use in research studies.
15.	EAD	Electrical Aerosol Detector	This instrument measures charge collected by particles and gives a continuous signal that is proportional to the integral of the particle diameter.
16.	—	Integrating nephelometer	Light scattering by suspended particles, collected over a large solid angle, provides an indicator for particle mass including particle-bound water unless the air sample is dried by heating or dehumidification.

2.2.10 Measurements of Individual Particles

Recently, several researchers have developed instruments for real-time *in situ* analysis of single particles (e.g., Noble and Prather, 1996; Gard et al., 1997; Johnson and Wexler, 1995; Silva and Prather, 1997; Thomson and Murphy, 1994). Although the technique varies from one laboratory to another, the underlying principle is to fragment each particle into ions, using either a high-power laser or a heated surface and, then, a time-of-flight mass spectrometer (TOFMS) to measure the ion fragments in a vacuum. Each particle is analyzed in a suspended state in the air stream (i.e., without collection), avoiding sampling artifacts associated with impactors and filters. The technique is called aerosol time-of-flight mass spectrometry (ATOFMS). By measuring both positive and negative ions from the same particle, information can be obtained about the composition, of individual particles of known aerodynamic diameter. This information is especially useful in determining sources of particles. Noble and Prather (1996) used ATOFMS to provide compositionally resolved particle-size distributions. Their instrument is capable of analyzing size and chemical composition of 50 to 100 particles/min at typical ambient concentrations and up to 600/min at high particle concentrations. Four systems for measurement of single particles using mass spectroscopy are reviewed by Middlebrook (2002). An example of the type of information that can be determined is shown in Figure 2-25.

Because particles are analyzed individually, biases in particle sampling (the efficiency of particle transmission into the sensor chamber as a function of size; particle size measurement, and detection of particles prior to fragmentation) represent a major challenge for these instruments. Moreover, the mass spectrometer has a relatively large variability in ion yields (i.e., identical samples would yield relatively large differences in mass spectrometer signals [Thomson and Murphy, 1994]); therefore, quantitation is inherently difficult (Murphy and Thomson, 1997). Quantitation will be even more challenging for complex organic mixtures because of the following two reasons: (1) a large number of fragments are generated from each molecule, and (2) ion peaks for organics can be influenced or obscured by inorganic ions (Middlebrook et al., 1998). Nonetheless, scientists have been successful in using these techniques to identify the presence of organics in atmospheric particles and laboratory-generated particles (i.e., as contaminants in laboratory-generated sulfuric acid droplets) as well as the identification of specific compound classes such as PAHs in combustion emissions (Castaldi and Senkan, 1998; Hinz et al., 1994; Middlebrook et al., 1998; Murphy and Thomson, 1997;

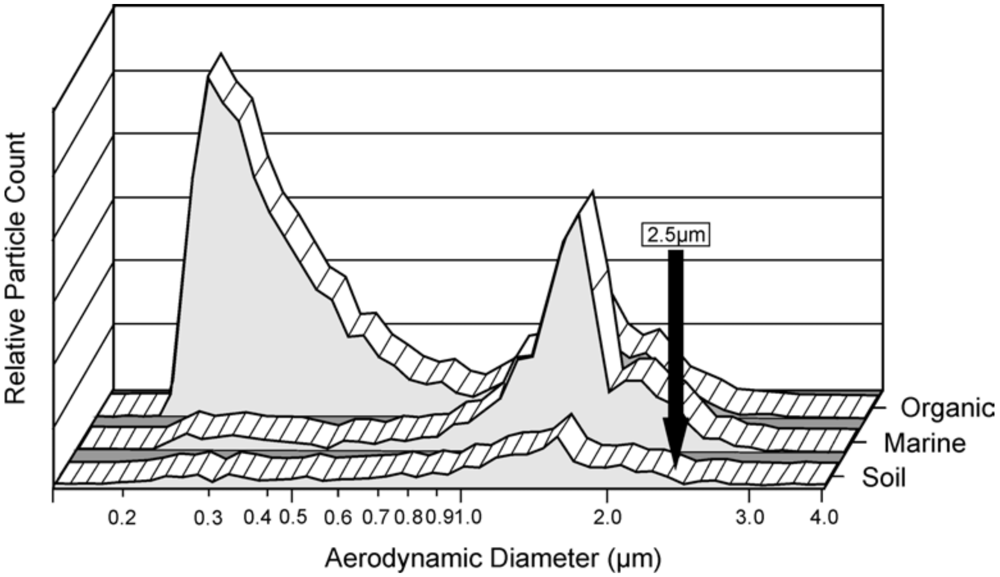

Figure 2-25. Size distribution of particles divided by chemical classification into organic, marine, and crustal.

Source: Noble and Prather (1998).

Neubauer et al., 1998; Noble and Prather, 1998; Reilly et al., 1998; Silva and Prather, 1997). A new multivariate technique for calibration of ATOFMS using microorifice impactors shows promise for simplifying the calibration process (Fergenson et al., 2001). This calibration technique has been applied to gasoline and diesel particles to demonstrate the feasibility of using this technique for the source apportionment of gasoline and diesel particles in an atmospheric mixture (Song et al., 2001).

Until recently, ATOFMS systems have only been able to characterize particles that are larger than approximately 0.2 to 0.3 µm in diameter. Wexler and colleagues (Carson et al., 1997; Ge et al., 1998) have developed an ATOFMS instrument that is able to size, count, and provide chemical composition on individual particles ranging in size from 10 nm to 2 µm.

2.2.11 Low Flow Filter Samples for Multiday Collection of Particulate Matter

For some purposes, such as demonstrating attainment of an annual standard or as an exposure indicator for epidemiologic studies of chronic health effects, 24-h measurements are not essential. Annual or seasonal averages may be adequate. Multiday sampling techniques can result in lower costs for weighing, chemical analysis, and travel time to change filters. The multiday sampler serves a second purpose. Most commercially available samplers are optimized for collecting 24-h samples of the PM concentrations found in the U.S., Europe, or Japan. Many cities in other parts of the world have significantly higher PM concentrations. Under these conditions, the 16.7 L/min flow through 37 or 47 mm diameter filters may overload the filter and prevent the sampler from maintaining the prescribed flow rate for 24 h. A low flow sampler with a 0.4 L/min flow rate and a 47 mm diameter filter has been designed by Aerosol Dynamics, Inc. With this sampler, the sample collection time can be chosen to suit the ambient concentration level. This sampler, with a one-week collection period, has been used to characterize $PM_{2.5}$ in Beijing, PRC (He et al., 2001). With a two-week collection period, it is being used in a chronic epidemiologic study in southern California, USA (Gauderman, et al., 2000).

The sampler, as described by He et al. (2001), has three $PM_{2.5}$ channels. One channel collects PM on a Teflon filter for gravimetric mass measurement and elemental analysis by XRF. A second channel collects PM on a quartz filter for organic and elemental carbon analysis. A denuder to remove organic gases and a backup filter to collect semivolatile organic compounds may be added. The third channel uses a carbonate denuder to remove acid gases (HNO_3 and SO_2), a Teflon filter to collect PM for analysis of ions by ion chromatography, and a nylon filter to collect volatilized nitrate. The Teflon filter can also be weighed prior to extraction. Thus, the multiday sampler can provide the information needed for source apportionment by Chemical Element Balance techniques (Watson et al., 1990a,b; U.S. Environmental Protection Agency, 2002b).

For monitoring sites with high day-to-day variability in PM concentrations, a sample integrated over a week may provide a more accurate measurement of the annual average than can be obtained by 1-in-3 or 1-in-6 day sampling schedules. Daily PM data from Spokane, WA were resampled to simulate common sampling schedules and the error due to less-than-everyday sampling was computed (Rumburg et al., 2001). The error in the annual mean concentration for

$PM_{2.5}$, expressed as a percentage difference from the everyday sampling mean, was 1.7, 3.4, and 7.7% for 1-in-2 day, 1-in-3 day, and 1-in-6 day sampling, respectively.

2.3 SUMMARY AND KEY POINTS

2.3.1 Atmospheric Physics and Chemistry of Particles

Atmospheric particles originate from a variety of sources and possess a range of morphological, chemical, physical, and thermodynamic properties. The composition and behavior of aerosols are linked with those of the surrounding gas. Aerosol may be defined as a suspension of solid or liquid particles in air and includes both the particles and all vapor or gas phase components of air. However, the term aerosol often is used to refer to the suspended particles only.

A complete description of the atmospheric aerosol would include an accounting of the chemical composition, morphology, and size of each particle, and the relative abundance of each particle type as a function of particle size. Recent developments in single particle analysis techniques are bringing such a description closer to reality.

The diameter of a spherical particle may be determined geometrically, from optical or electron microscopy, by light scattering and Mie theory, or by a particle's behavior (e.g., electrical mobility or its aerodynamic behavior). However, the various types of diameters may be different, and atmospheric particles often are not spherical. Therefore, particle diameters are described by an "equivalent" diameter. Aerodynamic diameter, D_a (the diameter of a unit density sphere that would have the same terminal settling velocity as the real particle), and the Stokes diameter, D_p (the diameter of a sphere of the same density as the particle that would have the same aerodynamic resistance or drag), are the most widely used equivalent diameters.

Atmospheric size distributions show that most atmospheric particles are quite small, below 0.1 µm; whereas most of the particle volume (and therefore most of the mass) is found in particles greater than 0.1 µm. An important feature of the mass or volume size distributions of atmospheric particles is their multimodal nature. Volume distributions, measured in ambient air in the United States, are almost always found to have a minimum between 1.0 and 3.0 µm. That portion of the size distribution that contains particles that are mostly larger than the minimum is called "coarse" particles or the "coarse" mode. That portion of the size distribution that contains particles that are mostly smaller than the minimum is called "fine" particles and includes several modes. "Accumulation-mode" refers to that portion of fine particles with diameters above about 0.1 µm. That portion of fine particles with diameters below 0.1 µm are usually called "ultrafine" by toxicologists and epidemiologists and "nanoparticles" by aerosol physicists and material scientists. In the number distribution of ultrafine particles, particles in the size range below 0.01 are called the nucleation mode and particles between 0.01 and 0.1 are called the Aitken mode. The Aitken mode can be observed as a separate mode in mass or volume distributions only in clean or remote areas or near sources of new particle formation by nucleation.

The aerosol community uses three different approaches or conventions in the classification of particles by size: (1) modes, based on the observed size distributions and formation mechanisms; (2) cut point, usually based on the 50% cut point of the specific sampling device, including legally specified, regulatory sizes for air quality standards; and (3) dosimetry or occupational sizes, based on the entrance into various compartments of the respiratory system. Over the years, the terms fine and coarse as applied to particle sizes have lost the original precise meaning of fine and coarse. In any given article, therefore, the meaning of fine and coarse, unless defined, must be inferred from the author's usage. In particular, $PM_{2.5}$ and fine particles are not equivalent. $PM_{2.5}$ refers to the aggregate sample of PM that is collected following a size-selective inlet with a specified penetration as a function of size and a 50% cutpoint of 2.5 µm D_a. It may also be used to refer to number (or other measure of particles suspended in the atmosphere that would be collected by such a sampler). PM_{10} is defined similarly. $PM_{10\text{-}2.5}$ refers to the sample that would be collected if the $PM_{2.5}$ component could be removed from a PM_{10} sample.

Several processes influence the formation and growth of particles. New particles may be formed by nucleation from gas phase material. Particles may grow by condensation as gas phase material condenses onto existing particles. Particles may also grow by coagulation as two particles combine to form one. Gas phase material condenses preferentially on smaller particles, and the rate constant for coagulation of two particles decreases as the particle size increases. Therefore, nuclei mode particles grow into the accumulation mode, but growth of accumulation mode particles into the coarse mode is rare.

The major constituents of atmospheric PM are sulfate, nitrate, ammonium, and hydrogen ions; particle-bound water; elemental carbon; a great variety of organic compounds; and crustal material. Atmospheric PM contains a large number of elements in various compounds and concentrations and hundreds of specific organic compounds. Particulate material can be primary or secondary. PM is called primary if it is in the same chemical form in which it was emitted into the atmosphere. PM is called secondary if it is formed by chemical reactions in the atmosphere. Primary coarse particles are usually formed by mechanical processes; whereas primary fine particles are emitted from sources either directly as particles or as vapors that rapidly condense to form particles.

Most of the sulfate and nitrate and a portion of the organic compounds in atmospheric particles are secondary. Secondary aerosol formation depends on numerous factors including the concentrations of precursors; the concentrations of other gaseous reactive species such as ozone, hydroxyl radical, peroxy radicals, and hydrogen peroxide; atmospheric conditions, including solar radiation and relative humidity; and the interactions of precursors and preexisting particles within cloud or fog droplets or on or in the liquid film on solid particles. As a result, it is considerably more difficult to relate ambient concentrations of secondary species to sources of precursor emissions than it is to identify the sources of primary particles.

The lifetimes of particles vary with particle size. Coarse particles can settle rapidly from the atmosphere within minutes or hours and normally travel only short distances. However, when mixed high into the atmosphere, as in dust storms, the smaller-sized, coarse-mode particles may have longer lives and travel greater distances. Accumulation-mode particles are kept suspended by normal air motions and have a lower deposition velocity than coarse-mode particles. They can be transported thousands of kilometers and remain in the atmosphere for a number of days. Accumulation-mode particles are removed from the atmosphere primarily by cloud processes. Dry deposition rates are expressed in terms of a deposition velocity that varies with the particle size, reaching a minimum between 0.1 and 1.0 μm aerodynamic diameter.

PM is a factor in acid deposition. Particles serve as cloud condensation nuclei and contribute directly to the acidification of rain. In addition, the gas-phase species that lead to dry deposition of acidity are also precursors of particles. Therefore, reductions in SO_2 and NO_x emissions will decrease both acid deposition and PM concentrations. Sulfuric acid, ammonium nitrate, and organic particles also are deposited on surfaces by dry deposition and can contribute to ecological effects.

2.3.2 Measurement of Atmospheric Particles

The decision by the EPA to revise the PM standards by adding daily and yearly standards for $PM_{2.5}$ has led to a renewed interest in the measurement of atmospheric particles and to a better understanding of the problems in developing precise and accurate measurements of particles. Unfortunately, it is very difficult to measure and characterize particles suspended in the atmosphere.

PM monitoring is used to develop information to guide implementation of standards (i.e., to identify sources of particles; to determine whether or not a standard has been attained; and to determine health, ecological, and radiative effects). Federal Reference Methods (FRM) specify techniques for measuring PM_{10} and $PM_{2.5}$. Particles are collected on filters and mass concentrations are determined gravimetrically. The PM_{10} FRM sampler consists of a PM_{10} inlet/impactor and a 47-mm Teflon filter with a particle collection efficiency greater than 99.7%. The $PM_{2.5}$ FRM is similar except that it includes a $PM_{2.5}$ impactor with an oil-covered impaction substrate to remove particles larger than 2.5 μm. Both techniques provide relatively precise (±10%) methods for determining the mass of material remaining on a Teflon filter after equilibration. Despite considerable progress in measuring the atmospheric PM mass concentration, numerous uncertainties continue to exist as to the relationship between the mass and composition of material remaining on the filter as measured by the FRMs and the mass and composition of material that exists in the atmosphere as suspended PM. There is no reference standard for particles suspended in the atmosphere, nor is there an accepted way to remove particle-bound water without losing some of the semivolatile components of PM such as ammonium nitrate and semivolatile organic compounds. It also is difficult to cleanly separate fine and coarse PM. As a result, EPA defines accuracy for PM measurements in terms of agreement of a candidate sampler with a reference sampler. Therefore, intercomparisons of samplers become very important in determining how well various samplers agree and how various design choices influence what is actually measured.

Current filtration-based mass measurements lead to significant evaporative losses of a variety of semivolatile components (i.e., species that exist in the atmosphere in dynamic equilibrium between the condensed phase and gas phase) during and possibly after collection. Important examples include ammonium nitrate, semivolatile organic compounds, and particle-bound water. Loss of these components may significantly affect the quality of the measurement and can lead to both positive and negative sampling artifacts. Negative artifacts resulting from loss of ammonium nitrate and semivolatile organic compounds may occur during sampling because of changes in temperature, relative humidity, or composition of the aerosol or because of the pressure drop across the filter. Negative artifacts also may occur during handling and storage because of evaporation. Positive artifacts occur when gas-phase compounds (H_2O, HNO_3, SO_2, and organic compounds) absorb onto or react with filter media or collected PM or when some particle-bound water is not removed.

Sampling systems for semivolatile PM components make use of denuders to remove the gas-phase fraction and absorptive filters to remove the condensed phase and retain any material that subsequently evaporates from the collected PM. The loss of particulate nitrate may be determined by comparing nitrate collected on a Teflon filter to that collected on a nylon filter (which absorbs nitric acid which evaporates from ammonium nitrate particles) preceded by a denuder to remove gas-phase nitric acid. In two studies in southern California, the $PM_{2.5}$ mass lost because of volatilization of ammonium nitrate was found to represent 10 to 20% of the total $PM_{2.5}$ mass and almost a third of the nitrate. Denuder/absorptive filter sampling systems also have been developed for measuring particulate phase organic compounds. This technique is an improvement over the filter/adsorbent collection method. However, the denuder systems currently discussed in the literature are not straightforward in their use, and the user must have a thorough understanding of the technology. The FRM for $PM_{2.5}$ will likely suffer loss of particulate nitrates and semivolatile organic compounds, similar to the losses experienced with other single filter collection systems.

It is generally desirable to collect and measure ammonium nitrate and semivolatile organic compounds as part of particulate matter mass. However, it is usually desirable to remove the particle-bound water before determining the mass. In some situations, it may be important to know how much of the suspended particle's mass or volume results from particle-bound water. Calculations and measurements indicate that aerosol water content is strongly dependent on relative humidity and composition. Particle-bound water can represent a significant mass fraction of the PM concentration at relative humidities above 60%. A substantial fraction of accumulation-mode PM is hygroscopic or deliquescent. The more hygroscopic particles tend to contain more sulfates, nitrates, and secondary organic compounds, while the less hygroscopic particles tend to contain more elemental carbon, primary organic compounds, and crustal components. Fresh, submicron-size soot particles may tend to shrink with increasing relative humidity because of a structural change. The effects of relative humidity on the sorption of semivolatile organic compounds on particles are not well understood. The amount of water sorbed to an atmospheric aerosol may be affected by the presence of an organic film on the particle, which may impede the transport of water across the surface.

Fine and coarse particles differ not only in formation mechanisms and size, but also in sources; composition; and chemical, physical, and biological properties. Fine and coarse particles overlap in the intermodal size range (1-2.5 µm D_a). As relative humidity increases, fine particles grow into this size range; as relative humidity decreases, more coarse particles may be suspended in this size range. It is desirable to measure fine PM and coarse PM separately in order to properly allocate health effects to either fine PM or coarse PM and to correctly determine sources by factor analysis or chemical mass balance. The selection of a cut point of 2.5 µm as a basis for EPA's 1997 NAAQS for fine particles (Federal Register, 1997) and its continued use in many health effects studies reflects the importance placed on more complete inclusion of accumulation-mode particles, while recognizing that intrusion of coarse-mode particles can occur under some conditions with this cut point.

In addition to FRM sampling of equilibrated mass to determine compliance with PM standards, EPA requires states to conduct speciation sampling primarily to determine source categories and trends. The current speciation samplers collect $PM_{2.5}$ on three filters: (1) a Teflon filter for gravimetric determination of mass and for analysis of heavy elements by X-ray fluorescence; (2) a Nylon filter preceded by a nitric acid denuder for artifact-free determination of nitrate and measurement of other ionic species by ion chromatography; and (3) a quartz filter for measurement of elemental carbon (EC) and organic carbon (OC). In addition, IMPROVE (Interagency Monitoring of Protected Visual Environments) samplers provide information on regional PM background and transport. IMPROVE samplers, in addition to the three types of filters collected by the speciation samplers, also collect a PM_{10} sample. The IMPROVE and speciation networks use slightly different methods for determination of EC and OC. The two methods agree on total carbon but differ in the split of total carbon into EC and OC. The two methods also differ in their correction for positive artifacts due to absorption of volatile organic compounds on the quartz filters. Neither EC/OC method provides for any correction for negative artifacts due to evaporation of semivolatile organic compounds from the collected particles.

The EPA expects that monitoring agencies will operate continuous PM monitors; and EPA is in the process of providing guidance regarding appropriate continuous monitoring techniques. All currently available techniques for continuous measurements of suspended particle mass, e.g., the integrating nephelometer, the beta-absorption monitor, and the Tapered Element Oscillating Microbalance (TEOM), share the problem of dealing with semivolatile PM components: that is, in order not to include particle-bound water as part of the mass, the particle-bound water must be removed by heating or dehumidification; however, heating also causes ammonium nitrate and semivolatile organic compounds to evaporate. The TEOM monitor operates at a constant, but higher than ambient, temperature to remove particle-bound water; whereas, the FRM is required to operate at no more than 5 °C above the ambient temperature. Subsequently, much of the particle-bound water is removed during equilibration at 40% relative humidity. This difference in techniques for removal of particle-bound water causes differences in the measured mass concentration between the TEOM and FRMs.

Several new techniques for continuous PM mass measurements are currently being field tested. The Real-Time Total Ambient Mass Sampler (RAMS) measures the total mass of collected particles including semivolatile species with a TEOM monitor using a “sandwich filter.” The sandwich contains a Teflon-coated particle-collection filter followed by a charcoal-impregnated filter to collect any semivolatile species lost from the particles during sampling. The RAMS uses a Nafion dryer to remove particle-bound water from the suspended particles and a particle concentrator to reduce the quantity of gas phase organic compounds that must be removed by the denuder. The Continuous Ambient Mass Monitor (CAMM) estimates ambient particulate matter mass by measurement of the increase in the pressure drop across a membrane filter caused by particle loading. It also uses a Nafion dryer to remove particle-bound water. A new differential TEOM offers the possibility of measuring both nonvolatile and semivolatile PM mass. In addition to continuous mass measurement, a number of techniques for continuous measurement of sulfate, nitrate, or elements are being tested.

2.3.3 Key Points

Fine and Coarse Particles

Particle size distributions show that atmospheric particles exist in two classes, fine particles and coarse particles. Fine and coarse particles are defined primarily in terms of their formation mechanisms and size; an they also differ in sources, chemical composition, and removal processes (see Table 2-1). Subsequent chapters will show that fine and coarse particles also differ in aspects of concentration, exposure, dosimetry, toxicology, and epidemiology.

These differences support the setting of separate standards for fine and coarse particles. Fine and coarse particles overlap in the size range between 1 and 3 µm aerodynamic diameter where particulate matter (PM) concentrations are at a minimum. Coarse particles are generally larger than this minimum and are generally formed by mechanical processes. Coarse particles and coarse-mode particles are equivalent terms. Fine particles are generally smaller than the minimum and are generally formed by coagulation and condensation of gases. Fine particles are subdivided into accumulation, Aitkin, and nucleation modes. In earlier texts, nuclei mode referred to the size range now split into the Aitkin and nucleation modes (see Figures 2-4 and 2-5).

Measurement of Mass and Composition

Nonvolatile PM. Analytical techniques exist for measurement of the mass and chemical composition of PM retained on a filter (nonvolatile mass) in terms of elements (except carbon) and certain key ions (sulfate, nitrate, hydrogen, and ammonium). Acceptable measurements can be made of the total carbon retained on a filter. However, the split into organic carbon and elemental carbon depends on the operational details of the analytical methods and varies somewhat among methods. Determination of the various organic compounds in the organic carbon fraction remains a challenge.

Semivolatile PM. Important components of atmospheric PM (particle-bound water, ammonium nitrate, and many organic compounds) are termed semivolatile because significant amounts of both the gaseous and condensed phases may exist in the atmosphere in equilibrium. Particle-bound water is not considered a pollutant. Most of the particle-bound water is removed by heating the particles or by equilibration of the collected particles at a low relative humidity

(40%) for 24 hours. However, these processes also cause the loss of other semivolatile components. Semivolatile components also evaporate from the filter during sampling due to the pressure drop across the filter or due to a reduction in the atmospheric concentration during the sampling time. Filter collection and equilibration techniques for PM, such as prescribed by the Federal Reference Methods, lose a fraction of the semivolatile PM. Continuous methods must dry the PM to remove particle-bound water. If heating is used to dry the particles, more of the semivolatile components may be removed than are lost in filter sampling. Collection and retention of ammonium nitrate and semivolatile organic compounds represents a major challenge in the effort to move to continuous measurement of PM mass. The use of diffusion dryers, which dehumidify the air stream without heating, represents a promising approach. Uncertainty in the efficiency of retention of ammonium nitrate and organic compounds on filters also impacts source category attribution and epidemiologic studies.

Separation of Fine and Coarse PM

Techniques are available to separate fine particles from coarse particles and collect the fine particles on a filter. No such technique exists for coarse particles. As yet, no consensus exists on the best technique for collecting a coarse particle sample for determination of mass and composition. Candidates include multistage impaction, virtual impaction, and difference (subtracting $PM_{2.5}$ mass or composition from PM_{10} mass or composition). Advances in the theory and practice of virtual impaction suggest that it would be possible to design virtual impactors with much less than the 10% of fine PM collected in the coarse PM sample as is now the case for the dichotomous samplers used in air quality studies and with penetration curves as sharp as those used in the current Federal Reference Method for $PM_{2.5}$.

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APPENDIX 2A. TECHNIQUES FOR MEASUREMENT OF SEMIVOLATILE ORGANIC COMPOUNDS

Use of Denuder Systems To Measure Semivolatile Organic Compounds

Phase distribution of semivolatile organic species has been the subject of several studies that have employed denuder technology (see Gundel et al., 1995; Gundel and Lane, 1999) to directly determine the phase distributions while avoiding some of the positive and negative sampling artifacts associated with using back-up quartz filters. In an ideal system with a denuder that is 100% efficient, the gas phase would be collected in the denuder and the particle phase would be the sum of the material collected on the filter and the adsorbent downstream. Denuder collection efficiency depends on the denuder surface area (+), the diffusivity (+) and vapor pressure (−) of the compound, the temperature (−) and flow rate (−) of the air stream, and the presence of competing species (−), including water vapor (Cui et al., 1998; Kamens and Coe, 1997; Lane et al., 1988). (The + and – symbols in parentheses indicate qualitatively the effect increasing each parameter would have on efficiency). In a system with a denuder collection efficiency less than 100%, the collection efficiency must be known to accurately attribute adsorbed organics from denuder breakthrough to the gas phase and adsorbed organics volatilized from collected particles to the particle phase. In calculating the overall phase distributions of SVOC PAH from a denuder system, the collection efficiency for each compound is needed.

The efficiency of silicone-grease-coated denuders for the collection of polynuclear aromatic hydrocarbons was examined by Coutant et al. (1992), who examined the effects of uncertainties in the diffusion coefficients and in the collisional reaction efficiencies on the overall phase distributions of SVOC PAH calculated using denuder technology. In their study, they used a single stage, silicone-grease-coated aluminum annular denuder with a filter holder mounted ahead of the denuder and an XAD trap deployed downstream of the denuder. In a series of laboratory experiments, they spiked the filter with a mixture of perdeuterated PAH, swept the system with ultra-high purity air for several hours, and then analyzed the filter and the XAD. They found that the effects of these uncertainties, introduced by using a single compound as a surrogate PAH (in their case, naphthalene) for validation of the denuder collection efficiency, are less significant than normal variations because of sampling and analytical effects. Results on field studies using their sampling system have not been published.

For measuring particulate phase organic compounds, the denuder-based sampling system represents an improvement over the filter/adsorbent collection method (Turpin et al., 1993). Some researchers, however, have reported that denuder coatings themselves can introduce contamination (Mukerjee et al., 1997) and that the adsorbed species may be difficult to remove from the coating (Eatough et al., 1993).

In a study conducted in southern California (Eatough et al., 1995), the Brigham Young University Organic Sampling System (BOSS; Eatough et al., 1993) was used for determining POM composition, and a high-volume version (BIG BOSS; flow rate 200 L/min) was utilized for determining the particulate size distribution and the chemical composition of SVOC in fine particles. The BOSS, a multi-channel diffusion denuder sampling system, consists of two separate samplers (each operating at 35 L/min). The first sampler consists of a multi-parallel plate diffusion denuder with charcoal-impregnated filter papers as the collection surfaces followed by a two-stage quartz filter pack and a two-stage charcoal-impregnated filter pack. The second sampler operating in parallel with the first consists of a two-stage quartz filter pack, followed by the parallel plate denuder, followed by the two-stage charcoal-impregnated filter pack. The filter samples collected by the BOSS sampler were analyzed by temperature-programmed volatilization analysis. The second channel allows calculations of the efficiency of the denuder in removing gas-phase specifics that would be absorbed by the charcoal impregnated filter. Eatough et al. (1995) also operated a two-stage quartz filter pack alongside the BOSS sampler. The BIG BOSS system (Tang et al., 1994) consists of four systems (each with a flowrate of 200 L/min). Particle size cuts of 2.5, 0.8, and 0.4 μm are achieved by virtual impaction, and the sample subsequently flows through a denuder, then is split, with the major flow (150 L/min) flowing through a quartz filter followed by an XAD-II bed. The minor flow is sampled through a quartz filter backed by a charcoal-impregnated filter paper. The samples derived from the major flow (quartz filters and XAD-II traps) were extracted with organic solvents and analyzed by gas chromatography (GC) and GC-mass spectroscopy. The organic material lost from the particles was found to represent all classes of organic compounds.

Eatough et al. (1996) operated the BOSS sampler for a year at the IMPROVE site at Canyonlands National Park, UT, alongside the IMPROVE monitor and alongside a separate sampler consisting of a two-stage quartz filter pack. They found that concentrations of particulate carbon determined from the quartz filter pack sampling system were low on average by 39%, and this was attributed to volatilization losses of SVOC from the quartz filters. In another study conducted with the BOSS in southern California, losses of 35% of the POM, on average, were found and attributed to losses of the SVOC during sampling (Eatough et al., 1995).

The denuder used in the various BOSS samplers consists of charcoal-impregnated cellulose fiber filter material. Denuder collection efficiencies of greater than 95% have been reported for organic gases that adsorb on quartz and charcoal-impregnated filters (Eatough et al., 1999a; Ding et al., 2002; Lewtas et al., 2001). However, because the mass concentration of gas phase species that adsorb on quartz and charcoal-impregnated filters is so much greater than the mass of semivolatile organic material in the particulate phase, it is necessary to measure and account for the inefficiency of the denuder in the BOSS samplers. To address this problem, Brigham Young University (BYU) developed a particle-concentrator (PC)-BOSS system (Ding et al., 2002; Eatough et al., 1999b; Lewtas et al., 2001; Modey et al., 2001; Pang et al., 2001, 2002a,b). The PC-BOSS includes a virtual impactor upstream of the denuder to improve the denuder collection efficiency by removing a majority of the gases from the aerosol flow. With this system, denuder collection efficiencies of greater than 99% have been reported for organic gases, SO_2(g), HNO_3(g) and other species that adsorb on quartz and charcoal-impregnated filters (Pang et al., 2001). Since the concentrations of semivolatile organic and other gases in the presence of the concentrated particles is not altered by this process the virtual impaction concentration of accumulation mode particles (except possibly by slight changes in pressure), it is anticipated that the gas-particle distribution will not be significantly altered by the concentration process. The virtual impactor has a 50% cut point at 0.1 μm aerodynamic diameter. As a result, some particles in the 0.05 to 0.2 μm diameter size range will be removed in the major flow along with the majority of the gases. Therefore, the mass collection efficiency of the virtual impactor concentrator will be a function of the particle size distribution in the 0.05 to 0.1 μm size range. This collection efficiency is measured by comparing the concentration of nonvolatile components measured in the concentrated sample with that measured in an unconcentrated sample. The concentration efficiency varies from 50 to 75%. It is relatively constant over periods of weeks but varies by season and site, presumably as the particle size distribution changes. Previous studies at Harvard (Sioutas et al., 1995a,b) have shown that the composition of the sampled aerosol is little changed by the concentration process. The BYU studies listed above have shown that the concentration efficiencies for sulfate, organic carbon (OC) and elemental carbon (EC) are comparable for a given sampling location. Furthermore, the concentrations of these species and of fine particulate nitrate determined using the PC-BOSS have been shown to be comparable to those determined using more conventional samplers for sulfate or EC or using simpler denuder systems for OC and nitrate.

Ding et al. (1998a) developed a method for the determination of total n-nitroso compounds in air samples and used the method to examine organic compounds formed from NO_x chemistry in Provo, UT (Ding et al., 1998b). In their method, n-nitroso compounds are selectively decomposed to yield nitric oxide, which is then detected using chemiluminescence. From the samples from Provo, they found that the majority of the n-nitroso and nitrite organic compounds that were present in fine particulate matter were semivolatile organic compounds that could be evaporated from the particles during sampling. They found particulate n-nitroso compound concentrations ranging between <1 and 3 nmoles/m^3 and gas-phase n-nitroso compound concentrations in the same range. Particulate organic nitrite concentrations were found in the range of <1 to ≈5 nmoles/m^3, and gas-phase concentrations as high as 10 nmoles/m^3 were found.

Turpin et al. (1993) developed a sampling system that corrects for the loss of semivolatile organic compounds during sampling by removal of most of the gas phase material from the particles in a diffusion separator sampling system. Unlike the previously mentioned systems, wherein the particulate phase is measured directly, in the system of Turpin et al. (1993) the gas-phase is measured directly. In the laminar flow system, ambient, particle-laden air enters the sampler as an annular flow. Clean, particle-free air is pushed through the core inlet of the separator. The clean air and ambient aerosol join downstream of the core inlet section, and flow parallel to each other through the diffusion zone. Because of the much higher diffusivities for gases compared to particles, the SVOC in the ambient air diffuses to the clean, core flow. The aerosol exits the separator in the annular flow, and the core flow exiting the separator now contains a known fraction of the ambient SVOC. Downstream of the diffusion separator, the core exit flow goes into a polyurethane foam (PUF) plug, where the SVOC is collected. The adsorbed gas phase on the PUF plug is extracted with supercritical fluid CO_2 and analyzed by gas chromatography/mass-selective detection (GC/MSD). The gas-phase SVOC is thus determined. Ultimately, to determine particulate phase SVOC concentrations, the total compound concentration will also be measured and the particulate phase obtained by difference.

The system was tested for the collection of PAH. The diffusional transport of gas-phase PAHs and particle concentrations agreed well with theory. Breakthrough was problematic for low molecular weight PAHs (MW < 160). Detection limits ranged from 20 to 50 pg of injected mass for all PAHs.

Gundel et al. (1995) recently developed a technique for the direct determination of phase distributions of semivolatile polycyclic aromatic hydrocarbons using annular denuder technology. The method, called the integrated organic vapor/particle sampler (IOVPS), uses a cyclone inlet with a 50% cutpoint of 2.5 μm at a sampling rate of 10 L/min. The airstream then goes through two or three sandblasted glass annular denuders that are coated with ground adsorbent resin material (XAD-4 was initially examined) that traps vapor-phase organics. The airstream subsequently passes through a filter, followed by a backup denuder. The denuder collection efficiency is high and compares well with predictions based on the diffusivity of the compounds. The denuder can also be extracted to obtain gas-phase concentrations directly (Gundel and Lane, 1999). Particle-phase PAHs are taken to be the sum of material on the filter and XAD adsorbent downstream after correction for denuder collection efficiency. The IOVPS was tested for sampling semivolatile PAH in laboratory indoor air and in environmental tobacco smoke (ETS). After exposure, the denuders, filters, and sorbent traps were extracted with cyclohexane (Gundel et al., 1995) and analyzed for PAHs from naphthalene to chrysene using dual-fluorescence detection (Mahanama et al., 1994). Recoveries from both denuders and filters were approximately 70% for 30 samples. Detection limits (defined as 3 times the standard deviation of the blanks) for gas-phase SVOC PAHs ranged from 0.06 ng for anthracene to 19 ng for 2-methylnaphthalene. The 95% confidence interval for reproduction of an internal standard concentration was 6.5% of the mean value. Relative precision, from a propagation of errors analysis or from the 95% confidence interval from replicate analyses of standard reference material SRM 1649 (urban dust/organics), was 12% on average (8% for naphthalene to 22% for fluorene). Sources of error included sampling flow rate, internal standard concentration, and co-eluting peaks. Gundel and Lane (1999) reported that roughly two-thirds of particulate PAH fluoranthene, pyrene, benz[*a*]anthracene, and chrysene were found on the postfilter denuders, so that it is likely that considerable desorption from the collected particles took place.

Solid adsorbent-based denuder systems have been investigated by other researchers as well. Bertoni et al. (1984) described the development of a charcoal-based denuder system for the collection of organic vapors. Risse et al. (1996) developed a diffusion denuder system to sample aromatic hydrocarbons. In their system, denuder tubes with charcoal coating and charcoal paper precede a filter pack for particulate collection and an adsorption tube to capture particle blow-off from the filter sample. Breakthrough curves for benzene, toluene, ortho-xylene, and meta-xylene were developed for 60-, 90-, and 120-cm denuder tubes. The effects of relative humidity on the adsorption capacities of the denuder system were examined, and it was found that the capacity of the charcoal was not affected significantly by increases in relative humidity. The feasibility of outdoor air sampling with the system was demonstrated.

Krieger and Hites (1992) designed a diffusion denuder system that uses capillary gas chromatographic columns as the tubes for SVOC collection. The denuder was followed by a filter to collect particles, which in turn was followed by a PUF plug to collect organic material volatilizing off the filter. Denuder samples were analyzed by liquid solvent extraction (CH_2Cl_2) followed by GC-mass spectrometric analysis. The PUF plugs and filters were extracted with supercritical fluid extraction using supercritical N_2O. Using this system, an indoor air sample was found to contain primarily chlorinated biphenyls, ranging from trichlorobiphenyls (vapor pressures $10^{-3} – 10^{-4}$ Torr at 25 °C) to octachlorobiphenyls ($10^{-6} – 10^{-7}$ Torr). This demonstrated that the sampler collects compounds with a wide range of volatility. They also found that on-line desorption is successful in maintaining good chromatographic peak shape and resolution. The entire method, from sample collection to the end of the chromatographic separation, took 2 h.

Organic acids in both the vapor and particulate phases may be important contributors to ambient acidity, as well as representing an important fraction of organic particulate matter. Lawrence and Koutrakis (1996a,b) used a modified Harvard/EPA annular denuder system (HEADS) to sample both gas and particulate phase organic acids in Philadelphia, PA, in the summer of 1992. The HEADS sampler inlet had a 2.1-µm cutpoint impactor (at 10 L/min), followed by two denuder tubes, and finally a filter pack with a Teflon filter. The first denuder tube was coated with potassium hydroxide (KOH) to trap gas phase organic acids. The second denuder tube was coated with citric acid to remove ammonia and thus to avoid neutralizing particle phase acids collected on the filter. The KOH-coated denuder tube was reported to collect gas phase formic and acetic acids at better than 98.5% efficiency and with precisions of 5% or better (Lawrence and Koutrakis, 1994). It was noted that for future field measurements of particulate organic acids, a Na_2CO_3-coated filter should be deployed downstream of the Teflon filter to trap organic acids that may evaporate from the Teflon filter during sampling.

Role of the Collection Media

The role of the collection media was recently examined in a study conducted in Seattle (Lewtas et al., 2001). In that study, the influence of denuder sampling methods and filter collection media on the measurement of SVOC associated with $PM_{2.5}$ was evaluated. Activated carbon and XAD collection media were used in diffusion denuders and impregnated back-up filters in two different samplers, the Versatile Air Pollution Sampler (VAPS) and the PC-BOSS. XAD-coated glass annular denuders and charcoal-impregnated cellulose fiber (CIF) filter denuders also were used. CIF filters also were compared to XAD-coated quartz filters as backup filter collection media. Lewtas et al. (2001) found that the two denuder types resulted in an equivalent measurement of particulate organic carbon and particle mass. The carbon-coated denuders in the BOSS sampler were more efficient than the XAD-coated denuders for the collection of the more highly volatile organic compounds (MHVOC). Lewtas et al. (2001) concluded that this MHVOC that is collected in the carbon-coated BOSS denuder does not contribute substantially to the particle mass or to the SVOC measured as OC on quartz filters. However, this MHVOC would be captured in the carbon impregnated filters placed behind the quartz filters, so that, in the XAD denuder configuration, the captured MHVOC would cause a higher OC concentration and an overestimation of the SVOC.

Some of the recent research in denuder technology also has focused on reduction in the size of the denuder, optimization of the residence time in the denuder, understanding the effect of diffusion denuders on the positive quartz filter artifact, identifying changes in chemical composition that occur during sampling, determining the effects of changes in temperature and relative humidity, and identifying possible losses by absorption in coatings.

Reducing the Size of Denuders

The typical denuder configuration is an annular diffusion denuder tube of significant length (e.g., 26.5 cm for 10 L/min [Koutrakis et al., 1988a,b]). A more compact design based on a honeycomb configuration was shown to significantly increase the capacity (Koutrakis et al., 1993). However, in intercomparisons with an annular denuder/filter pack system (Koutrakis et al., 1988), significant losses of ammonia and nitric acid were observed for the honeycomb configuration and were attributed to the large inlet surface area and long sample residence time of the honeycomb design relative to the annular denuder system. Sioutas et al. (1996a) subsequently designed a modified glass honeycomb denuder/filter pack sampler (HDS) with an inlet that minimizes vapor losses on the inlet surfaces. The modified HDS has reduced inlet surfaces and decreased residence time for sampled gases (NH_3 and HNO_3) compared to its predecessor (Sioutas et al., 1994d). Sioutas et al. (1996b) also tested various inlet materials (glass, PFA, and polytetrafluoroethylene [PTFE]) in laboratory tests and found that a PTFE Teflon coated inlet minimized loss of sampled gases (1 to 8% loss of HNO_3 observed, and −4 to 2% loss of NH_3 observed). The highest inlet losses were observed for HNO_3 lost to PFA surfaces (14 to 25%). The modified HDS was tested in laboratory and field tests and found to agree within 10% with the annular denuder system.

Residence Time in the Denuder

The efficiency of a diffusion denuder sampler for the removal of gas phase material can be improved by increasing the residence time of the sampled aerosol in the denuder. However, the residence time can only be increased within certain limits. Because the diffusion denuder reduces the concentration of gas-phase semivolatile organic material, semivolatile organic matter present in the particles passing through the denuder will be in a thermodynamically unstable environment and will tend to outgas SVOC during passage through the denuder. The residence time of the aerosol in the denuder, therefore, should be short enough to prevent significant loss of particulate phase SVOC to the denuder. Various studies have suggested that the residence time in the denuder should be less than about 2 s (Gundel and Lane, 1999; Kamens and Coe, 1997; Kamens et al., 1995). The residence times in the various denuder designs described by Gundel and Lane (1999) are from 1.5 to 0.2 s. The equilibria and evaporation rates are not as well understood for organic components as they are for NH_4NO_3 (Zhang and McMurry, 1987, 1992; Hering and Cass, 1999).

Effect of Diffusion Denuders on the Positive Quartz Filter Artifact

The adsorption of organic compounds by a second quartz filter has been shown to be reduced, but not eliminated, in samples collected in the Los Angeles Basin if a multi-channel diffusion denuder with quartz filter material as the denuder collection surface preceded the quartz filters (Fitz, 1990). This artifact can be further reduced by the use of activated charcoal as the denuder surface and the use of a particle concentrator to reduce the amount of gas phase organic compounds relative to condensed phase organic compounds (Cui et al., 1997, 1998; Eatough, 1999). Other experiments (Cotham and Bidleman, 1992; Cui et al., 1998; Eatough et al., 1995, 1996) have shown that the quartz filter artifact can result both from the collection of gas phase organic compounds and from the collection of semivolatile organic compounds lost from particles during sampling. Thus, results available to date suggest that both a "positive" and a "negative" artifact can be present in the determination of particulate phase organic compounds using two tandem quartz filters.

The importance of the adsorption of organic vapors on filters or PM relative to the volatilization of organic compounds from PM collected on a filter continues to be a topic of active debate. The relative importance of positive and negative artifacts will be different for denuded and undenuded filters; will depend on face velocity, sample loading, and the vapor pressures of the compounds of interest; and may vary with season and location because of variations in the composition of volatile and semivolatile organic material. Evidence exists for substantial positive and negative artifacts in the collection of organic PM.

Changes in Chemical Composition During Sampling

The use of sampling systems designed to correctly identify the atmospheric gas and particulate phase distributions of collected organic material has been outlined above. An additional sampling artifact that has received little consideration in the collection of atmospheric samples is the potential alteration of organic compounds as a result of the sampling process. These alterations appear to result from the movement of ambient air containing oxidants and other reactive compounds past the collected particles. The addition of NO_2 (<1ppm) or O_3 (<200 ppb) to the sampled air stream (0 to 5 °C) for a high-volume sampler reduced the concentrations of benzo[*a*]pyrene and benzo[*a*]anthracene from a few % to 38%, with the observed reduction increasing with increased concentration of the added gases (Brorström et al., 1983). Spiking a filter with an amine resulted in an increase in measured concentrations of nitrosamines in both the filter and a following XAD sorbent bed for a mid-volume sampler (Ding et al., 1998a,b). Similar results have been obtained for the exposure of a deuterated amine on a filter to NO_x (Pellizzari and Krost, 1984). When Tenax columns spiked with deuterated styrene and cyclohexene were exposed to ppm concentrations of ozone or halogens, oxygenated and halogenated compounds were formed (Pellizzari and Krost, 1984). Similar oxidation of aldehydes and peroxyacetylnitrate (PAN) during sampling has been observed (Grosjean and Parmar, 1990). Collected PAH compounds can be oxygenated or nitrated on a filter (Davis et al., 1987; Lindskog and Brorstrom-Lunden, 1987), but 1-nitropyrene has been shown to be resistant to additional nitration (Grosjean, 1983). These various chemical transformations of collected organic compounds can be eliminated by removal of the gas phase oxidants, NO_x, HNO_3, etc., by reaction or adsorption prior to collection of the particles (Ding, 1998a,b; Grosjean and Parmar, 1990; Parmar and Grosjean, 1990; Pellizzari and Krost, 1984; Williams and Grosjean, 1990). The BOSS denuder should be effective in eliminating most of the chemical transformation artifacts because reactive gases are removed by the charcoal denuder that precedes the particle collection filter.

Temperature and Relative Humidity Effects

The problems of sampling artifacts associated with SVOC adsorption and evaporation are compounded by temperature and relative humidity effects (Pankow and Bidleman, 1991; Pankow et al., 1993; Falconer et al., 1995; Goss and Eisenreich, 1997). Effects of temperature on the partitioning of PAH were examined by Yamasaki et al. (1982), who found that the partition coefficient (PAH_{vapor}/PAH_{part}) was inversely related to temperature and could be described using the Langmuir adsorption concept. The dissociation of ammonium nitrate aerosol is also a function of temperature. Bunz et al. (1996) examined the dissociation and subsequent redistribution of NH_4NO_3 within a bimodal distribution using a nine-stage low-pressure Berner impactor followed by analysis by ion chromatography and found a strong temperature dependency on the redistribution. Bunz et al. (1996) found that at lower temperatures (below 10 ˚C) there was little change in the aerosol size distribution. At temperatures between 25 and 45 ˚C, however, the lifetime of NH_4NO_3 particles decreases by more than a factor of 10, and size redistribution, as measured by average ending particle diameter, increased more for higher temperatures than for lower temperatures.

The effects of relative humidity on the sorption of SVOC on particles are not well understood. In a series of laboratory experiments, Goss and Eisenreich (1997) examined the sorption of both nonpolar (hydrocarbons and chlorinated hydrocarbons) and polar (ethyl ether and acetone) volatile organic compounds onto combustion soot particles as a function of temperature and relative humidity. The soot particles used in their experiments were collected from oil furnaces and contained 60% (w/w) iron sulfate (water-soluble fraction) and 9% (w/w) elemental and organic carbon. They found that, for all compounds, the sorption of VOC onto soot particles decreased with increasing relative humidity over the range of 10 to 95%. They also observed hysteresis in the relative humidity dependency, with sorption coefficients at a given relative humidity higher when the RH is being increased than when the RH is being decreased. The sorption coefficients were fit with an exponential function to the RH so that the slope of the regression line would provide a measure of the influence of relative humidity. Based on the magnitude of the slope, they concluded that the RH-dependency of sorption was stronger for water-soluble organic compounds.

In another study by Jang and Kamens (1998), humidity effects on gas-particle partitioning of SVOC were examined using outdoor environmental chambers and the experimentally determined partitioning coefficients were compared to theoretical values. They examined the partitioning of SVOC onto wood soot, diesel soot, and secondary aerosols and concluded that “the humidity effect on partitioning was most significant for hydrophobic compounds adsorbing onto polar aerosols.” Although these two studies seem to be contradictory, on closer examination, it is difficult to compare the two studies for several reasons. The experiments conducted by Jang and Kamens (1998) were conducted in outdoor chambers at ambient temperatures and humidities. Their model was for absorptive partitioning of SVOC on *liquid-like* atmospheric particulate matter. In contrast, the results of Goss and Eisenreich (1997) were obtained from a gas chromatographic system operated at 70 ˚C higher than ambient conditions. The model of Goss and Eisenreich (1997) was for adsorptive partitioning of VOC on *solid-like* atmospheric particulate matter. In the study of Jang and Kamens (1998), calculated theoretical values for water activity coefficients for diesel soot were based on an inorganic salt content of 1 to 2%; whereas, the combustion particles studied by Goss and Eisenreich (1997) contained 60% water-soluble, inorganic salt content. Jang and Kamens (1998) obtained their diesel soot from their outdoor chamber, extracted it with organic solvent (mixtures of hexane and methylene chloride), and measured the organic fraction. The resulting salt content of 2% of the particulate matter studied in Jang and Kamens (1998) is enough to affect water uptake but presumably not to affect the sorption partitioning of organics.

Impactor Coatings

Impactors are used as a means to achieve a size cutpoint and as particle collection surfaces. Particles collected on impactors are exposed to smaller pressure drops than filter-collected particles, making them less susceptible to volatile losses (Zhang and McMurry, 1987). However, size resolution can be affected by bounce when samples are collected at low humidities (Stein et al., 1994). There are other sources of error inherent in some of the currently acceptable practices that could potentially affect particulate mass concentration measurements and that will surely become even more important as more emphasis is placed on chemical speciation. Allen et al. (1999a) reported that the practice of greasing impaction substrates may introduce an artifact from the absorption of semivolatile species from the gas phase by the grease because the grease could artificially increase the amount of PAHs and other organic compounds attributed to the aerosol. Allen et al. (1999b) offer several criteria to ensure that this absorption artifact is negligible, including selecting impaction oils in which analytes of interest are negligibly soluble and ensuring that species do not have time to equilibrate between the vapor and oil phases (criterion is met for nonvolatile species). They recommend using oiled impaction substrates only if the absorption artifact is negligible as determined from these criteria. Application of greases and impaction oils for preventing or reducing bounce when sampling with impactors is not suitable for carbon analysis because the greases contain carbon (Vasilou et al., 1999).

Kavouras and Koutrakis (2001) investigated the use of polyurethane foam (PUF) as a substrate for conventional inertial impactors. The PUF impactor substrate is not rigid like the traditional impactor substrate so particle bounce and reentrainment artifacts are reduced significantly. Kavouras and Koutrakis (2001) found that the PUF impaction substrate resulted in a much smaller 50% cut point at the same flow rate and Reynolds number. Moreover, the lower 50% cut point was obtained at a lower pressure drop than with the conventional substrate, which could lead to a reduction of artifact vaporization of semivolatile components.

APPENDIX 2B. ANALYTICAL TECHNIQUES

2B.1 INORGANIC ELEMENTS

2B.1.1 Energy Dispersive X-Ray Fluorescence (EDXRF)

EDXRF has usually been the method of choice for analysis of trace elements on filters. EDXRF is preferred for aerosol analysis over wavelength dispersive XRF because it allows fast and simultaneous analysis over the total spectrum, allowing for the analysis of numerous elements simultaneously. EDXRF can accommodate small sample sizes and requires little sample preparation or operator time after the samples are placed into the analyzer. It also leaves the sample intact after analysis; so, further analysis is possible. XRF irradiates a uniform particle deposit on the surface of a membrane filter with 1 to 50 kev x-rays that eject inner shell electrons from the atoms of each element in the sample (Dzubay and Stevens, 1975; Jaklevic et al., 1977; Billiet et al., 1980; Potts and Webb, 1992; Piorek, 1994; Bacon et al., 1995; deBoer et al., 1995; Holynska et al., 1997; Török et al., 1998; Watson et al., 1999). When a higher energy electron drops into the vacant lower energy orbital, a fluorescent x-ray photon is released. The energy of this photon is unique to each element, and the number of photons is proportional to the concentration of the element. Concentrations are quantified by comparing photon counts for a sample with those obtained from thin-film standards of known concentration (Dane et al., 1996). The previous 1996 PM AQCD included a detailed discussion of EDXRF.

Emitted x-rays with energies less than ~4 kev (affecting the elements sodium, magnesium, aluminum, silicon, phosphorus, sulfur, chlorine, and potassium) are absorbed in the filter, in a thick particle deposit, or even by large particles in which these elements are contained. Very thick filters also scatter much of the excitation radiation or protons, thereby lowering the signal-to-noise ratio for XRF and PIXE. For this reason, thin membrane filters with deposits in the range of 10 to 50 $\mu g/cm^2$ provide the best accuracy and precision for XRF and PIXE analysis (Davis et al., 1977; Haupt et al., 1995).

2B.1.2 Synchrotron Induced X-ray Fluorescence (S-XRF)

S-XRF is a form of EDXRF in which the exciting x-rays are derived from a synchrotron. Bremmstrahlung x-rays are generated when energetic electrons (generally several GeV in energy) are forced by a magnetic field to make a bend in their path. The advantages of the technique are that an extremely high flux of x-rays may be obtained and that the x-rays are 100% polarized in the plane of the electron beam. The former allows for x-ray beams generally of 50 to 500 µm in diameter. However, the beams can be focused into x-ray microprobes, with spot sizes on the order of one µm diameter. The x-ray polarization allows for removal of most of the background normally found under the characteristic x-ray peaks, greatly improving sensitivity compared to other XRF techniques. The primary disadvantages are the limited number of synchrotrons, and that few synchrotrons have S-XRF capabilities. Thus, the technique has been relatively little used for PM, and then generally for special problems such as the smoke from the Kuwaiti oil fires (Cahill et al., 1992, Reid et al., 1994). However, with the increasing availability of S-XRF facilities dedicated to PM analysis, the first of which was the Advanced Light Source opened at Lawrence Berkeley National Laboratory last year, utilization of S-XRF for PM analysis is increasing.

2B.1.3 Proton (or Particle) Induced X-ray Emission (PIXE)

PIXE differs from XRF analysis in the excitation source for producing fluorescence. The filter deposit is bombarded with high-energy protons to remove inner shell electrons and the resulting characteristic x-rays are analyzed as in XRF (Johansson, 1970, Cahill, 1981, 1985; Zeng et al., 1993). Small accelerators, generally Van de Graaffs, generate intense beams of low energy protons, generally of a few MeV in energy. These have the ability to remove electrons from inner shells of atoms of any element. Thus, PIXE can see a very wide range of elements in a single analysis. The cross section for producing x-rays using protons of a few MeV in energy tends to favor lighter elements, Na through Ca, but sensitivities for equivalent PIXE and multi-wavelength XRF analysis are roughly comparable. The technique has been widely used in the U.S. (Flocchini et al., 1976, Malm et al., 1994) and around the world, as many universities have the small accelerators needed for the method. Like S-XRF, the proton beams can be focused into µm size beams, but these have been relatively little used for PM. However, the mm size beams used in both S-XRF and PIXE are well suited to analyzing the limited mass and small deposits that result from detailed particle size measurements by impactors (Perry et al., 1999).

2B.1.4 Proton Elastic Scattering Analysis (PESA)

With the routine availability of elemental analyses for all elements sodium and heavier, organic components remain the major unmeasured species for mass balance. For programs like IMPROVE (Malm et al., 1994), parallel filters are collected for separate organic and elemental carbon determinations. Aerosol programs that use PIXE can directly measure hydrogen simultaneously by scattering protons from Teflon filters that lack hydrogen (Cahill et al., 1989, 1992). Generally, results from organic matter by carbon combustion from quartz filters and organic matter by hydrogen from Teflon filters are in agreement, assuming certain assumptions about the chemical states of sulfates and nitrates are met (Malm et al., 1994, Cahill et al., 1996).

2B.1.5 Total Reflection X-ray Fluorescence (TRXRF)

One of the limitations of the EDXRF method is the minimum detection limit, which may be high due to high background values (Streit et al., 2000). By implementation of x-ray optical geometries that use the total reflection of the primary radiation on flat surfaces, scattering on the substrate is reduced, so that detection limits can be reduced. This is the basis for the total reflection x-ray fluorescence (TRXRF) method (Aiginger and Streli, 1997). This modification to the EDXRF technique improves detection limits and avoids the need to correct for matrix effects. Despite its apparent advantages, TRXRF has not yet become widely in use for atmospheric aerosol analysis but has been used in the analysis of marine aerosol (Stahlschmidt et al., 1997) and at a high elevation site (Streit et al., 2000). Streit et al. sampled ambient air at the High Alpine Research Station (3580 m above sealevel) in the Bernese Alps, Switzerland, using a nine-stage, single-jet, low-pressure, cascade impactor equipped with quartz impactor plates coated with silicon oil diluted in 2-propanol. The typical sample volume for a weekly sample was 10 m^3. The quartz plates were analyzed directly by TRXRF. Streit et al. reported that the minimum detection limits, defined by the 3σ values of the blanks, ranged from 25 ng for S, decreased monotonically with increasing atomic number down to 5 pg for Rb, and decreased after that. The use of TRXRF is expected to increase as EDXRF users become aware of the method. A relatively low-cost, add-on unit has been developed that would allow EDXRF users to test the TRXRF technique (Aiginger, 1991).

2B.1.6 Instrumental Neutron Activation Analysis (INAA)

INAA irradiates a sample in the core of a nuclear reactor for few minutes to several hours, depending on the elements being quantified (Dams et al., 1970; Zoller and Gordon, 1970; Nadkarni, 1975; Landsberger, 1988; Olmez, 1989; Ondov and Divita, 1993). The neutron bombardment chemically transforms many elements into radioactive isotopes. The energies of the gamma rays emitted by these isotopes identify them and, therefore, their parent elements. The intensity of these gamma rays is proportional to the amount of the parent element present in the sample. Different irradiation times and cooling periods are used before counting with a germanium detector. In source apportionment studies, it is possible to use a combination of XRF and INAA to develop a relatively complete set of elemental measurements. Between these two analytical techniques, good sensitivity is possible for many elements, including most of the toxic metals of interest. In general, XRF provides better sensitivity for some metals (e.g., Ni, Pb, Cu, and Fe); whereas INAA provides better sensitivity for others (Sb, As, Cr, Co, Se, and Cd). Both methods provide similar detection limits for still other elements (V, Zn, and Mn). INAA does not quantify some of the abundant species in ambient particulate matter such as silicon, nickel, tin, and lead. While INAA is technically nondestructive, sample preparation involves folding the sample tightly and sealing it in plastic, and the irradiation process makes the filter membrane brittle and radioactive. These factors limit the use of the sample for subsequent analyses.

INAA has been used to examine the chemical composition of atmospheric aerosols in several studies either as the only method of analysis or in addition to XRF (e.g., Yatin et al., 1994; Gallorini, 1995). INAA has higher sensitivity for many trace species, and it is particularly useful in analyzing for many trace metals. Landsberger and Wu (1993) analyzed air samples collected near Lake Ontario for Sb, As, Cd, In, I, Mo, Si, and V using INAA. They demonstrated that using INAA in conjunction with epithermal neutrons and Compton suppression produces very precise values with relatively low detection limits.

Enriched rare-earth isotopes have been analyzed via INAA and used to trace sources of particulate matter from a coal-fired power plant (Ondov et al., 1992), from various sources in the San Joaquin Valley (Ondov, 1996), from intentially tagged (iridium) diesel emissions from sanitation trucks (Suarez et al., 1996; Wu et al., 1998), and from iridium-tagged emissions from school buses (Wu et al., 1998).

An intercomparison was conducted in which 18 pairs of filters were sent to participants in the Coordinated Research Program (CRP) on Applied Research on Waste Using Nuclear Related Analytical Techniques (Landsberger et al., 1997). As part of that study, participants used PIXE, INAA, XRF, or AAS to analyze the samples. Many of the results for XRF and PIXE in the coarse fraction were observed to be biased low compared to INAA. The authors speculated that there is a systematic error because of self-attenuation of the x-rays resulting from the particle size effect.

2B.1.7 Atomic Absorption Spectrophotometry (AAS)

AAS is applied to the residue of a filter extracted in a strong solvent to dissolve the solid material; the filter or a portion of it is also dissolved during this process (Ranweiler and Moyers, 1974; Fernandez, 1989; Jackson and Mahmood, 1994; Chow et al., 2000a). A few milliliters of this extract are injected into a flame where the elements are vaporized. Elements absorb light at certain wavelengths in the visible spectrum, and a light beam with wavelengths specific to the elements being measured is directed through the flame to be detected by a monochrometer. The light absorbed by the flame containing the extract is compared with the absorption from known standards to quantify the elemental concentrations. AAS requires an individual analysis for each element, and a large filter or several filters are needed to obtain concentrations for a large variety of elements. AAS is a useful complement to other methods, such as XRF and PIXE, for species such as beryllium, sodium, and magnesium which are not well-quantified by these methods. Airborne particles are chemically complex and do not dissolve easily into complete solution, regardless of the strength of the solvent. There is always a possibility that insoluble residues are left behind and that soluble species may co-precipitate on them or on container walls.

AAS was used to characterize the atmospheric deposition of trace elements Zn, Ni, Cr, Cd, Pb, and Hg to the Rouge River watershed by particulate deposition (Pirrone and Keeler, 1996). The modeled deposition rates were compared to annual emissions of trace elements that were estimated from the emissions inventory for coal and oil combustion utilities, iron and steel manufacturing, metal production, cement manufacturing, and solid waste and sewage sludge incinerators. They found generally good agreement between the trend observed in atmospheric inputs to the river (dry + wet deposition) and annual emissions of trace elements, with R^2s varying from ≈0.84 to 0.98. Both atmospheric inputs and emissions were found to have followed downward trends for Pb. For the period of 1987 to 1992, steady increases were observed for Cd (major sources are municipal solid waste incineration, coal combustion, sludge incineration, and iron and steel manufacturing), Cr and Ni (major sources are iron and steel production and coal combustion), and Hg (major sources are coal, the contribution from which had decreased from 53 to 45%, and municipal, solid, and medical waste incineration, the contribution from which has increased).

2B.1.8 Inductively Coupled Plasma with Atomic Emission Spectroscopy (ICP-AES)

ICP-AES introduces an extracted sample into an atmosphere of argon gas seeded with free electrons induced by high voltage from a surrounding Tesla coil (Fassel and Kniseley, 1974; McQuaker et al., 1979; Lynch et al., 1980; Harman, 1989; Tyler, 1992; Baldwin et al., 1994). The high temperatures in the induced plasma raise valence electrons above their normally stable states. When these electrons return to their stable states, a photon of light is emitted that is unique to the element that was excited. This light is detected at specified wavelengths to identify the elements in the sample. ICP-AES acquires a large number of elemental concentrations using small sample volumes with acceptable detection limits for atmospheric samples. As with AAS, this method requires complete extraction and destruction of the sample.

2B.1.9 Inductively Coupled Plasma with Mass Spectroscopy (ICP-MS)

ICP-MS has been applied in the analysis of personal exposure samples (Tan and Horlick, 1986; Gray and Williams, 1987a,b; Nam et al., 1993; Munksgaard and Parry, 1998; Campbell and Humayun, 1999). Ion species generated from ICP and from the sample matrix can produce a significant background at certain masses resulting in formation of polyatomic ions that can limit the ability of ICP-MS to determine some elements of interest. Cool plasma techniques have demonstrated the potential to detect elements at the ultra-trace level (Nham et al., 1996) and to minimize common molecular ion interferences (Sakata and Kawabata, 1994; Turner, 1994; Plantz, 1996). Detection limits of ICP-MS using a one-second scan are typically in the range of 10^{-3} ng/m^3, which is an order of magnitude lower than other elemental analysis methods. The instrument can also be set up to analyze a wide dynamic range of aerosol concentrations.

Isotope analysis can also be performed with ICP-MS. Intercomparison studies are needed to establish the comparability of ICP-MS with other non-destructive filter analysis methods.

Keeler and Pirrone (1996) used ICP-MS to determine trace elements Cd, Mn, V, As, Se, and Pb in atmospheric fine particulate ($PM_{2.5}$) and total suspended particulate samples collected in two Detroit sites. The results were used in a deposition model with additional measurements using AAS to estimate the dry deposition flux of trace elements to Lake Erie.

2B.1.10 Scanning Electron Microscopy (SEM)

Mamane et al. (2001) investigated the use of computer-controlled scanning electron microscopy (CCSEM) as a way of supplementing XRF analysis and providing automated analysis of particle size, chemistry, and particle classification. An ambient coarse particulate sample from Baltimore was collected on a polycarbonate filter for this analysis. CCSEM analyses were conducted for 2819 particles in 78 randomly selected fields of view during an unattended 8-h run. Mamane et al. confirmed the stability of the CCSEM instrument over several hours of operation. The physical properties of the sample such as particle diameter, mass loading per field, and particle number per field were well represented by analyzing approximately 360 particles with little additional information gained by analyzing more particles. Teflon filters are not well suited for SEM analyses. Analysis of fine PM is expected to pose analytical challenges not addressed in the present study (Mamane et al., 2001).

Nelson et al. (2000) applied Raman chemical imaging and SEM (Raman/SEM) to study the size, morphology, elemental and molecular composition, and molecular structure of fine particulate matter. In their study, filter compatibility was examined, and Raman/SEM chemical imaging was conducted for several standard materials as well as for ambient $PM_{2.5}$ samples. Polycarbonate was determined to be a suitable substrate for both SEM and Raman chemical imaging analysis.

Conner et al. (2001) used CCSEM with individual X-ray analysis to study the chemical and physical attributes of indoor and outdoor aerosols collected around a retirement home in Baltimore. The CCSEM technique was demonstrated to be capable of identifying spherical particles typical of combustion or other high temperature (presumably industrial) processes as well as pollens and spores. Indoor particles originating from cosmetics were also identified.

2B.2 ORGANIC AND INORGANIC CARBON

Large scale efforts to characterize carbonaceous aerosol require cost effective methods that can analyze samples rapidly. Commercial thermal/optical (TO) instruments were developed to serve this need. The US EPA IMPROVE and STN networks have employed these instruments to accumulate large datasets, including measurements taken over the past 18 years by the IMPROVE network and over the past 3 years by STN. In addition to the protocols developed for IMPROVE and STN networks, a number of alternative TO-based protocols and techniques have been employed by the academic research community. Protocols vary in temperature range and step size, in the duration of heating at each step, in the timing for introduction of oxygen for the conversion of black carbon into CO_2, and in the assignment of organic carbon (OC) and elemental carbon (EC) fractions. Figure 2B-2 shows examples of two protocols in current use. These operational differences have complicated efforts to compare and combine data sets from studies using different TO protocols.

Thermal-Optical Reflectance

The thermal optical reflectance (TOR) method of carbon analysis developed by Huntzicker et al. (1982) has been adapted by several laboratories for the quantification of organic and elemental carbon in PM collected on quartz-fiber filters. Although the principle applied by these laboratories is identical to that of Huntzicker et al. (1982), the details differ with respect to calibration standards, analysis time, temperature ramping, and volatilization/combustion temperature. The IMPROVE network employs a version of the TOR method for its OC/EC analyses.

In the most commonly used version of the TOR method (Chow et al., 1993), a punch from the filter sample is heated to temperatures ranging from ambient to 550 ˚C in a pure helium atmosphere. In principle, the organic carbon fraction of the PM contained by the filter punch will vaporize, leaving behind only refractory elemental carbon. The organic carbon that evolves at each temperature step is first oxidized to CO2, then converted to methane and finally quantified with a flame ionization detector (FID). The filter punch is incubated at 550 ˚C for a period sufficient to allow the flame ionization signal to return to its baseline value. The punch is then exposed to a 2% oxygen and 98% helium atmosphere and heated from 550 ˚C to 800 ˚C with several temperature ramping steps. The reflectance from the deposit side of the filter punch is monitored throughout the analysis. This reflectance decreases during OC volatilization in the helium atmosphere owing to the pyrolysis of involatile organic material present in the filter punch. When oxygen is added, the reflectance increases as light-absorbing carbon is combusted and removed. It is assumed that the first light-absorbing carbon compounds to combust are pyrolysis artifacts from the first phase of the analysis. Therefore, the organic carbon mass is defined as that fraction that evolves up to the introduction of oxygen plus the oxidized carbon that evolves up to the point when the filter reflectance signal is restored to its pre-analysis value. Once the original reflectance level is re-attained, all further carbon evolving from the sample punch is assigned to the elemental carbon fraction. Accordingly, "organic carbon" (OC) is carbon that does not absorb light at the laser wavelength (632.8 nm) typically used by TOR instruments, and all other carbon is defined as "elemental carbon" (EC).

Thermal-Optical Transmission

The primary difference between TOR and thermal optical transmission methods is in the choice of absorption detection — light transmission through the filter punch, rather than its reflectance, is monitored throughout the analysis. The TOT method of Birch and Cary (1996) also uses a pure helium atmosphere for volatilizing organic carbon, but the second stage involves a higher oxygen/helium (10%) gas mixture to oxidize the black carbon remaining on the filter punch. The temperature is raised to approximately 820 °C in the helium phase, during which both organic and carbonate carbon are volatilized from the filter. In the second stage, the oven temperature is reduced then raised to about 860 °C. During this stage, pyrolysis correction and the EC measurement is made. Figure 2B-1 is an example of a TOT thermogram, showing temperature, transmittance, and FID response traces. The peaks that correspond to the concentrations of CO_2 that evolve from the filter punch during the course of the analysis are assigned to OC, carbonate carbon (CC), pyrolitic carbon (PC), and EC. The high temperature in the first stage of the TOT thermal profile is included for the purpose of decomposing carbonate carbon and for volatilization of very high-boiling organic compounds. However, many organic carbon compounds will pyrolyze at this temperature to generate PC. The ability to quantify PC is particularly important in high OC/EC regions such as wood smoke-impacted air sheds. Wood smoke aerosol contains many complex compounds that generate substantial PC. Significant error in the EC fraction can result in the absence of a careful PC correction.

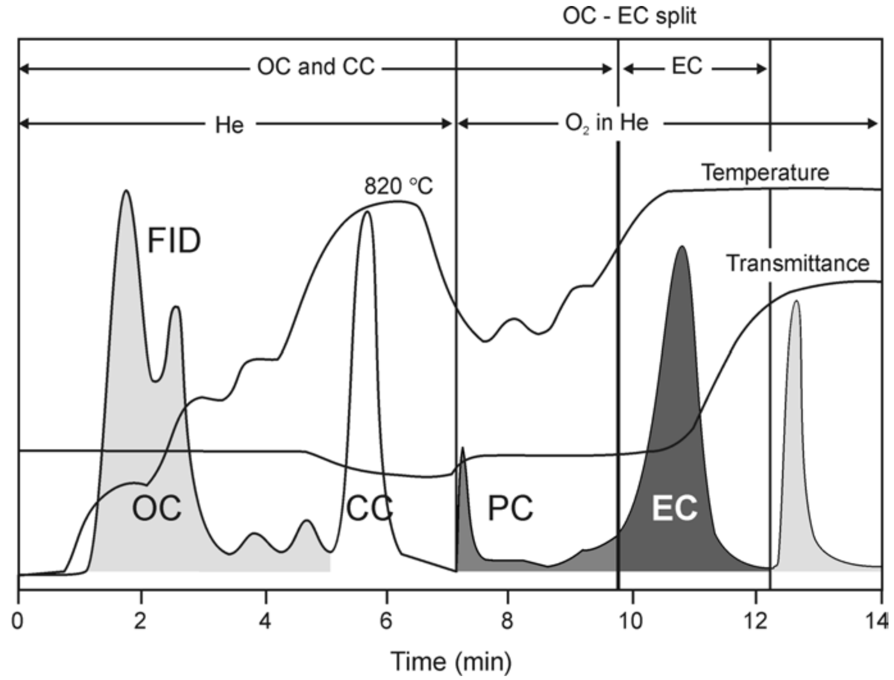


Figure 2B-1. This thermogram, for a sample containing rock dust (a carbonate source) and diesel exhaust, shows three traces that correspond to temperature, filter transmittance, and FID detector response. Peaks correspond to organic (OC), carbonate (CC), pyrolytic (PC), and elemental (EC) carbon. The final peak is a methane calibration peak.

Source: Birch and Cary (1996).

Informal intercomparisons among different filter transmission methods have shown high correlations of absorption, but differences of up to a factor of two in absolute values (Watson et al., 1988a,b). These differences are functions of the type of filter, filter loading, the chemical and physical nature of the deposit, the wavelengths of light used, calibration standards, and light diffusing methods. At the current time, there is no agreement on which combination most accurately represents light absorption in the atmosphere.

The National Institute for Occupational Safety and Health (NIOSH) Method 5040 is based on the TOT method (Birch and Cary, 1996). The NIOSH protocol consists of a two-stage process with the first stage being conducted in a pure helium atmosphere at temperatures of 250, 500, 650, and 850 ˚C for a total of 4.5 minutes and the second stage conducted in a 2% oxygen/98% helium mix at temperatures of 650, 750, 850, and 940 ˚C for 4 minutes.

A pyrolysis base correction is made based on the transmittance measurement. The U.S. EPA adopted a modified version of the NIOSH Method 5040 protocol for use in its Speciation Trends Network (STN).

IMPROVE versus NIOSH protocols

Although the IMPROVE protocol and the NIOSH protocol in use by the STN network yield closely comparable total carbon (TC) values, the differences in thermal profiles and operational definitions of organic versus black carbon result in very different mass assignments to these fractions. Other methodological differences may make data comparisons difficult, including the different choice of absorption detection, e.g. reflectance versus transmission, the different temperature ranges and incubation periods and the different approaches used to account for background OC. Examples of thermograms obtained with the IMPROVE and NIOSH protocols are shown in Figure 2B-2.

Using both the IMPROVE and NIOSH protocols, Chow et al. (2000) analyzed 60 quartz filter samples on a prototype reflectance/transmittance analyzer that represented a wide variety of aerosol compositions and concentrations. The two TC data sets possessed no statistically significant differences. However, marked differences were found in the fraction of TC that is attributed to EC as determined by the IMPROVE versus NIOSH thermal evolution protocols. The IMPROVE EC measurements were typically higher than the NIOSH EC measurements. When the NIOSH protocol was modified to exclude the helium-only 850 ºC temperature step, however, the OC/EC ratios came into agreement between the two methods. Because OC and EC are operationally defined parameters, Chow et al. (2000) pointed out that it is important to retain ancillary information when reporting EC and OC by these analytical methods, so that comparisons can be made among measurements taken at different sites using these two methods.

The NIOSH and IMPROVE protocols both require correction for positive organic artifacts due to absorption of background organic vapor by the heat-treated quartz filters used for OC/EC measurements. Both the IMPROVE and STN science teams have evaluated the presence of carbon artifacts in their measurements. The IMPROVE team has established that heat-treated quartz filters adsorb organic carbon vapors up to a saturation threshold over the course of a few days in the field. The STN science team has observed that positive carbon artifacts can vary with sampler type. Total carbon artifacts for the samplers used by the STN range from 9.5 to

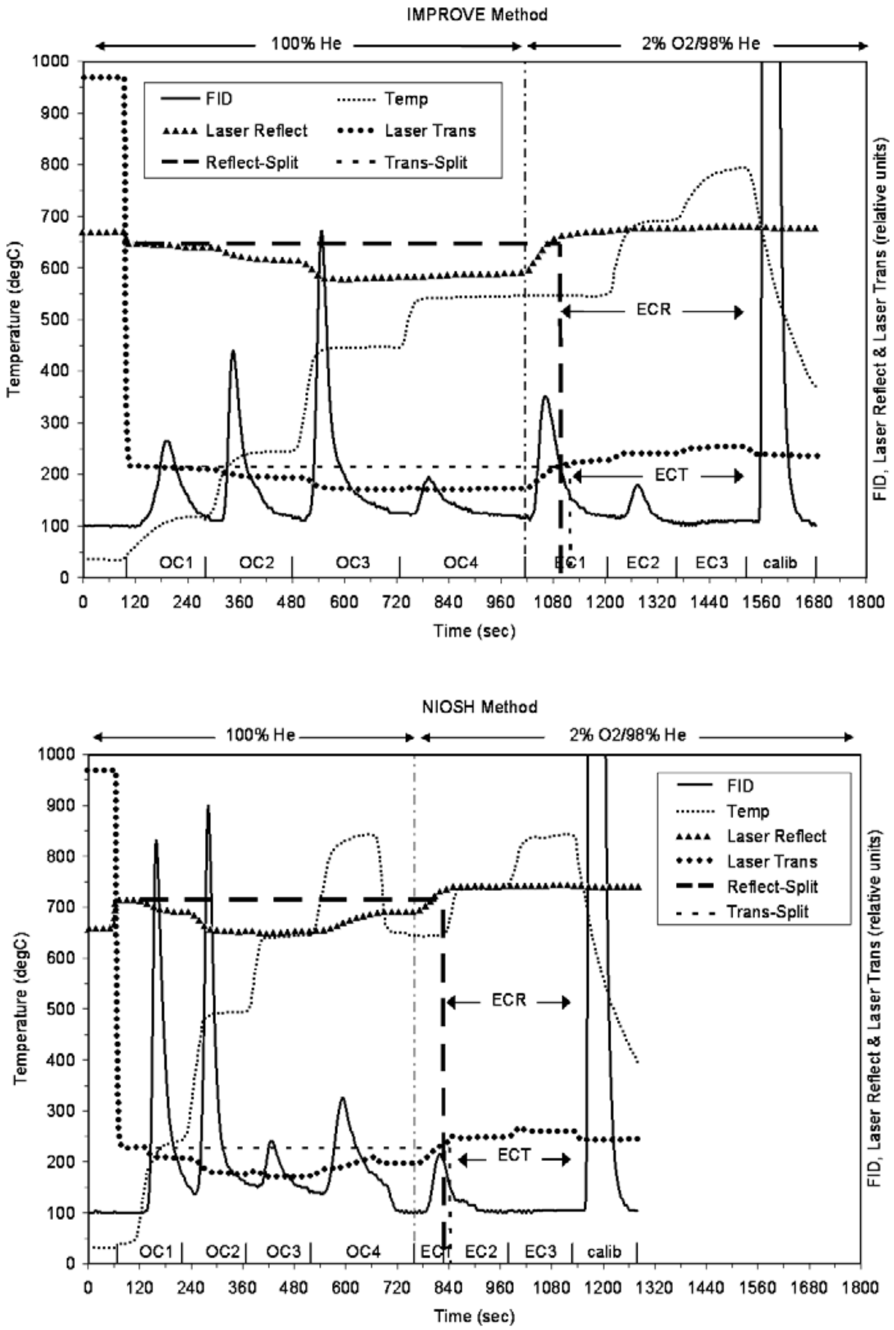


Figure 2B-2. **Examples of thermograms obtained by (a) the IMPROVE protocol, and by (b) the NIOSH protocol. Flame ionization detection is used in both examples. FID denotes the observed signal intensity. The intervals denoted ECR/ECT, i.e., elemental carbon reflectance/transmittance, refer to the time and temperature intervals during which EC is oxidized and filter "blackness" is monitored by laser reflectance or transmission at the He-Ne wavelength, 633 nm.**

Source: Birch and Cary (1996).

33.9% of the carbon collected during a typical ambient measurement. Documents describing the issues regarding blank subtraction and the current protocols used by the IMPROVE and STN networks are available on the network websites:

IMPROVE – http://vista.cira.colostate.edu/improve
STN – http://www.epa.gov/ttn/amtic/files/ambient/pm25/spec

Pyrolitic Carbon (PC) and Other Confounders

In a methods comparison study, Countess (1990) determined that it is necessary to minimize or correct for PC and that OC found in wood smoke and automobile exhaust samples which pyrolyze to create interferences during the course of some thermal optical protocols. Pyrolysis of organic compounds occurs during analysis by both TO methods, although the greater temperature to which samples are exposed in the NIOSH protocol is likely to produce larger quantities of pyrolysis-derived EC. During the initial heating phase, pyrolysis is indicated by an increase in optical density (blackness) by the filter sample. Both methods distinguish artifact pyrolysis-derived EC from ambient EC at the point when the transmittance or reflectance signal is restored to the pre-heating level. The assumption made is that heating does not alter the absorption properties of the material collected on the filter. This assumption is reasonable if the only light absorbing species of carbon is strictly a graphite-like elemental carbon that is unlikely to undergo a change in its absorption properties over the temperature ranges used by TO methods. The effects of heat-induced changes to the light absorption and chemical properties of atmospheric organic compounds on TO analysis are being evaluated by NIST. NIST has identified three assumptions that must be met in order for TO methods to reliably measure EC: (1) absorptivity of carbonaceous PM remains constant up to the point of pyrolysis; (2) once formed, pyrolyzed carbon (char) absorbs at the analytic wavelength and its absorptivity remains constant within the high temperature step; (3) pyrolyzed OC has the same absorptivity as EC that is native to the sample. Using urban dust, forest fire emissions and ambient laboratory aerosol, they observed changes in the absorptivities of these materials during heating before and during the formation of pyrolysis artifacts, up to the OC/EC split point. NIST, therefore, recommends that standard TOR/T protocols be developed that account for these changes.

Light-absorbing carbon includes a large number of compounds that may be altered, not only in their light-absorbing properties but also in their oxidation chemistry. The materials responsible for defining the original blackness of the filter sample may be altered during the initial heating phase of TO analysis, so that the mix present during the oxidation cycle may not be representative of the original, atmospherically-derived black carbon. An error in determining the mass of EC would arise, for example, if a heavy, but weakly light-absorbing compound were transformed into a material that possesses a higher absorption coefficient and higher resistance to oxidation than absorbing compounds collected from the atmosphere. The pyrolized form of this compound would resist oxidation past the OC-EC split point in the analysis, leading to a falsely high EC fraction.

Chow et al. (2000) noted that neither the IMPROVE nor NIOSH methods were able to accurately detect further blackening on optically dense, i.e., very black, filters that are typical of source profile samples. Predictions of artifact pyrolysis carbon by TOR and TOT differed widely. Note that both transmittance and reflectance methods rely on derivations of optics laws (i.e., the Beer-Lambert and Lambert Laws) that predict a linear transmittance/reflectance signal response with species concentration, but only for optically thin samples (Strobel and Heineman, 1989). Very black filters exceed this limitation; thus, the signal response of these methods may not be a linear or otherwise predictable function of black carbon concentration.

Another important source of error in any TO measurement of aerosol OC/EC arises when samples contain transition metal oxides, such as iron oxide. Many transition metal oxides are found in crustal material. Fung et al.(2002) report that such oxides can serve as oxidizing agents for BC at high temperatures. The consequence of such an effect is an elevation of the signal usually assigned to OC and corresponding reduction in apparent BC.

Thermal Manganese Oxidation

The thermal manganese oxidation (TMO) method (Mueller et al., 1982; Fung, 1990) uses manganese dioxide in contact with the sample throughout the analysis as the oxidizing agent. Temperature is relied upon to distinguish between organic and elemental carbon. Carbon evolving at 525 °C is classified as organic carbon, and carbon evolving at 850 °C is classified as elemental carbon. TMO does not correct for pyrolized OC, which may lead to overestimation of EC. This method has been used in the SCENES (Subregional Cooperative Electric Utility, Department of Defense, National Park Services, and Environmental Protection Agency Study); (Sutherland and Bhardwaja, 1987; Mueller et al., 1986) visibility network, as well as in the SCAQS (Southern California Air Quality Study) (Chow et al., 1994a,b; Watson et al., 1993, 1994a,b).

OC/EC Methods Intercomparisons

Chow et al. (1993) document several variations of the thermal (T), thermal/optical reflectance (TOR), thermal/optical transmission (TOT), and thermal manganese oxidation (TMO) methods for organic and elemental carbon. Comparisons among the results of the majority of these methods show that they yield comparable quantities of total carbon in aerosol samples, but the distinctions between organic and elemental carbon are quite different (Cadle and Groblicki, 1982; Cadle and Mulawa, 1990; Countess, 1990; Hering et al., 1990; Birch, 1998; Schmid et al., 2001). For the sum of organic and elemental carbon, these methods reported agreement within 5% to 15% for ambient and source samples (Houck et al., 1989; Kusko et al., 1989; Countess, 1990; Shah and Rau, 1990) and within 3% on carefully prepared standards. Evaluation of these methods thus is a matter of assessing how they differentiate between organic and elemental carbon. The EC/TC ratio for samples is method dependent.

An international methods intercomparison study on the analysis of carbonaceous aerosols on quartz fiber filters was organized by the Vienna University of Technology and involved seventeen laboratories and nine different thermal and optical methods (Schmid et al., 2001). All laboratories were sent punches from three 150-mm quartz fiber filters that had been exposed for 24 h near a high traffic street in Berlin.

Five laboratories employed the German official standard VDI 2465 methods. Two of these laboratories used the VDI 2465/1 method that determines extractable organic carbon, non-extractable organic carbon, and elemental carbon by way of a solvent-based extraction protocol. Other laboratories participating in the intercomparison used variations of the VDI 2465 standard that rely upon differences in thermal stability to accomplish the separation of carbonaceous aerosol fractions. A range of thermal protocols, total carbon determination techniques and CO2 detection schemes were employed by the participating laboratories.

Good agreement of the TC results was obtained by all laboratories with only two outliers in the complete data set. The relative standard deviation between laboratories for the TC results, were 6.7, 10.6, and 8.8% for the three samples. In contrast, the EC results were much more variable. The relative standard deviation between laboratories for the EC results, were 36.6, 24.4, and 45.5% for the three samples. The VDI methods, especially the VDI 2465/2, were found to give generally higher amounts of EC than the thermal-optical methods. This trend was detected for all samples. The authors recognized that uncorrected thermal methods are prone to positive artifacts by charring during pyrolysis. They also noted that when using solvent extraction methods, the dissolution of polymeric aerosol constituents may not be successful. Both of these effects would lead to overestimation of the EC fraction. When the laboratories were grouped according to their methods, the relative standard deviation between laboratories was much smaller. This study demonstrates that the TC measurement can yield similar results from a variety of methods, but the EC measurement is highly dependent upon the method used. The problems associated with the determination of EC are exacerbated by the lack of a standard reference material and consistent definitions of EC.

Measuring Black Carbon (BC) Instead of EC

Light absorbing or black carbon (BC) can be measured by optical techniques (Penner and Novakov, 1996). Both EC and BC define a similar fraction of aerosol; but EC is defined in terms of both the thermal and light-absorption properties of the sample, whereas BC is based on solely on its light-absorption properties. The aethalometer, the integrating sphere sunphotometer and photoacoustic spectroscopy (described in Section 2B.3) are example techniques for determining BC.

Hitzenberger et al. (1996) investigated the feasibility of using an integrating sphere photometer as an adequate measurement system for the BC content and the absorption coefficient. In another study (Hitzenberger et al., 1999), the integrating sphere method was compared to an aethalometer (Hansen et al., 1984), the thermal method of Cachier et al. (1989), and the thermal/optical method of Birch and Cary (1996). The absorption coefficients that were obtained from both the integrating sphere and the aethalometer were comparable. The BC mass concentrations obtained from the aethalometer were 23% of those obtained from the integrating sphere. Compared to the thermal method, the integrating sphere overestimated the BC mass concentrations by 21%. Compared to the thermal/optical method, the integrating sphere was within 5% of the 1:1 line. However, the data were not well correlated.

The Carbonaceous Species Methods Comparison Study (CSMCS), as mentioned in the 1996 PM AQCD (U.S. Environmental Protection Agency, 1996a) was conducted in Los Angeles in 1986. Hansen and McMurry (1990) compared the thermal manganese method with the aethalometer for aerosol elemental carbon. The first involved collection of impactor samples backed by a quartz fiber after-filter followed by EC analysis by oxidation in helium over a MnO_2 catalyst; the other conducted real-time measurements using an aethalometer (an optical absorption technique). They found good agreement between these two very different methods. The CSMCS interlaboratory precision for total carbon was 4.2% (Turpin et al., 2000). However, because the split between OC and EC is operationally defined, there was substantial interlaboratory variability in OC and EC (e.g., 34% for EC [Turpin et al., 1990]).

EC/OC Summary. With the limitations and precautions described above, laboratory analyses for the carbonaceous properties of collected particles have matured to the point where they can be performed with commercially-available instruments following established standard operating procedures. However, carbon analysis continues to be a subject of active research within the atmospheric sciences community and EPA, and carbon speciation methods comparisons are being undertaken during such studies as the Atlanta Supersite. The state of the art for carbonaceous PM measurements continues to advance; and, although progress is being made, the definitions of OC, EC and BC continue to be operationally defined in reference to the method employed. Reports of EC/OC measurements should therefore include mention of the method with which the species were determined. Finally, if possible, all ancillary data should be retained, to allow later comparison to other methods.

2B.3 CONTINUOUS METHODS

2B.3.1 Continuous Measurement of Mass

Tapered Element Oscillating Microbalance (TEOM)

The advantages of continuous PM monitoring and the designation of the TEOM as an equivalent method for PM_{10}, have led to the deployment of the TEOM at a number of air monitoring sites. The TEOM also is being used to measure $PM_{2.5}$. The TEOM differs from the federal reference methods for particulate mass in that it does not require equilibration of the samples at a specified temperature and relative humidity. The TEOM samples at a constant temperature and is typically heated to some temperature higher than the ambient temperature (Meyer et al., 1995; Meyer and Rupprecht, 1996); whereas the FRM samples at the ambient temperature. Thus, the TEOM does not provide data equivalent to the FRM because of losses of volatile species. Volatilization losses in the TEOM sampler can be reduced by operating the instrument at 30 ˚C, rather than the typical 50 ˚C specified, or by using a Nafion diffusion dryer instead of heating to dehumidify the particles (with a 30 °C temperature).

This difference in operation and implications for fine particle measurements was examined by researchers at Commonwealth Scientific and Industrial Research Organisation (CSIRO) Atmospheric Research in Australia (Ayers et al., 1999). That group compared 24-h mean $PM_{2.5}$ mass concentrations as determined by a TEOM and by two manual, gravimetric samplers (a low-volume filter sampler and a MOUDI sampler) in four Australian cities, on 15 days in the winter half-year. The TEOM was operated at 50 ˚C at one location and at 35 ˚C at the other three locations. A systematically low TEOM response in comparison to the integrated gravimetric methods was observed. In a comprehensive study, Allen et al. (1997) reported results in which TEOM data collected at 10 urban sites in the United States and Mexico were compared with 24 h integrated mass concentrations for both PM_{10} and $PM_{2.5}$. They collected a large data set that included both winter and summer seasons. Allen et al. (1997) concluded that, especially for urban areas, a significant fraction of PM_{10} could be semivolatile compounds that could be lost from the heated filter in the TEOM leading to a systematic difference between the TEOM and the EPA FRM for PM_{10}. They suggested that this difference is likely to be larger for $PM_{2.5}$ than it is for PM_{10} (Allen et al., 1997).

In a similar study conducted in Vancouver, British Columbia, the effect of equilibration temperature on PM_{10} concentrations from the TEOM was examined. Two collocated TEOM monitors operated at 30 and 50 ˚C, respectively, were operated in the Lower Fraser Valley in British Columbia for a period of approximately 17 months (Mignacca and Stubbs, 1999).
A third TEOM operating at 40 ˚C was operated for 2 months during this period. They found that, on average, the 1-h average PM_{10} from the TEOM operating at 30 ˚C was consistently greater than that from the TEOM operated at 50 ˚C. For the period during which the third TEOM was operated (at 40 ˚C), the PM_{10} from that instrument was between those values for the other two instruments. They also found that the differences in masses were proportional to the

PM_{10} loading, and more strongly correlated to the PM_{10} from the TEOM operated at the lower temperature. They recommended that the TEOM monitors be operated at 40 ºC as opposed to operating at 50 ˚C in summer and 30 ˚C in winter, in order to avoid introducing a methodological seasonal bias.

A new sample equilibration system (SES) was developed to reduce losses of semivolatile species from the $PM_{2.5}$ TEOM by conditioning the sample stream to lower humidity and temperature (Meyer et al., 2000). The SES utilizes humidity sensors and a Nafion dryer designed for low particle loss. The dryer fits between the flow splitter that follows the size-selective inlet and the sensor unit. A dry purge gas flows over the exterior of the Nafion tubing and allows for self-regeneration. A TEOM with $PM_{2.5}$ inlet and equipped with an SES was operated at 30 ˚C alongside another TEOM operating at 50 ˚C without the SES in Albany, NY, over a 6-day period during a summertime high-temperature, high-relative-humidity episode. The SES maintained the sample air relative humidity under 30%, and the TEOM with the SES generally measured more mass than the other TEOM. The TEOM with SES also was operated alongside an FRM-type sampler for the period of June 6 through September 25, 1999. The correlation between the FRM and TEOM/SES showed a slope of 1.0293 and R^2 of 0.9352; whereas the correlation between the FRM and the TEOM without SES and operating at 50 ˚C showed a slope of 0.8612 and R^2 of 0.8209. The SES can be installed on existing TEOM monitors.

Beta-Gauge Techniques

The use of absorption of beta radiation as a indicator of particle mass has been used effectively to measure the mass of equilibrated particulate matter collected on Teflon filters (Jaklevic et al., 1981a; Courtney et al., 1982). The technique also has been used to provide near real-time measurements with time intervals on the order of an hour (Wedding and Weigand, 1993). However, real-time beta gauge monitors experience the same problems as other continuous or near real-time particulate matter mass monitoring techniques. Particle-bound water must be removed to reduce the sensitivity of the indicated mass to relative humidity. However, the simplest technique, mild heating, will remove a portion of the ammonium nitrate and the semivolatile organic compounds as well as the particle-bound water.

An intercomparison study of two beta gauges at three sites indicated that the Wedding beta gauge and the Sierra Anderson (SA) 1200 PM_{10} samplers were highly correlated, $r > 0.97$ (Tsai and Cheng, 1996). The Wedding beta gauge was not sensitive to relative humidity but yielded results approximately 7% lower. This suggests that the mild heating in the beta gauge causes losses comparable to those caused by equilibration, although the differences could result from slight differences in the upper cut points. The Kimoto beta gauge that was operated at ambient temperature was sensitive to relative humidity yielding significantly higher mass concentrations relative to the SA 1200 for RH > 80% than for RH < 80% even though the correlation with the SA 1200 was reasonable ($r = 0.94$ for RH > 80% and 0.83 for RH < 80%).

Piezoelectric Microbalance

Piezoelectric crystals have mechanical resonances that can be excited by applying an alternating electrical voltage to the crystal. As the resonance frequencies are well defined, such crystals (quartz in particular) have found applications as secondary time and frequency standards in clocks and watches. As for all mechanical resonators, the resonance frequency is a function of mass. Therefore, by monitoring the resonance frequency in comparison with a second crystal, one can continuously measure the mass deposited on the crystal (Sem et al., 1977; Bowers and Chuan, 1989; Ward and Buttry, 1990; Noel and Topart, 1994). Comparison with a second crystal largely compensates for the effect of temperature changes on the resonance frequency.

The piezoelectric principle has been used to measure particle mass by depositing the particles on the crystal surface either by electrostatic precipitation or by impaction (Olin and Sem, 1971). The collection efficiency of either mechanism has to be determined as function of particle size to achieve quantitative measurements. In addition, the mechanical coupling of large particles to the crystal is uncertain. Both single and multi-stage impactors have been used (Olin and Sem, 1971; Fairchild and Wheat, 1984). Quartz crystals have sensitivities of several hundred hertz per microgram. This sensitivity results in the ability to measure the mass concentration of a typical 100 $\mu g/m^3$ aerosol to within a few percent in less than one minute (Olin and Sem, 1971).

Coarse Particle Mass

The RAMS and CAMM are only appropriate for fine particle measurements ($PM_{2.5}$ or PM_1). However, the TEOM, beta gauge, and piezoelectric microbalance may be used to measure either $PM_{2.5}$ or PM_{10} (or a sample with any specified upper 50% size cut). A pair of such samplers may be used to measure thoracic coarse PM mass concentration ($PM_{10\text{-}2.5}$) by difference between the PM_{10} and $PM_{2.5}$ concentrations. However, concerns have been raised concerning the quality of the data from such difference calculations and the resulting potential biases in exposure assessment and risk determinations (Wilson and Suh, 1997; White, 1998). Misra et al. (2001) describe the development and evaluation of a continuous coarse particle monitor (CCPM) that may provide direct measurements of coarse mode PM mass concentrations at short time intervals (on the order of 5-10 min). The basis of the CCPM is enrichment of the coarse particle concentrations through use of virtual impaction while maintaining fine particle concentrations at ambient levels. The resulting aerosol mixture is analyzed using a standard TEOM for which the response is now dominated by the enriched coarse PM mass. The coarse PM concentrations determined from the CCPM were compared to those obtained with a MOUDI, operating with only the 10- and 2.5-micron cutpoint stages, and a Partisol dichotomous sampler. The CCPM coarse particulate concentrations were highly correlated with both the MOUDI ($R^2 = 0.88$) and the Partisol ($R^2 = 0.88$) coarse PM concentrations. By operating the CCPM at a coarse particle enrichment factor of 25, the coarse PM concentration can be determined *a priori* without determination of the fine particle concentration, so long as the fine-to-coarse particle concentration ratios are not unusually high (i.e., 4-6). Misra et al. (2001) also concluded from field experiments that the coarse particulate concentrations determined from the CCPM were independent of the ambient fine-to-coarse particulate concentration ratio due to the decrease in particle mass median diameter that should accompany fine-to-coarse particulate concentration ratios during stagnation conditions.

2B.3.2 Continuous Measurement of Organic and/or Elemental Carbon

Testing and refinement of models that simulate aerosol concentrations from gas and particle emissions require air quality measurements of approximately 1-h time resolution to reflect the dynamics of atmospheric transport, dispersion, transformation, and removal. Below instruments are described that have been used to collect and analyze atmospheric organic PM with better than 2-h resolution. These instruments were all present at the Atlanta Supersite experiment during the summer of 1999, and an intercomparison of results is underway.

Automated Carbon Analyses

Turpin et al. (1990) describe an *in situ*, time-resolved analyzer for particulate organic and elemental carbon that can operate on a time cycle as short as 90 min. This analyzer collects particulate matter on a quartz fiber filter mounted in a thermal-optical transmittance carbon analyzer (Turpin et al., 1990). A second quartz fiber filter behind a Teflon filter in a second sampling port may also be analyzed to provide an estimate of the positive sampling artifact (i.e., gas adsorption on the quartz sampling filter). The organic material in the collected PM is thermally desorbed from the filter at 650 °C and oxidized at 1000 °C over a MnO_2 catalyst bed. The evolved CO_2 is converted to methane over a nickel catalyst, and the methane is measured in a flame ionization detector. Then the elemental carbon is oxidized at 350 °C in a 98% He-2% O_2 atmosphere. Correction is made for pyrolytic conversion of some of the organic particulate matter. The instrument was operated with a 2-h resolution during SCAQS in 1987 (Turpin and Huntzicker, 1991;1995), as well as during CSMCS in 1986 (Turpin et al., 1990). By using elemental carbon as a tracer for primary, combustion-generated organic carbon, these authors estimated the contributions of primary sources (i.e., material emitted in particulate form) and secondary sources (i.e., particulate material formed in the atmosphere) to the total atmospheric particulate organic carbon concentrations in these locations.

An automated carbon analyzer with 15-min to 1-h resolution is now commercially available (Rupprecht et al., 1995) and has been operated in several locations including the Atlanta Supersite. It collects samples on a 0.1-µm impactor downstream of an inlet with a 2.5-µm cutpoint. Use of an impactor eliminates gas adsorption that must be addressed when filter collection is used. However, this collection system may experience substantial particle bounce and loss of a sizable fraction of EC since some EC is in particles < 0.2 µm. It is possible that ongoing research, in which particle size is increased by humidification prior to impaction, may result in an improvement in collection efficiency. In the analysis step, carbonaceous compounds are removed by heating in filtered ambient air. Carbonaceous material removed below 340 °C is reported as organic carbon, and material removed between 340 and 750 °C is reported as elemental carbon. Turpin et al. (2000) comment that it would be more appropriate to report carbon values obtained by this method as “low-” and “high-temperature” carbon, because some organics are known to evolve at temperatures greater than 340 °C (e.g., organics from woodsmoke).

Aethalometer for EC

As discussed earlier, black carbon (BC), a carbon fraction very similar to EC, is most commonly measured using an aethalometer, a commercially available, automated, time-resolved instrument (i.e., 5- to 15-min sample duration) that measures the light attenuation of aerosol particles collected on a filter tape (Hansen et al., 1984). The concentration of elemental carbon is derived from the light absorption measured on a filter using an estimate of the specific absorption (m^2/g) of elemental carbon on the filter; the specific absorption value is derived from laboratory and atmospheric tests and is specified by the manufacturer. The specific absorption value could be expected to vary with location, season, and source mix. Comparisons in atmospheric experiments at some locations with EC values measured by thermal methods confirm that the aethalometer provides a statistically meaningful estimate of EC concentration (Allen et al., 1999c; Liousse et al., 1993). For instance, Allen et al. (1999c) found the following statistical relationship for Uniontown, PA, during summer 1990: black carbon (aethaometer) = 0.95*EC (thermal) – 0.2 (r^2 = 0.925, n not specified but appears to be >50, EC range from 0 to 9 $\mu g/m^3$). Another source of error in aethalometer measurements arises from the sampling procedure. Particles are trapped within a three-dimensional filter matrix. Therefore, scattering of transmitted and reflected light may erroneously be attributed to absorption, thus causing errors in the BC calculation. Ballach et al. (2001) investigated immersing the filter in oil of a similar refractive index as a means to minimize the interferences due to light scattering effects from the filter, similar to a procedure common in microscopy. BC measurements determined using the oil immersion technique were compared to those from an integrating sphere, a polar photometer, and Mie calculations. Aerosols tests included several pure carbon blacks from different generating procedures that were used to calibrate the immersion technique, pure ammonium sulfate aerosol, and external and internal mixtures of ammonium sulfate with varying amounts of carbon blacks. The oil immersion technique was also tested on ambient air samples collected at two different sites in the cities of Frankfurt am Main and Freiburg, Germany. Optical measurements, both of blank and loaded filters, show that the oil immersion technique minimizes scattering losses. Ballach et al. (2001) found that site-related effects were reduced and that there was reasonably good agreement with the other optical techniques as well as with the Mie calculations.

Photoacoustic Measurement of EC

Measurement of aerosol light absorption utilizing photoacoustic spectroscopy has been examined as a continuous method for measuring elemental carbon mass concentrations (Petzold and Niessner, 1996; Arnott et al., 1999; 2000). Like the aethalometer, this method measures light absorption; however, unlike most other light absorption methods, the photoacoustic technique does not require a filter. The photoacoustic spectrometer of Arnott and coworkers was demonstrated during the Northern Front Range Air Quality Study and compared to an aethalometer (Moosmuller et al., 1998). Neither the aethalometer nor the photoacoustic spectrometer measure elemental carbon mass directly. Because the photoacoustic spectrometer measures the absorption coefficient directly, the specific absorption efficiency must be known or assumed in order to determine elemental carbon mass. Assuming a light absorption efficiency of 10 m^2 g^{-1}, Arnott et al. (1999) reported a lower detection limit for light absorption of 0.4 M m^{-1} corresponding to a mass concentration of elemental carbon of approximately 40 ngm^{-3}.

2B.3.3 Continuous Measurements of Nitrate and Sulfate

Nitrate

An integrated collection and vaporization cell was developed by Stolzenburg and Hering (2000) that provides automated, 10-min resolution monitoring of fine particulate nitrate. In this system, particles are collected by a humidified impaction process and analyzed in place by flash vaporization and chemiluminescent detection of the evolved nitrogen oxides. In field tests in which the system was collocated with two FRM samplers, the automated nitrate sampler results followed the results from the FRM, but were offset lower. The system also was collocated with a HEADS and a SASS speciation sampler (MetOne Instruments). In all these tests, the automated sampler was well correlated to other samplers with slopes near 1 (ranging from 0.95 for the FRM to 1.06 for the HEADS) and correlation coefficients ranging from 0.94 to 0.996.

During the Northern Front Range Air Quality Study in Colorado (Watson et al., 1998), the automated nitrate monitor captured the 12-minute variability in fine particle nitrate concentrations with a precision of approximately ±0.5 µg/m^3 (Chow et al., 1998). A comparison with denuded filter measurements followed by ion chromatographic analysis (Chow and Watson, 1999) showed agreement within ±0.6 µg/m^3 for most of the measurements, but exhibited a discrepancy of a factor of two for the elevated nitrate periods. More recent intercomparisons took place during the 1997 Southern California Ozone Study (SCOS97) in Riverside, CA. Comparisons with 14 days of 24-hour denuder-filter sampling gave a correlation coefficient of $R^2 = 0.87$ and showed no significant bias (i.e., the regression slope is not significantly different from 1). As currently configured, the system has a detection limit of 0.7 µg/m^3 and a precision of 0.2 µg/m^3.

Sulfate

Continuous methods for the quantification of aerosol sulfur compounds first remove gaseous sulfur (e.g., SO_2, H_2S) from the sample stream by a diffusion tube denuder followed by the analysis of particulate sulfur (Cobourn et al., 1978; Durham et al., 1978; Huntzicker et al., 1978; Mueller and Collins, 1980; Tanner et al., 1980). Another approach is to measure total sulfur and gaseous sulfur separately by alternately removing particles from the sample stream. Particulate sulfur is obtained as the difference between the total and gaseous sulfur (Kittelson et al., 1978). The total sulfur content is measured by a flame photometric detector (FPD) by introducing the sampling stream into a fuel-rich hydrogen-air flame (e.g., Stevens et al., 1969; Farwell and Rasmussen, 1976) that reduces sulfur compounds and measures the intensity of the chemiluminescence from electronically excited sulfur molecules (S_2*).

Because formation of S_2* requires two sulfur atoms, the intensity of the chemiluminescence is theoretically proportional to the square of the concentration of molecules that contain a single sulfur atom. In practice, the exponent is between one and two and depends on the sulfur compound being analyzed (Dagnall et al., 1967; Stevens et al., 1971). Calibrations are performed using both particles and gases as standards. The FPD can also be replaced by a chemiluminescent reaction with ozone that minimizes the potential for interference and provides a faster response time (Benner and Stedman, 1989, 1990).

Capabilities added to the basic system include *in situ* thermal analysis and sulfuric acid speciation (Cobourn et al., 1978; Huntzicker et al., 1978; Tanner et al., 1980; Cobourn and Husar, 1982)). Sensitivities for particulate sulfur as low as 0.1 µg/m^3, with time resolution ranging from 1 to 30 min, have been reported. Continuous measurements of particulate sulfur content have also been obtained by on-line x-ray fluorescence analysis with resolution of 30 min or less (Jaklevic et al., 1981b). During a field-intercomparison study of five different sulfur instruments, Camp et al. (1982) reported four out of five FPD systems agreed to within ±5% during a one-week sampling period.

2B.4 OTHER CONTINUOUS MEASUREMENTS

Continuous Ion Chromatography of Water-Soluble Ions

Dasgupta and Slanina have independently developed particle collection systems that grow particles by increasing the relative humidity and collect the particles in an aqueous solution suitable for injection into an ion chromatography (Simon and Dasgupta, 1995; Khlystov et al., 1995). Automation of these systems yield semi-continuous monitors for those ions that can be determined using ion chromatography. A similar system suing a particle size magnifier has been reported by Weber et al. (2001).

Determination of Aerosol Surface Area in Real Time

Aerosol surface area is an important aerosol property for health effects research. However, methods for on-line measurement of surface area are not widely available. Woo et al. (2001b) used three continuous aerosol sensors to determine aerosol surface area. They used a condensation particle counter (CPC, TSI, Inc., Model 3020), an aerosol mass concentration monitor (MCM, TSI, Inc., Model 8520), and an electrical aerosol detector (EAD, TSI, Inc., Model 3070) for measuring particle charge concentration. The three sensor signals were inverted to obtain the aerosol size distribution, using a log-normal size distribution model (by minimizing the difference between the measured signals and the theoretical values based upon a size distribution model, the instrument calibration, and its theoretical responses). The log-normal function was then integrated to calculate the total surface area concentration. Woo et al. (2001b) demonstrated that this method can give near real-time measurements of aerosol surface area.

Light Scattering

A variety of types of nephelometers that integrate aerosol light scattering over various solid angles are available (McMurry, 2000). When used to measure visibility, e.g., to provide pilots with realtime data on visual range, it is desirable to include the light scattering due to particle-bound water. However, when used as an indicator of fine particle mass, it is desirable to exclude particle-bound water. This is frequently done by heating the ambient aerosol to a low reference relative humidity of 40%. However, this heating has the potential of also causing the loss of semivolatile components of the aerosol. The evaporation of ammonium nitrate aerosol in a heated nephelometer has been examined. Bergin et al. (1997) conducted laboratory experiments at low relative humidity (~10%) and as a function of temperature (27-47 °C), mean residence time in the nephelometer, and initial particle size distribution. The evaporation of ammonium nitrate aerosol was also modeled for comparison and was found to describe accurately the decrease in aerosol scattering coefficient as a function of aerosol physical properties and nephelometer operating conditions. Bergin et al. (1997) determined an upper limit estimate of the decrease in the aerosol light scattering coefficient at 450 nm due to evaporation for typical field conditions. The model estimates for their worst-case scenario suggest that the decrease in the aerosol scattering coefficient could be roughly 40%. Under most conditions, however, they estimate that the decrease in aerosol scattering coefficient is generally expected to be less than 20%.

3. CONCENTRATIONS, SOURCES, AND EMISSIONS OF ATMOSPHERIC PARTICULATE MATTER

3.1 INTRODUCTION

This chapter discusses topics covered in Chapter 5 (Sources and Emissions of Atmospheric Particles) and Chapter 6 (Environmental Concentrations) of the previous document, Air Quality Criteria for Particulate Matter or “1996 PM AQCD” (U.S. Environmental Protection Agency, 1996) and presents updates to these materials where available.

Information about concentrations, the composition, and the spatial and temporal variability of ambient particles across the United States is presented in Section 3.2. Ambient concentration data obtained during the first three years of operation of the recently deployed nationwide network of Federal Reference Method $PM_{2.5}$ monitors in twenty-seven metropolitan statistical areas (MSAs) are presented and analyzed in Appendix 3A. Initial data from the pilot method evaluation study for the national speciation network are presented in Appendix 3B. Results of field studies that have characterized the composition of organic compounds in ambient particles are summarized in Appendix 3C to complement the data for the inorganic composition of ambient particles presented in Appendix 6A of the 1996 PM AQCD and Appendix 3B of this document. Data for characterizing the daily and seasonal variability of $PM_{2.5}$ concentrations are discussed in Section 3.2.1; the intra-day variability of $PM_{2.5}$ concentrations is discussed in Section 3.2.2; relationships among different size fractions are discussed in Section 3.2.3; interrelationships and correlations among PM components are discussed in Section 3.2.4; and the spatial variability of various PM components is discussed in Section 3.2.5.

Unlike gaseous criteria pollutants (SO_2, NO_2, CO, O_3), which are well-defined chemical entities, atmospheric particulate matter (PM) is composed of a variety of particles differing in size and chemical composition. Therefore, sources of each component of the atmospheric aerosol must be considered in turn. Differences in the composition of particles emitted by different sources also will lead to spatial and temporal heterogeneity in the composition of the atmospheric aerosol. The nature of the sources and the composition of the emissions from these sources are discussed in Section 3.3. The chemistry of formation of secondary PM from gaseous precursors is discussed in Section 3.3.1. Estimates of contributions of various sources to ambient PM levels given by source apportionment studies also are presented in Section 3.3.2. More detailed information about the composition of emissions from various sources is given in Appendix 3D. The determination of "policy-relevant background" (PRB) concentrations, including contributions from natural local sources and the long-range transport of PM from sources outside the United States, is discussed in Section 3.3.3. Reviews of transport of PM and its precursors within the United States can be found in the North American Research Strategy for Tropospheric Ozone (NARSTO) Fine Particle Assessment (NARSTO, 2002). More detailed information regarding sulfur and nitrogen species can be found in Hidy (1994). Further information about PM concentrations observed at relatively remote monitoring sites (RRMS), i.e., monitoring sites located in relatively remote areas that are not obviously influenced by local anthropogenic sources, is given in Appendix 3E. Because PM is composed of both primary and secondary constituents, emissions of both the primary components and the gaseous precursors of secondary PM must be considered. Nationwide emissions estimates of primary PM and precursors to secondary PM are discussed in Section 3.3.4, and uncertainties in emissions estimates in Section 3.3.5.

The organization of topics in this chapter (ambient measurements, source characterization and apportionment, and emissions inventories) reflects, in a broad sense, the order in which these topics are addressed in scientific studies and, arguably, the increasing levels of uncertainty that are associated with these topics.

3.2 PATTERNS AND TRENDS IN AMBIENT PM CONCENTRATIONS

Considerable data exists for characterizing PM_{10} mass concentrations and trends, and those available at the time were presented in the 1996 PM AQCD. In contrast, data sets for characterizing $PM_{2.5}$ and $PM_{10-2.5}$ mass or trends were not as extensive. Sources of data for $PM_{2.5}$ (fine) and $PM_{10-2.5}$ (coarse) discussed in the 1996 PM AQCD include EPA's Aerometric Information Retrieval System (AIRS; U.S. Environmental Protection Agency, 2000a); Interagency Monitoring of Protected Visual Environments (IMPROVE; Eldred and Cahill, 1994; Cahill, 1996); the California Air Resources Board (CARB) Data Base (California Air Resources Board, 1995); the Harvard Six-Cities Data Base (Spengler et al., 1986; Neas, 1996); and the Harvard-Philadelphia Data Base (Koutrakis, 1995). The Inhalable Particulate Network (IPN)

(Inhalable Particulate Network, 1985; Rodes and Evans, 1985) provided TSP, PM_{15}, and $PM_{2.5}$ data but only a small amount of PM_{10} data.

New sources of PM data include the recently deployed nationwide $PM_{2.5}$ compliance-monitoring network, which provides mass measurements using a Federal Reference Method (FRM). This section summarizes data obtained by this network from 1999 to 2001 and provides an approximate characterization of nationwide $PM_{10-2.5}$ concentrations by comparing PM_{10} to $PM_{2.5}$ measurements at sites where both types of compliance monitors are located. Various aspects of these data are presented in greater detail in Appendix 3A. In addition, a small number of recent studies in which daily mass and composition measurements are available for extended periods are discussed in this section. The results of quality-assured aerosol composition data obtained by X-ray fluorescence (XRF) and by analyses of organic carbon (OC) and elemental carbon (EC) for thirteen urban areas from the methods evaluation study for the national $PM_{2.5}$ speciation network are presented in Appendix 3B. The terms organic carbon (OC) and elemental carbon (EC) are subject to some ambiguity, and the meanings of these terms discussed in Section 2.2.7 and Appendix 2.B.2 are applied here.

Organic compounds contribute from 10 to 70% of the dry fine particle mass in the atmosphere (see Appendix 3C). However, concentrations and the composition of organic PM are poorly characterized, and its formation mechanisms are poorly understood. Particulate organic matter is an aggregate of hundreds of individual compounds spanning a wide range of chemical and thermodynamic properties (Saxena and Hildemann, 1996). Some of the organic compounds are “semivolatile” (i.e., they have atmospheric concentrations and saturation vapor pressures such that both gaseous and condensed phases exist in equilibrium in the atmosphere). The presence of semivolatile or multiphase organic compounds complicates the sampling process. Organic compounds originally in the gas phase may be absorbed on glass or quartz filter fibers and create a positive artifact. Conversely, semivolatile compounds originally present in the condensed phase may evaporate from particles collected on glass, quartz, or Teflon filters creating a negative artifact. In addition, no single analytical technique is currently capable of analyzing the entire range of organic compounds present in atmospheric PM. Rigorous analytical methods are able to identify only 10 to 20% of the organic PM mass on the molecular level (Rogge et al., 1993), and only about 50% of the condensed phase compounds can be identified in smog chamber studies of specific compounds (Forstner et al., 1997a,b).

Measurement techniques and associated artifacts are discussed in Section 2.2.3.2. Information on the identification and concentration of the many different organic compounds identified in atmospheric samples obtained during the 1990s is given in Appendix 3C.

Summary tables giving the results of 66 field studies that obtained data for the composition of particles in the $PM_{2.5}$, $PM_{10-2.5}$, or PM_{10} size ranges were presented in Appendix 6A of the 1996 PM AQCD. The summary tables included data for mass, organic carbon, elemental carbon, nitrate, sulfate, and trace elements. Data from the studies were presented for the eastern, western, and central United States. It should be noted that these studies took place at various times and lasted for various durations over a 20-year period, and there may have been significant changes in the concentrations of many species between the times when these studies were conducted and now. These changes resulted from a number of factors (e.g., pollution controls, technological advances, land use changes, etc).

There were a number of discernible differences in the composition of particles across the United States evident in the data sets listed in Appendix 6A in the 1996 PM AQCD (cf., Figures 6-85a to 6-85c). However, these differences can only be discussed in the context of the uncertainties in the measurements of the main components (sulfate, organic carbon, elemental carbon, crustal material, ammonium, and nitrate). Sulfate, followed by crustal materials, has the smallest uncertainty associated with its measurement among all the components listed. Sulfate constituted about 38% of $PM_{2.5}$ in the aerosol composition studies in the eastern United States and was the major identifiable component of $PM_{2.5}$. However, it constituted only about 11% of $PM_{2.5}$ in the studies listed for the western United States. The contribution of crustal materials to $PM_{2.5}$ ranged from about 4% in the East to about 15% in the West. The contribution of unidentified material (possibly consisting mostly of water of hydration) ranged from 23% in the East to 0% in the West. The contribution of elemental carbon to $PM_{2.5}$ ranged from about 4% in the East to about 15% in the West. Organic compounds constituted about 21% of $PM_{2.5}$ in the eastern United States, reaching to about 39% for the studies listed in the western United States. However, uncertainties for organic carbon, elemental carbon, ammonium, and nitrate are larger than for sulfate and crustal material. Concentrations of organic carbon were multiplied by a factor of 1.4 when calculating mass to account for the presence of oxygen, nitrogen, and hydrogen in the organic compounds. This factor may vary among different areas and may represent the lowest reasonable estimate for an urban aerosol (Turpin and Lim, 2001).

In addition, the samples collected in the studies were subject to a number of sampling artifacts involving the adsorption of gases and the evaporation of volatile components that either formed on the filters or were present in the ambient particles. The values reported for organic carbon and elemental carbon in filter samples depend strongly on the specific analysis method used (Chow et al., 2002) as discussed extensively in Chapter 2.

Crustal materials constitute from 52% of $PM_{10-2.5}$ in the eastern United States to 70% of $PM_{10-2.5}$ in the western United States as indicated by the studies in Appendix 6A of the 1996 PM AQCD. The fraction of unidentified material in $PM_{10-2.5}$ varied from 41% in the eastern United States to 27% in the western United States. However, in the vast majority of these studies, no attempt was made to characterize organic components or nitrate in the $PM_{10-2.5}$ size fraction. It should also be remembered that a small fraction (typically about 10%) of $PM_{2.5}$ is entrained into the flow of the channel of the dichotomous sampler that collects the $PM_{10-2.5}$ sample and that there may be errors invoked during the procedure used to account for this entrainment. Even if analyses of total OC were available, they would not be able to distinguish between primary biological particles (PBP), which include microorganisms and fragments of living things, and organic compounds of miscellaneous origin in surface deposits on filters. A clear distinction should be made between PBP and primary OC emitted by organisms such as waxes coating the surfaces of leaves, seeds, fruits, stems, pollen, fungi, and on insects. Indeed, the fields of view of many photomicrographs of PM samples obtained by scanning electron microscopy, are dominated by large numbers of pollens, plant and insect fragments, and microorganisms. Bioaerosols such as pollens, fungal spores, and most bacteria are expected to be found mainly in the coarse size fraction. However, allergens from pollens can also be found in respirable particles (Monn, 2001; Taylor et al., 2002). Matthias-Maser (1998) summarized information about the size distribution of PBP in and around Mainz, Germany, in what is perhaps the most complete study of this sort. Matthias-Maser found that PBP constituted up to 30% of total particle number or volume in the size range from about 0.35 μm to about 50 μm on an annual basis. Additionally, whereas the contribution of PBP to the total aerosol volume did not change appreciably with season, the contribution of PBP to total particle number ranged from about 10% in December and March to about 25% in June and October.

Data for the chemical composition of particles in a number of national parks and remote areas have been collected for a number of years by the IMPROVE network. Concentrations have been reported for sulfate, nitrate, light absorbing carbon, organic carbon, and soil components. With the collection of compositional data by the speciation network, more synoptic (i.e., concurrent) coverage will be obtained for these constituents from relatively remote to urban environments across the United States.

PM_{10} Concentrations and Trends

Nationwide PM_{10} annual mean concentrations on a county-wide basis from the AIRS database for calendar years 1999, 2000, and 2001 are shown in Figure 3-1a. Concentrations in most areas of the country were below the level of the PM_{10} annual standard of 50 $\mu g/m^3$ from 1999 through 2001. Further information about the attainment status of different areas can be found in the U.S. Environmental Protection Agency's Air Quality Trends Reports. The median annual mean PM_{10} concentration for this three year period was about 23 $\mu g/m^3$; and the 95th percentile value was about 38 $\mu g/m^3$. Concentrations flagged as natural events (e.g., resulting form high winds, wildfires, volcanic eruptions) or exceptional events (e.g., construction, prescribed burning) are not included in the calculations. The procedures for calculating the annual means at the site level follow 40 Code of Federal Regulations (CFR) Part 50 Appendix K (requiring 75 percent completeness per quarter for all three years). The 98th percentile concentrations from the monitor showing the highest value in a given county over the three year period are shown in Figure 3-1b. In these and in similar maps for $PM_{2.5}$ and $PM_{10\text{-}2.5}$, cut points were chosen at the 50th and 95th percentile concentrations. These cut points were chosen as they represent the standard metrics for characterizing important aspects of human exposure used by the U.S. Environmental Protection Agency. Of course, any other percentiles or statistics that are believed to be useful for characterizing human exposures could also be used. As shown by the blank areas on the maps, the picture is not complete because some monitoring locations did not record valid data for all four quarters or recorded fewer than 11 samples in one or more quarters or counties simply did not have monitors. Similar considerations apply to the maps shown later for $PM_{2.5}$ and $PM_{10\text{-}2.5}$. It should also be noted that the area of counties can be much greater in the West than in the East. As a result, the density of monitors may appear to be greater in the West and air quality may appear to be worse over much larger areas in the West than in the East. Concentrations are shown at the county level because this is the typical scale

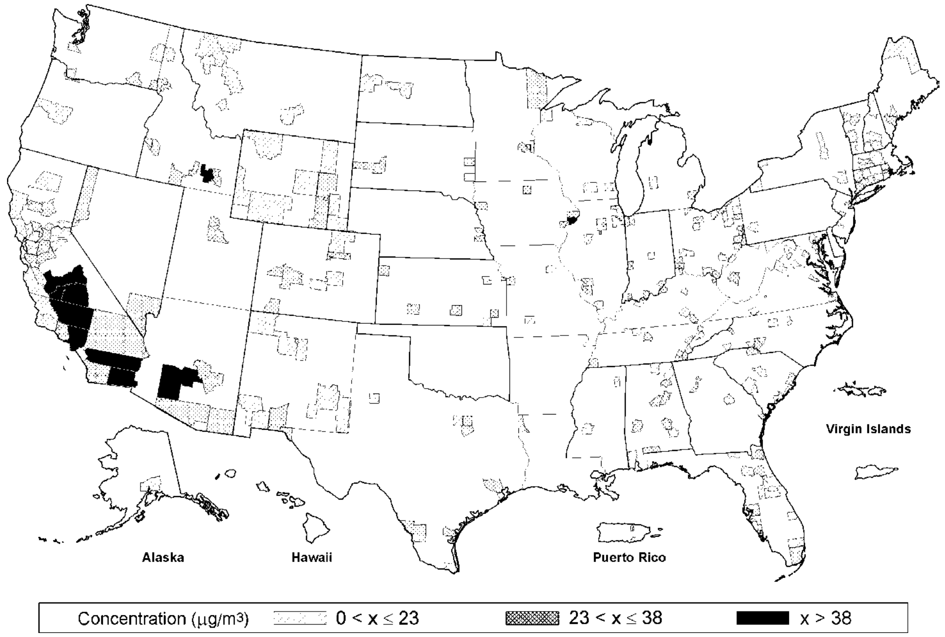


Figure 3-1a. **1999-2001 county-wide average annual mean PM_{10} concentrations (μg/m^3) for counties with PM_{10} monitors.**

Source: Aerometric Information Retrieval System (AIRS; U.S. Environmental Protection Agency, 2002b).

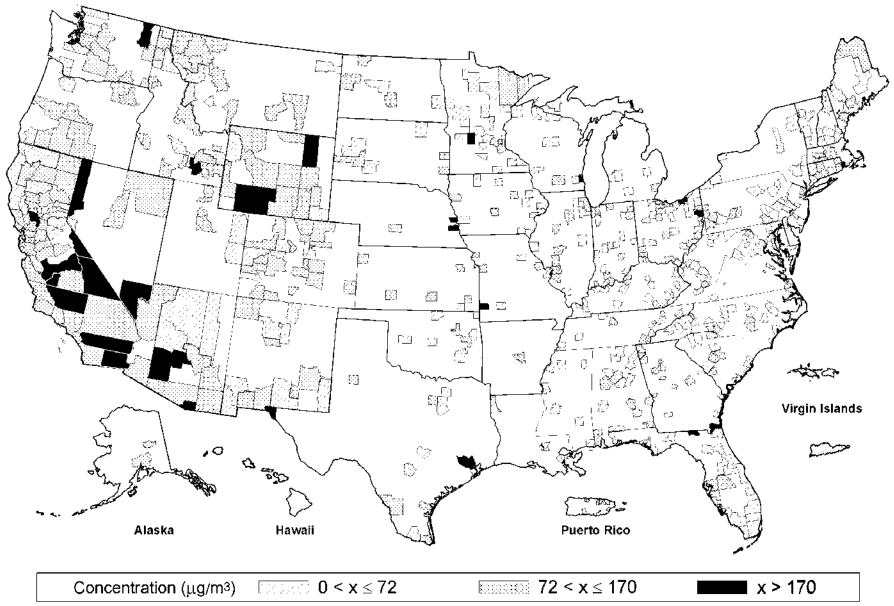


Figure 3-1b. **1999-2001 highest county-wide 98th percentile 24-h average PM_{10} concentrations (μg/m^3) for counties with PM_{10} monitors.**

Source: Aerometric Information Retrieval System (AIRS; U.S. Environmental Protection Agency, 2002b).

used in many health outcome studies. MSA or multi-county scales have also been used in a number of studies, e.g., Schwartz et al. (1996), or the NMMAPS study.

Nationwide trends in annual mean PM_{10} concentrations from 1992 through 2001 (based on data obtained at 119 rural sites, 297 suburban sites, and 316 urban sites reporting to AIRS) are shown in Figure 3-2 (U.S. Environmental Protection Agency, 2002a). Although average concentration levels differ among types of sites with higher levels at urban and suburban sites the nationwide data set shows a decrease of 14% that occurred mainly during the first half of the record. PM_{10} concentrations basically leveled off during the last few years of the record but there were indications of transient increases followed by decreases. Figure 3-3 shows the annual mean PM_{10} trend summarized by EPA region. Decreases in annual average PM_{10} concentrations from 1990 to 1999 were largest in the Northwest (9.6 $\mu g/m^3$) and smallest in the south-central United States (1.3 $\mu g/m^3$). Analyses of available TSP measurements obtained since 1950 indicate that mean TSP concentrations appear to have declined by about two- to three-fold in urban areas between 1950 and 1980 (Lipfert, 1998).

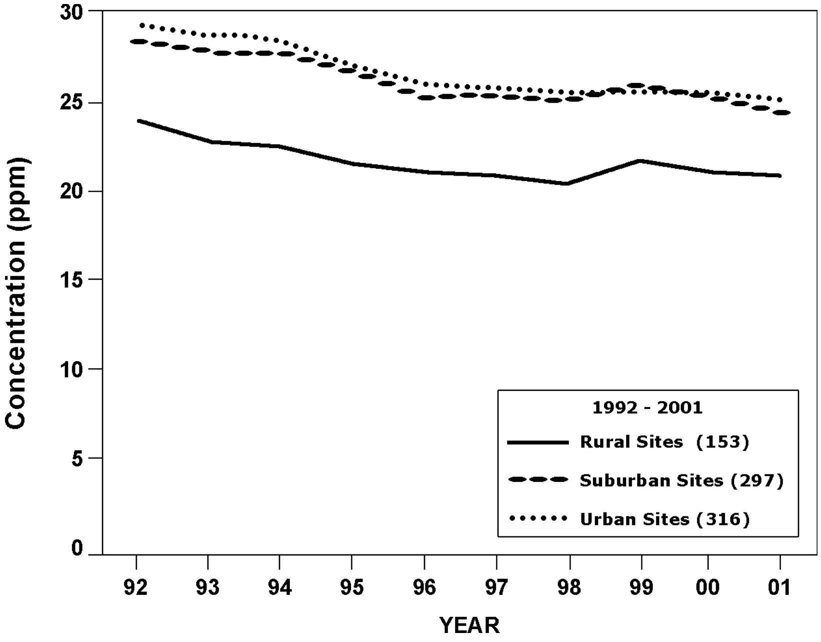
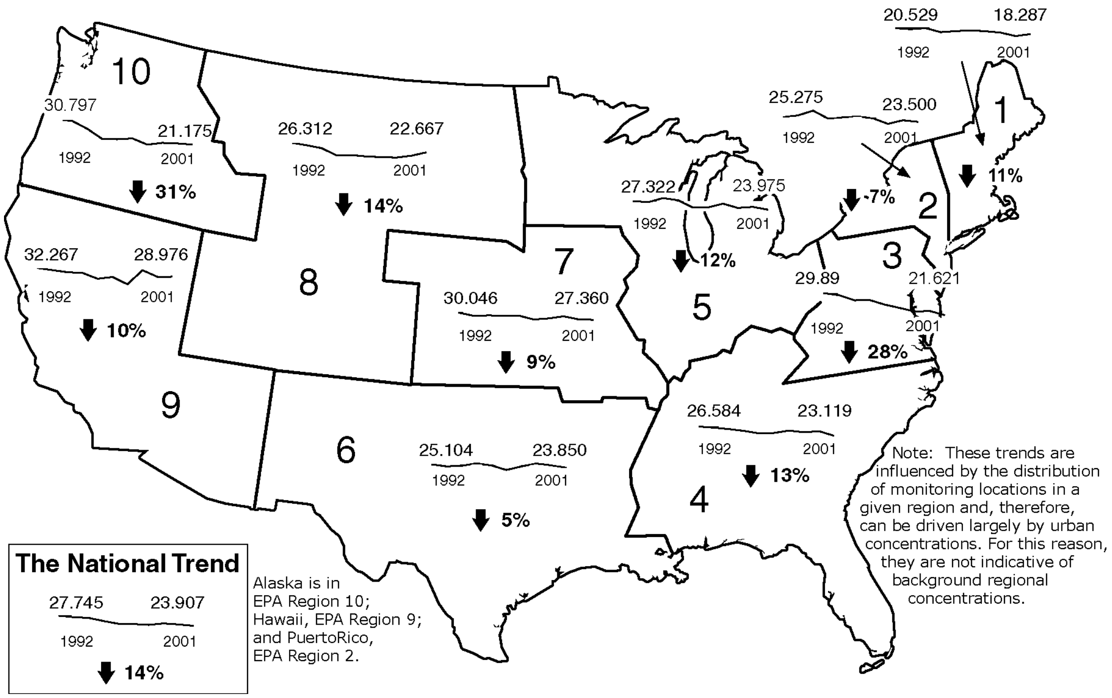


Figure 3-2. Nationwide trend in ambient PM_{10} concentration from 1992 through 2001.

Source: U.S. Environmental Protection Agency (2002a).



Alaska is in EPA Region 10; Hawaii, EPA Region 9; and PuertoRico, EPA Region 2.

Note: These trends are influenced by the distribution of monitoring locations in a given region and, therefore, can be driven largely by urban concentrations. For this reason, they are not indicative of background regional concentrations.

Figure 3-3. Trend in PM_{10} annual mean concentrations by EPA region, 1992 through 2001 ($\mu g/m^3$).

Source: U.S. Environmental Protection Agency (2002a).

$PM_{2.5}$ Concentrations and Trends

Nationwide annual mean $PM_{2.5}$ concentrations obtained from data collected during 1999, 2000, and 2001 are shown in Figure 3-4a; and 98th percentile concentrations are shown in Figure 3-4b. Quantities shown in Figure 3-4a and 3-4b were calculated for individual counties. Annual mean concentrations shown in Figure 3-4a were calculated on the basis of the latest 8 consecutive quarters containing at least 11 samples per quarter, and results from the highest monitor were used to produce Figure 3-4b. Data meeting these completeness criteria were obtained at 897 sites in 592 counties. The median $PM_{2.5}$ concentration nationwide was about 13 $\mu g/m^3$. Annual mean $PM_{2.5}$ concentrations were above 17 $\mu g/m^3$ at 5% of the sites, mainly in California and in the southeastern United States. The 98th percentile 24-h average concentrations (as defined earlier for PM_{10}) were below 47 $\mu g/m^3$ at 95% of the sites sampled. Most of the sites with levels above this value are located in California.

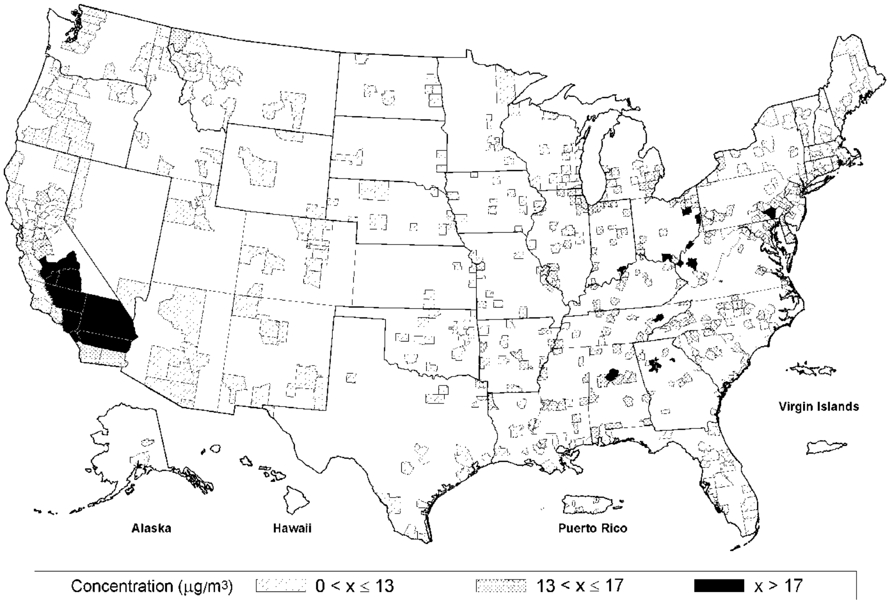


Figure 3-4a. 1999-2001 county-wide average annual mean $PM_{2.5}$ concentrations (µg/m^3) for counties with $PM_{2.5}$ monitors.

Source: Aerometric Information Retrieval System (AIRS; U.S. Environmental Protection Agency, 2002b).

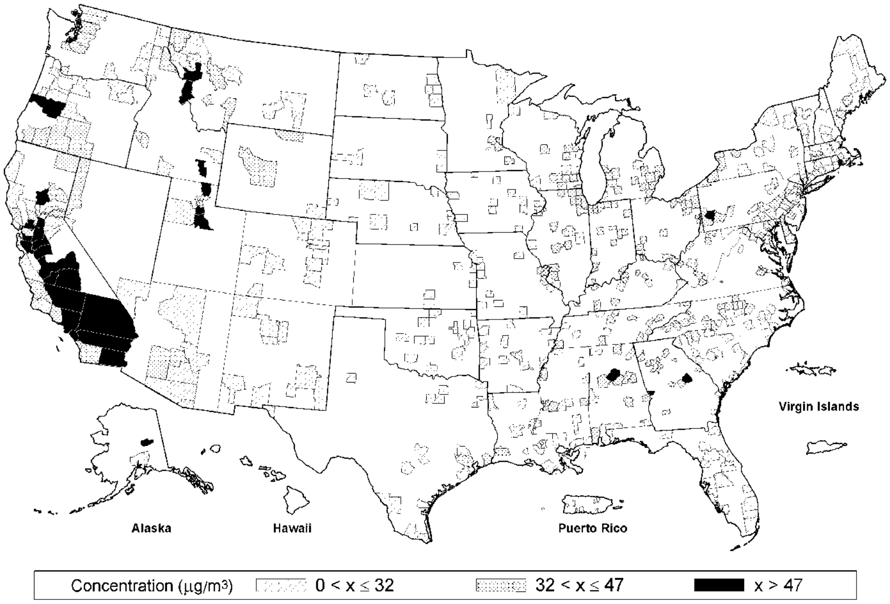


Figure 3-4b. 1999-2001 highest county-wide 98th percentile 24-h average $PM_{2.5}$ concentrations (µg/m^3) for counties with $PM_{2.5}$ monitors.

Source: Aerometric Information Retrieval System (AIRS; U.S. Environmental Protection Agency, 2002b).

Annual average $PM_{2.5}$ concentrations obtained as part of several health studies conducted in various locations in the United States and Canada from the late 1980s to the early 1990s are shown in Figure 3-5 (Bahadori et al., 2000a). These studies include the Harvard six-cities study (Steubenville, OH; Watertown, MA; Portage, WI; Topeka, KS; St. Louis, MO; and Kingston-Harriman, TN); Particle Total Exposure Assessment Methodology (PTEAMS; Riverside, CA); Metropolitan Acid Aerosol Characterization Study (MAACS; Philadelphia, PA; Washington, DC; and Nashville, TN); South Boston Air Quality and Source Apportionment Study (Boston, MA); and NPMRMN (Phoenix, AZ). The remaining sites were part of the 24-cities study (Spengler et al., 1996).

Sufficient data are not yet available to permit the calculation of nationwide trends of $PM_{2.5}$ and $PM_{10\text{-}2.5}$; however, some general emerging patterns can be discerned. Darlington et al. (1997) proposed that the consistent reductions in PM_{10} concentrations found in a wide variety of environments ranging from urban to rural may have resulted from common factors or controls that affected fine particles more strongly than coarse particles. This is because fine particles have longer atmospheric lifetimes than coarse particles and can be transported over longer distances and, hence, can affect larger areas. Apart from the IMPROVE network of monitoring sites located mainly in national parks, the longest time series of $PM_{2.5}$ concentration and composition data have been obtained by the California Air Resources Board (CARB). Their data show that annual average $PM_{2.5}$ concentrations decreased by about 50% in the South Coast Air Basin, 35% in the San Joaquin Valley, 30% in the San Francisco Bay Area, and 35% in the Sacramento Valley from 1990 to 1995 (Dolislager and Motallebi, 1999). $PM_{2.5}$ data were collected continuously from 1994 to 1998 as part of the children's health study in 12 southern California communities (Taylor et al., 1998). Data obtained at all sites show decreases in $PM_{2.5}$ ranging from 2% at Santa Maria to 37% at San Dimas/Glendora from 1994 through 1998. These decreases were accompanied by decreases in major components such as nitrate, sulfate, ammonium, and acids. Based on the analysis of $PM_{2.5}$ data sets collected prior to 1990, Lipfert (1998) found that $PM_{2.5}$ concentrations appear to have decreased by about 5% per year from 1970 to 1990 in a number of urban areas. These declines were also found to be consistent with decreases in emissions from combustion sources over that time period.

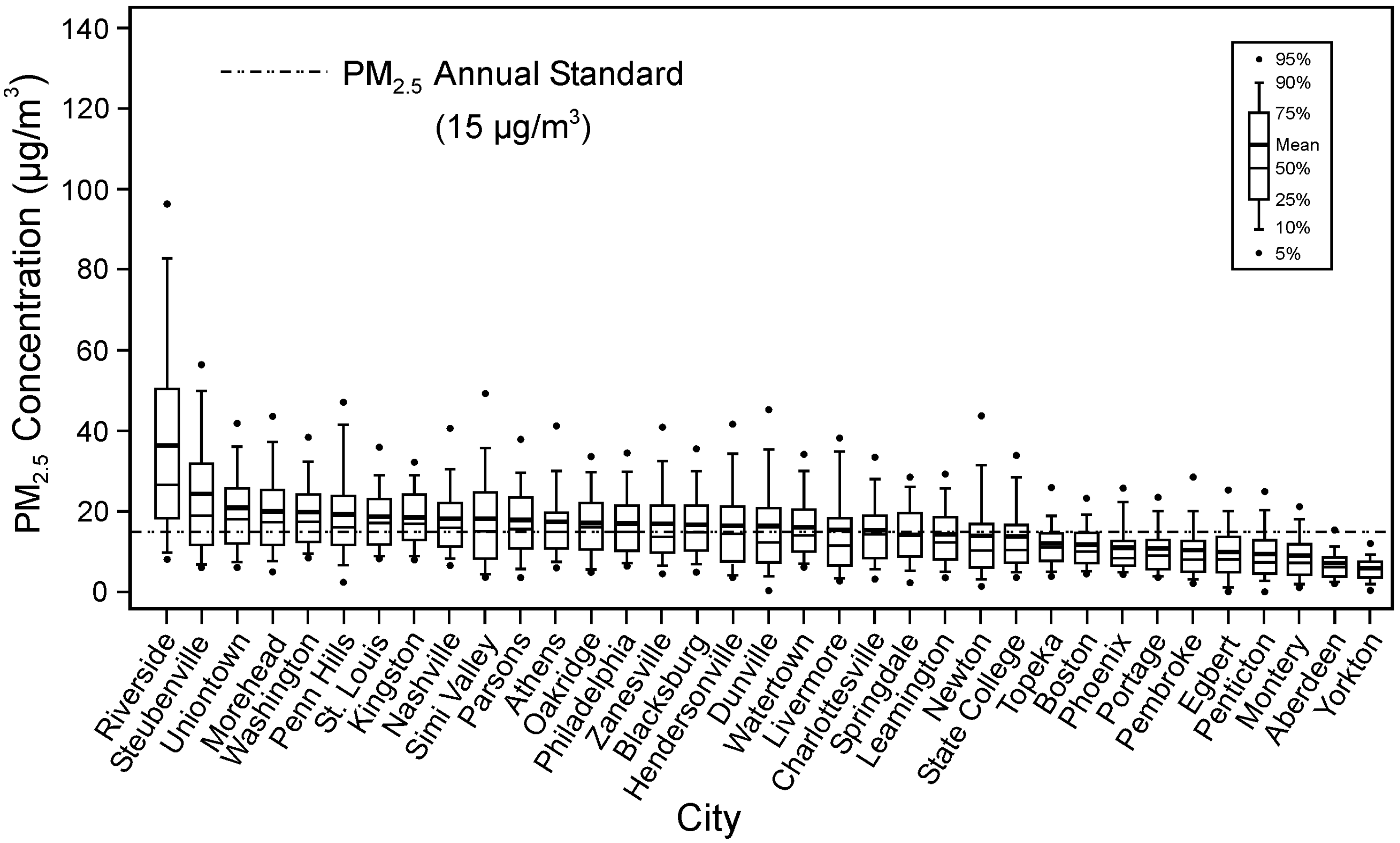


Figure 3-5. Collection of annual distribution of 24-h average PM$_{2.5}$ concentrations observed in U.S. and Canadian health studies conducted during the 1980's and early 1990's.

Source: Bahadori et al. (2000a).

$PM_{10-2.5}$ Concentrations

By using AIRS data for 1999, 2000, and 2001 obtained by the PM_{10} and $PM_{2.5}$ compliance networks, it is possible to construct a picture of the distribution of coarse PM across the country. This is accomplished by pairing data from 208 compliance monitoring sites in 196 counties where PM_{10} and $PM_{2.5}$ monitors are collocated and subtracting the mass concentrations of $PM_{2.5}$ from PM_{10}. Annual mean concentrations were calculated on the basis of the latest 8 consecutive quarters containing at least 11 samples per quarter. Nationwide annual mean $PM_{10-2.5}$ concentrations calculated by this approach are shown in Figure 3-6a. Annual mean $PM_{10-2.5}$ concentrations ranged from about 1 to about 50 $\mu g/m^3$; the nationwide median concentration was about 10 $\mu g/m^3$; and 5% of the sites had mean concentrations greater than 28 $\mu g/m^3$. The higher values occur mainly in the western United States, particularly in California. The highest county-wide 98th percentile $PM_{10-2.5}$ concentrations based on this same data set are shown in Figure 3-6b. Highest values in the western United States are caused by dust raised locally either by natural means or by anthropogenic activity. It is not clear what the contribution of PBP to these values may be. Elevated dust levels are also found in southern Florida as the result of dust storms in North Africa (Section 3.3.3) and trans-Atlantic transport. In many areas, combined errors in the $PM_{2.5}$ and PM_{10} measurements may be similar to or even greater than the calculated $PM_{10-2.5}$ concentrations. Because of this and other potential problems with this approach (Section 3.2.1), these results should be viewed with caution.

3.2.1 Seasonal Variability in PM Concentrations

$PM_{2.5}$

Aspects of the spatial and temporal variability of $PM_{2.5}$ concentrations for 1999, 2000, and 2001 in a number of metropolitan areas across the United States are presented in this and following subsections. Data for multiple sites in 27 urban areas across the United States have been obtained from the AIRS data base and analyzed for their seasonal variations and for their spatial correlations and spatial uniformity in concentrations. Selection of these 27 MSAs was based on the criteria that data be available for at least 15 days in each calendar quarter of either a three year period (1999, 2000, and 2001) or a two year period (2000 and 2001) at three or more sites within that MSA. In addition, a maximum of 11 sites per MSA were included for analysis.

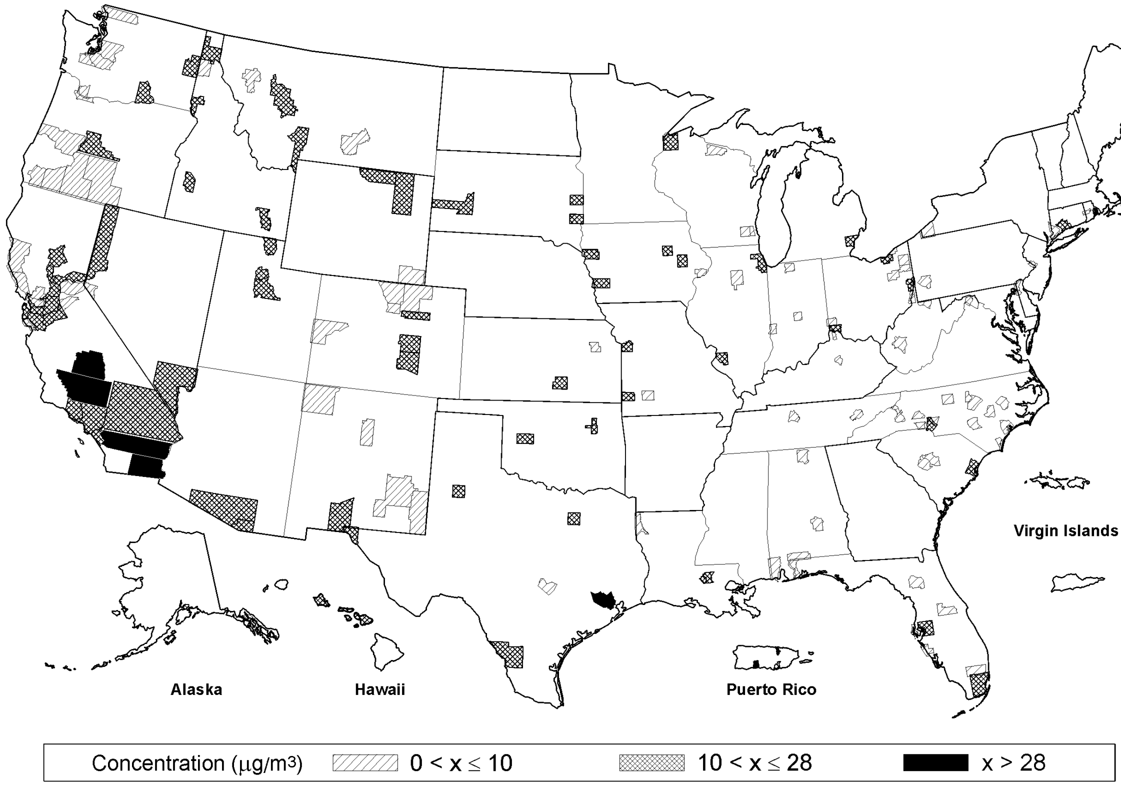


Figure 3-6a. 1999-2000 estimated county-wide average annual mean $PM_{10-2.5}$ concentrations ($\mu g/m^3$) for counties with collocated $PM_{2.5}$ and PM_{10} monitors.

Source: Aerometric Information Retrieval System (AIRS; U.S. Environmental Protection Agency, 2002b).

(In the Chicago and St. Louis MSAs, the 11 sites having the most observations were selected from a greater number of qualifying sites.) A number of aspects of the spatial and temporal variability of the 1999 $PM_{2.5}$ data set were presented in Rizzo and Pinto (2001) based in part on analyses given in Fitz-Simons et al. (2000).

Information regarding the seasonal variability in $PM_{2.5}$ concentrations in four MSAs (Philadelphia, PA; Cleveland, OH; Dallas, TX; and Los Angeles-Long Beach, CA) in the United States is summarized in Figures 3-7a through 3-7d. These four urban areas were chosen to illustrate some general features of the spatial and temporal variability found in the United States. The figures show lowest, lower quartile, median, upper quartile, and highest concentrations for each calendar quarter of 1999, 2000, and 2001 for the Cleveland, OH MSA and for 2000 and 2001 for Philadelphia, Dallas and Los Angeles MSAs. For each monitoring

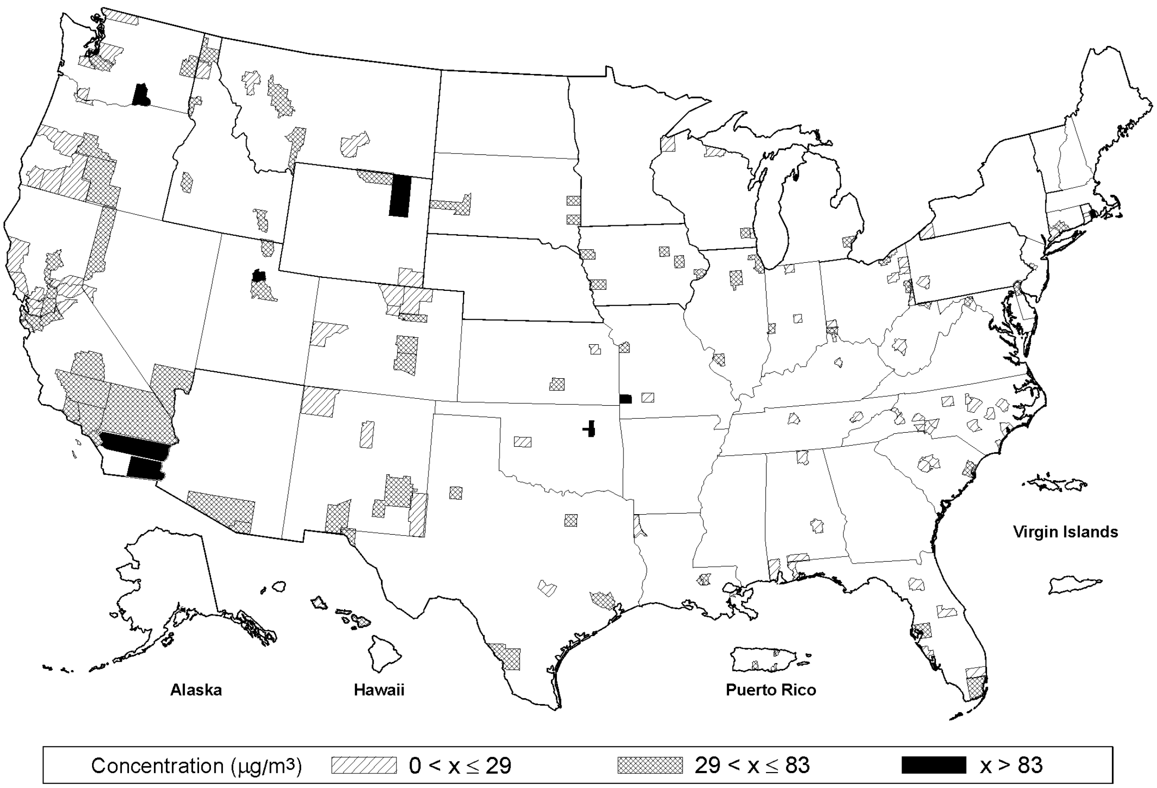


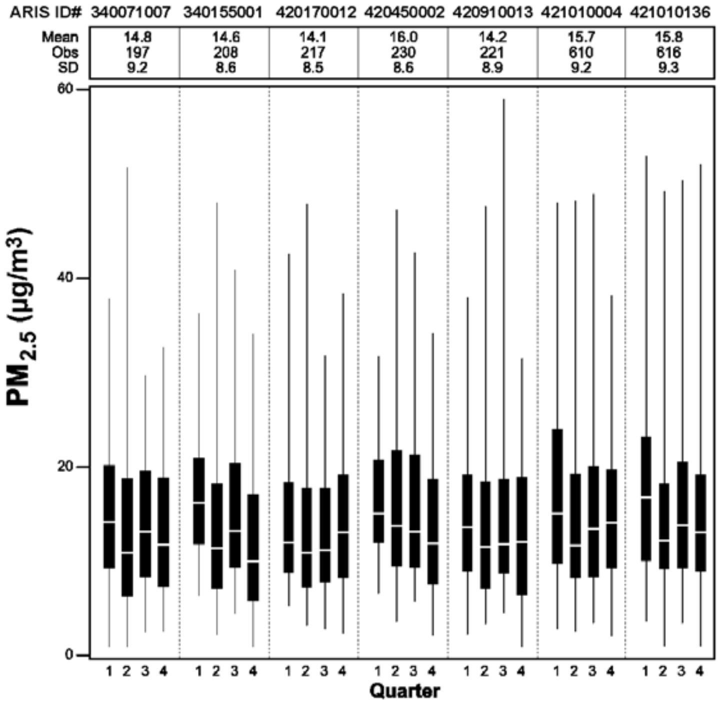
Figure 3-6b. 1999-2000 estimated county-wide highest 98th percentile 24-h $PM_{10-2.5}$ concentrations (µg/m^3) for counties with collocated $PM_{2.5}$ and PM_{10} monitors.

Source: Aerometric Information Retrieval System (AIRS; U.S. Environmental Protection Agency, 2002b).

site, the AIRS ID numbers, annual mean concentrations, the number of observations, and standard deviations are also shown. Data for multiple sites within these MSAs are shown to provide an indication of the degree of inter-site variability. Data for these MSAs and an additional twenty-three MSAs, criteria used for site selection, and additional descriptions of the data are given in Appendix 3A.

Annual mean $PM_{2.5}$ concentrations at individual monitoring sites in the MSAs examined ranged from about 6 µg/m^3 to about 30 µg/m^3. The lowest values were found in rural portions of the MSAs examined, typically near the perimeter of the MSA. The two highest mean concentrations were found in the Riverside and Los Angeles-Long Beach MSAs in southern California while the three lowest means were found in the Northwest (Portland, OR; Boise, ID; Seattle, WA). MSAs situated along the Eastern seaboard (Washington, DC; Philadelphia, PA;

a. Philadelphia, PA (2000 - 2001)



b. Cleveland, OH (1999 - 2001)

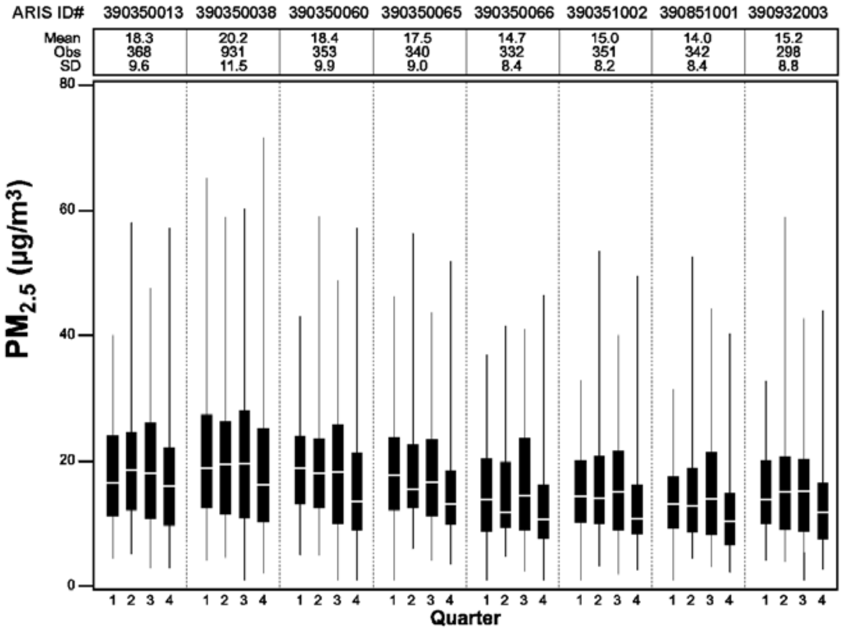
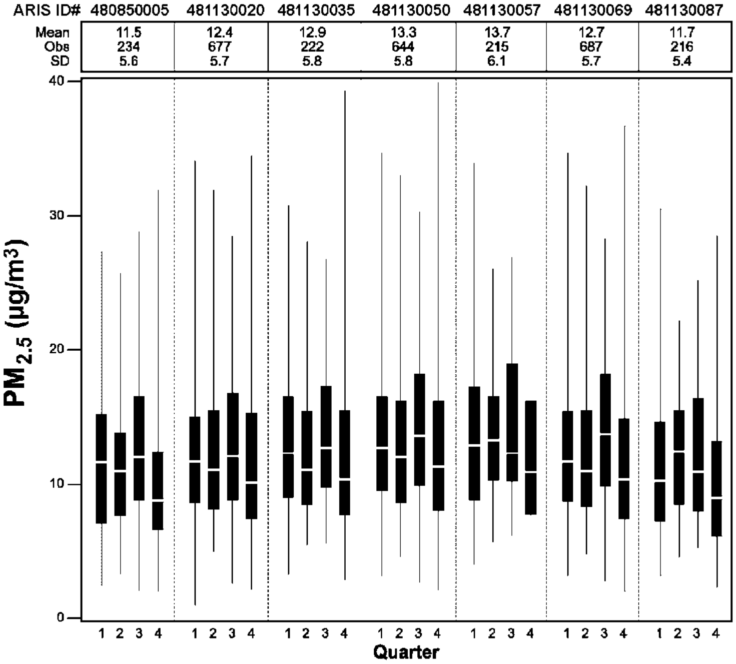


Figure 3-7a,b. Quarterly distribution of 24-h average PM$_{2.5}$ concentrations for selected monitors in the (a) Philadelphia, PA and (b) Cleveland, OH. Values for the lowest, lower quartile, median, upper quartile and highest concentrations are shown in the figures. The AIRS site ID number, annual mean concentration (µg/m^3), number of observations, and standard deviation of the data are shown above the figures for each site.

c. Dallas, TX (2000 - 2001)



d. Los Angeles, CA (2000 - 2001)

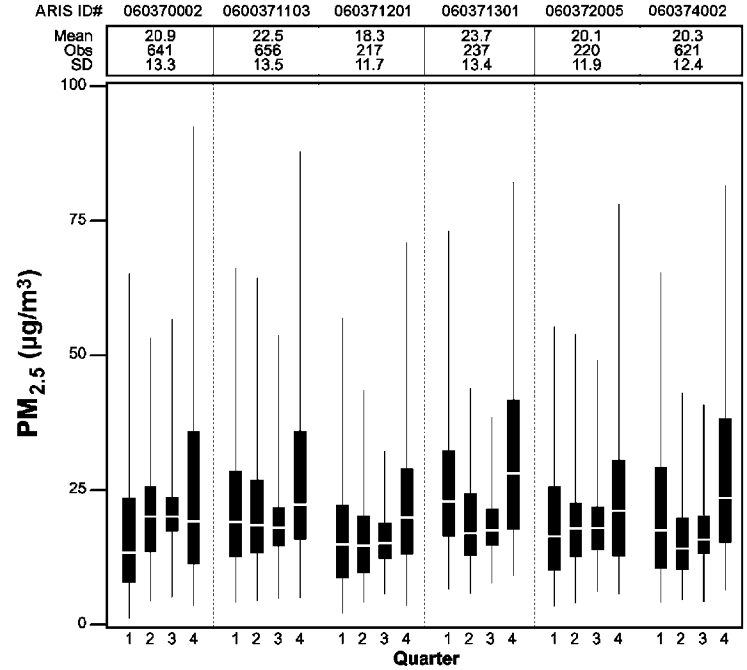


Figure 3-7c,d. **Quarterly distribution of 24-h average $PM_{2.5}$ concentrations for selected monitors in the (c) Dallas, TX and (d) Los Angeles, CA MSAs. Values for the lowest, lower quartile, median, upper quartile and highest concentrations are shown in the figures. The AIRS site ID number, annual mean concentration (µg/m^3), number of observations, and standard deviation of the data are shown above the figures for each site.**

Norfolk, VA) tend to have lower mean $PM_{2.5}$ concentrations than MSAs in the north-central United States (Steubenville, OH; Cleveland, OH; Pittsburgh, PA; Chicago, IL; Detroit, MI; Gary, IN; Appendix 3A). In addition, average $PM_{2.5}$ concentrations tended to be lower in 1999, 2000, and 2001 in urban areas given in Appendix 3A compared to the concentrations observed during pollution-health outcome studies conducted in those five urban areas where these overlap (Figure 3-5). It should be noted that there are no data demonstrating the comparability of the monitors used in the studies shown in Figure 3-5 and the FRM.

The patterns of seasonal variability observed in the MSAs examined are complex. In the Philadelphia, PA MSA, highest median concentrations occur at all but one site in the first quarter (cf., Figure 3-7a). First quarter maxima are also observed at all sites in the Detroit, MI and Chicago, IL MSAs (cf., Figures 3A-11 and 3A-14). The Cleveland, OH, MSA (Figure 3-7b) by contrast does not have a clear seasonal pattern. In several MSAs examined in the south and eastern United States (Atlanta, GA; Baton Rouge, LA; Birmingham, AL; Columbia, SC; and Washington, DC), highest median concentrations occur at all sites during the third calendar quarter (i.e., summer months; cf., Appendix 3A). Sites in Dallas, TX, (Figure 3-7c) as in the other southern cities mentioned above, generally exhibit third quarter median concentration maxima. Highest median concentrations occur during the fourth calendar quarter in MSAs in the western United States as in the Los Angeles, CA MSA (Figure 3-7d) although there are exceptions at individual sites in the Riverside, CA MSA (Figure 3A-26).

Lowest median concentrations occur mainly during the first or fourth quarters at most sites in the eastern United States as well as in Cleveland, OH and Dallas, TX (Figures 3-7b and 3-7c) while some occur during the second quarter (Philadelphia, PA; Figure 3-7a). Moving westward, the seasonal pattern is not as distinct: lowest median concentrations occur in any quarter, but usually in the second or third quarter as in the Chicago, Detroit, and Los Angeles-Long Beach (Figure 3-7d) MSAs. With the exception of Los Angeles, CA and Riverside, CA, sites in the West show lowest median concentrations in the second quarter. In most of the MSAs examined, seasonal variations follow a similar pattern at all of the sites within the MSA, but in a few MSAs there are noticeable differences in the seasonal pattern between sites. The large-scale differences in seasonal variability between MSAs tend to follow differences in the major categories of PM sources affecting the monitoring sites. Local heating by wood burning during the colder months is practiced more widely in the western United States than in the eastern United States.

Prolonged winter stagnation events are also more common in western mountain valleys during winter than in sections of the eastern United States located in relatively flat topography. Hence, winter maxima and greater variability in $PM_{2.5}$ concentrations across sites are expected in the West due to the influence of the local sources. On the other hand, photochemical production of secondary PM, especially sulfate, occurs over wide areas in relatively homogeneous air masses during the summer months in the eastern United States. Because sulfates (along with associated cations and water) constitute the major fraction of summertime $PM_{2.5}$ in the East, there is greater uniformity in third quarter PM concentrations within eastern MSAs (cf., Appendix 3A).

Maximum twenty-four hour average concentrations shown in the box plots in Figures 3-7a to 3-7d and in Figures 3A-1 to 3A-27 do not necessarily follow the same seasonal pattern as the median concentrations. There is no clear relation between the maximum and the median concentrations evident in the Philadelphia, PA data set (Figure 3-7a). In Cleveland, OH (Figure 3-7b), maximum concentrations occur during the second or fourth quarters, and highest median concentrations generally occur during the third or first quarters. In Dallas, TX (Figure 3-7c), maximum concentrations generally occur during the fourth quarter, but highest median concentrations tend to occur during the second or third quarter. In the Los Angeles-Long Beach MSA (Figure 3-7d), the maximum and highest median concentrations occur together in the fourth quarter with the exception of one site. Peak individual concentrations likely reflect the occurrence of transient events such as forest fires (mainly in the West) or episodes of secondary PM production (mainly in the East). However, chemical analyses of filter samples or other evidence should be used to determine specific causes in particular locations.

There have been a few studies that have characterized $PM_{2.5}$ and PM_{10} concentrations in major urban areas. The Metropolitan Aerosol Acidity Characterization Study (MAACS) (Bahadori et al., 2000b) characterized the levels and the spatial and temporal variability of $PM_{2.5,}$ PM_{10}, and acidic sulfate concentrations in four cities in the eastern United States (Philadelphia, PA; Washington, D.C.; Nashville, TN; and Boston, MA). Seasonal variations in $PM_{2.5}$ and PM_{10} concentrations obtained during the course of this study are shown in Figure 3-8. The data for the four cities included in MAACS are presented in a box plot showing the lowest, lowest tenth percentile, lowest quartile, median, highest quartile, highest tenth percentile, and highest $PM_{2.5}$ and PM_{10} values. Mean and highest $PM_{2.5}$ and PM_{10} concentrations are found during the summer

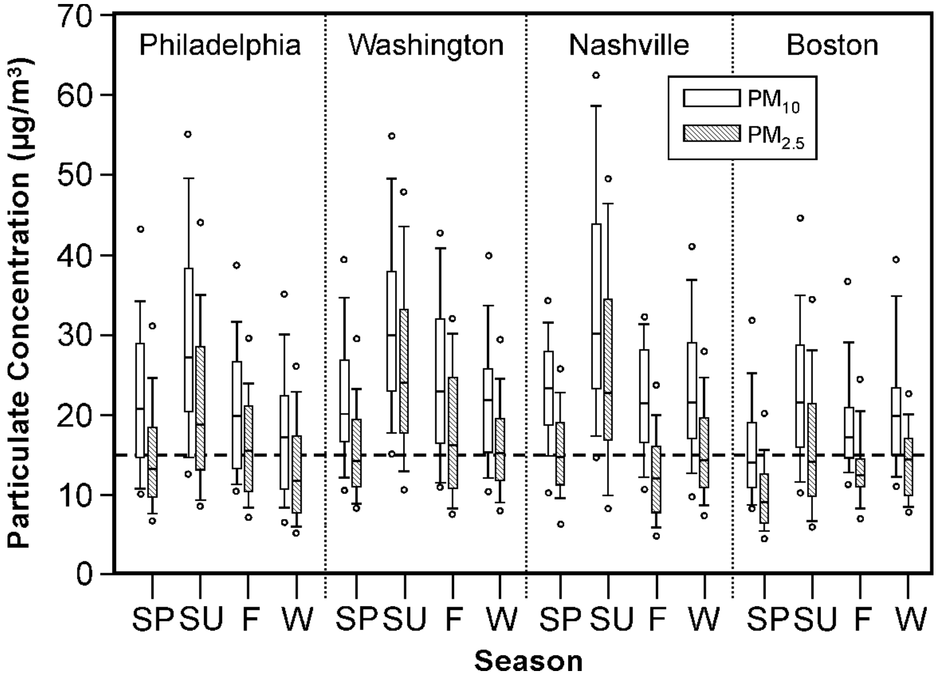


Figure 3-8. Seasonal concentrations of $PM_{2.5}$ and PM_{10} measured in the four MAACS cities. The data show the lowest, lowest tenth percentile, lowest quartile, median highest quartile, highest tenth percentile, and highest $PM_{2.5}$ 24-h average values. The dashed line shows the level of the annual $PM_{2.5}$ standard.

Source: Bahadori et al. (2000b).

in all four cities (in contrast with Figure 3-7a) although the seasonal pattern in Boston appears to be more nearly bimodal with an additional winter peak.

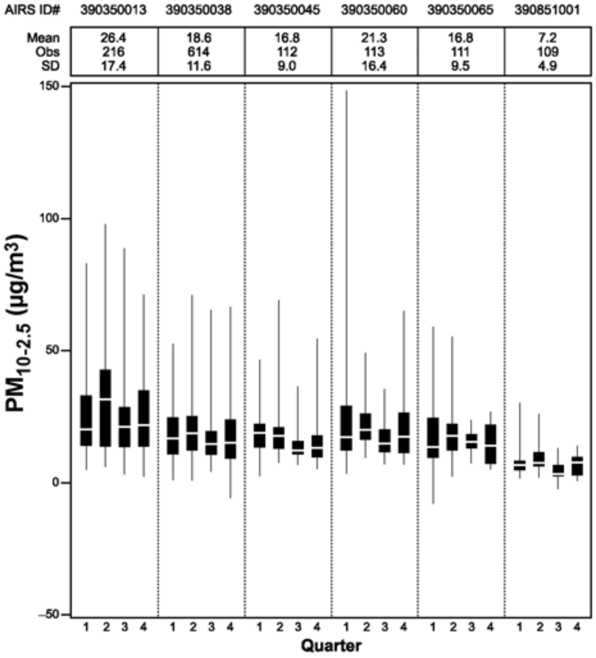
$PM_{10-2.5}$

Of the 27 MSAs selected for analysis of $PM_{2.5}$ data (Appendix 3A), 17 have multiple sites satisfying the $PM_{10-2.5}$ data completeness criteria. A subset of 53 qualifying sites were selected for analysis of $PM_{10-2.5}$ data. Each qualifying site has 11 or more observations per calendar quarter for twelve consecutive quarters (1999-2001, 2 MSAs), eight quarters (1999 + 2000 or 2000 + 2001, 7 MSAs) or four quarters (2000 or 2001, 8 MSAs). In addition, data from sites within the same MSA represent the same year (or years) of observations, so that intersite comparisons within an MSA are based on the same reporting period. However, comparisons between different MSAs can involve different annual reporting periods. As can be seen by comparing Figures 3-7a,b,c,d and Figures 3-9a,b,c the number of observations used for summarizing $PM_{10-2.5}$ data is much lower than that measured for $PM_{2.5}$. Unfortunately, fewer qualifying MSAs for $PM_{10-2.5}$ result in geographical coverage that is more spotty than with $PM_{2.5}$. Five of the seven MSAs representing the eastern United States for $PM_{2.5}$, for example, did not meet completeness criteria for $PM_{10-2.5}$, leaving only Tampa, FL, and Columbia, SC, to represent the East. Secondly, it can readily be seen, e.g., for Cleveland, OH (Figure 3-9a) and in Figures 3A-28 through 3A-44, that a number of $PM_{10-2.5}$ concentrations are negative. For example, in 2001, approximately one-fourth of all $PM_{10-2.5}$ concentrations at the three qualifying sites in the Gary, IN MSA were negative. (The negative estimates have been included in the calculation of mean concentrations.) There are a number of reasons for the negative concentration estimates, many of which arise because the ratios of $PM_{2.5}$ to PM_{10} are based on two independent measurements. Measurement imprecision plays a role when the ratios are large and concentrations are small. Differences in the behavior of semivolatile components in the two samplers could occur; and the results may also reflect errors in sampler placement, field, laboratory, or data processing procedures. For the reasons cited above, caution should be exercised when attempting to interpret results for $PM_{10-2.5}$ based on current network collocated $PM_{2.5}$ and PM_{10} monitors.

Annual mean $PM_{10-2.5}$ concentrations at individual monitoring sites range from about 6 $\mu g/m^3$ (Portland, OR) to about 33 $\mu g/m^3$ (Riverside, CA). (Gary, IN sites were excluded because of numerous negative $PM_{10-2.5}$ concentrations, and one site in Riverside, CA, affected by a local dust event was excluded.) The three highest annual mean concentrations are observed in Riverside, CA; Los Angeles-Long Beach, CA; and Salt Lake City, UT; and the lowest (excluding Gary) were observed in Portland, OR. For the remaining MSAs, there does not appear to be a significant geographical trend associated with the annual mean $PM_{10-2.5}$ concentration. Within MSAs, the lowest concentrations are frequently observed at sites near the perimeter of the MSA although it must be noted that the number of sites is limited.

Within each MSA, collocated $PM_{2.5}$ and $PM_{10-2.5}$ concentrations, averaged over the same years, were compared. The mean $PM_{2.5}$:$PM_{10-2.5}$ ratio was calculated for each of the 17 MSAs using as many sites as possible. The median mean $PM_{2.5}$:$PM_{10-2.5}$ ratio for the 17 MSAs was 1.2. For eight MSAs (Columbia, SC; Chicago, IL; Louisville, KY; Gary, IN; Tampa, FL;

a. Cleveland, OH (2000 - 2001)



b. Dallas, TX (2001)

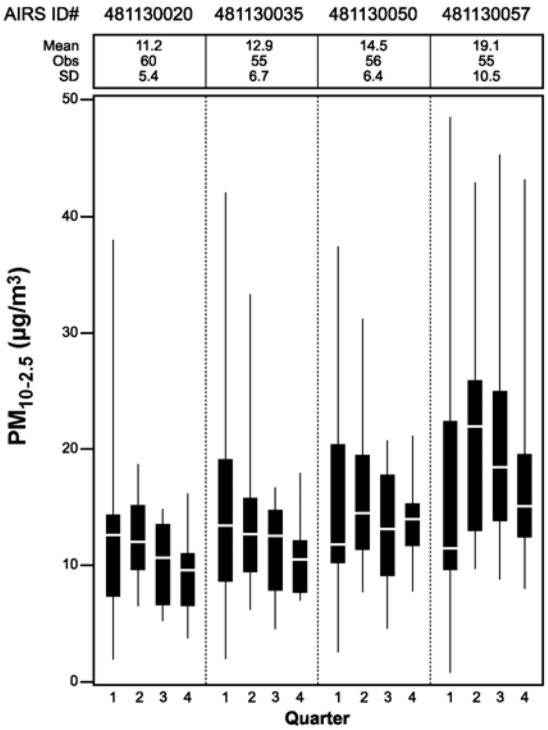


Figure 3-9a,b. Quarterly distribution of 24-h average PM$_{10-2.5}$ concentrations for selected sites in the (a) Cleveland, OH; (b) Dallas, TX MSAs. Values for the lowest, lower quartile, median, upper quartile and highest concentrations are shown in the figures. The AIRS site ID number, annual concentration, number and standard deviation are shown above the figures for each site.

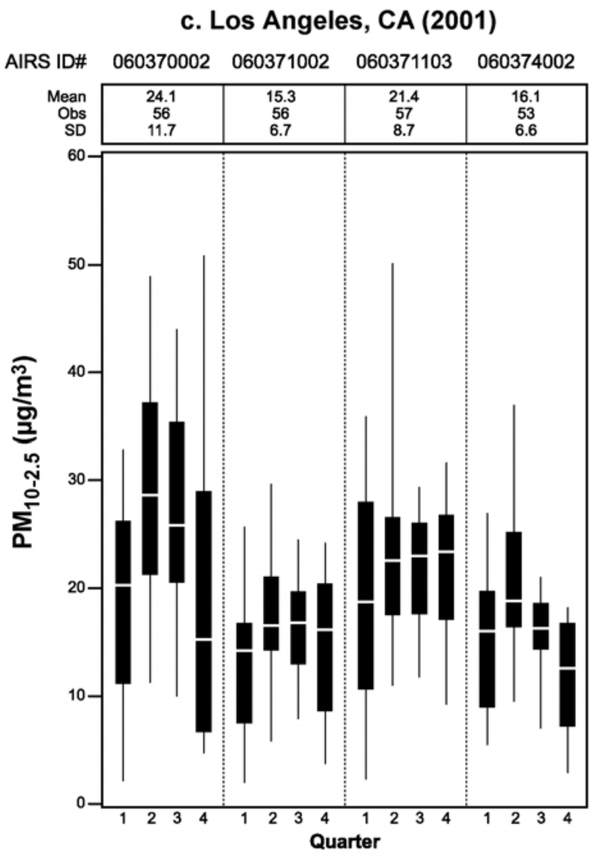


Figure 3-9c. Quarterly distribution of 24-h average $PM_{10-2.5}$ concentrations for selected sites in the Los Angeles, CA MSAs. Values for the lowest, lower quartile, median, upper quartile and highest concentrations are shown in the figures. The AIRS site ID number, annual concentration, number and standard deviation are shown above the figures for each site.

Source: AIRS Database.

Steubenville, WV; Portland, OR; Milwaukee, WI) the mean $PM_{2.5}$ concentration exceeded the mean $PM_{10-2.5}$ concentration. For an additional eight MSAs, the $PM_{2.5}$ and $PM_{10-2.5}$ concentration means were the same (within one SD). Salt Lake City was the only MSA for which the mean $PM_{10-2.5}$ concentration exceeded the mean $PM_{2.5}$ concentration.

Information regarding the seasonal variability in $PM_{10-2.5}$ concentrations in three MSAs (Cleveland, OH; Dallas, TX; Los Angeles-Long Beach, CA) is summarized in Figures 3-9a through 3-9c. The figures show lowest, lower quartile, median, upper quartile, and highest concentrations for each calendar quarter of 2000 and 2001 for the Cleveland, OH MSA (six sites); and of 2001 for the Dallas, TX and Los Angeles, CA MSAs (four sites each). Data for these and an additional 13 MSAs, as well as additional descriptions of the data, are given in Appendix 3A. The seasonal pattern for $PM_{10\text{-}2.5}$ median concentrations is different from that of $PM_{2.5}$ (Figures 3-7a,b,c,d, and Appendix 3A). Most seasonal median maxima in $PM_{10\text{-}2.5}$ occur during the second or third calendar quarters, i.e., spring and summer months (45% and 36% of all sites, respectively) as seen, for example, at most sites in Figures 3-9. Contributions from bioaerosols during the spring blooming season, which mostly affect $PM_{10\text{-}2.5}$ concentrations, might be a significant contributing factor in the second quarter $PM_{10\text{-}2.5}$ median maxima in some regions of the United States. Lowest median concentrations occur mainly in the first or fourth quarters 62% and 23% of all sites, respectively). Cleveland, OH, (Figure 3-9a) and Tampa, FL, where lowest medians generally are observed in the third quarter are exceptions (Figure 3A-29). At no site was the lowest median $PM_{10\text{-}2.5}$ concentration observed in the second quarter. By comparison with $PM_{10\text{-}2.5}$, seasonal $PM_{2.5}$ median maxima mostly occurred in the first or third quarters and $PM_{2.5}$ median minima are mostly observed in the second and fourth quarters. With few exceptions, collocated $PM_{2.5}$ and $PM_{10\text{-}2.5}$ seasonal medians at individual sites peak in different quarters. Likewise, at a given site, the lowest median concentrations for $PM_{2.5}$ and $PM_{10\text{-}2.5}$ rarely occur in the same quarter. In MSAs with several $PM_{10\text{-}2.5}$ sites, the seasonal patterns are typically reproduced at all sites within the MSA. In the Dallas, TX MSA, the maximum and minimum estimated $PM_{10\text{-}2.5}$ concentrations both occur in the first quarter at all four sites.

The ratio of $PM_{2.5}/PM_{10\text{-}2.5}$ seasonal median concentrations peak in the first quarter for MSAs in the central and north-central United States and tend to peak in the fourth quarter for western states. The largest ratios of $PM_{2.5}/PM_{10\text{-}2.5}$ seasonal median concentrations are observed in the central and north-central MSAs (Chicago, Cleveland, Detroit, and St. Louis); whereas smaller ratios are found in the western and southern United States.

As can be seen from Figure 3-9a and Figures 3A-40 and 3A-43, the maxima for $PM_{10\text{-}2.5}$ concentrations exceeded 100 $\mu g/m^3$ in Cleveland, OH, and Salt Lake City, UT, and 500 $\mu g/m^3$ in Riverside, CA. This latter value is related to a dust storm. In several urban areas (Cleveland, OH; Detroit, MI; Chicago, IL; Dallas, TX; and Riverside, CA) maxima in $PM_{10\text{-}2.5}$ concentrations were larger than those for $PM_{2.5}$. However, there is no clear geographic pattern.

The results described above should be viewed with caution because of inherently large errors in the technique used to derive them.

Frequency Distributions for $PM_{2.5}$ Data

Frequency distributions for $PM_{2.5}$ concentrations obtained in Philadelphia from 1992 through 1995 are shown in Figure 3-10 (data obtained by Bahadori et al., 2000b). Also shown, are concentrations predicted from the log-normal distribution, using geometric mean values and standard deviations derived from the data. In Philadelphia, the highest $PM_{2.5}$ values were observed when winds were from the southwest during sunny but hazy high pressure conditions. In contrast, the lowest values were found after significant rainstorms during all seasons of the year. Mean ± SD day-to-day concentration differences in the data set are $6.8 \pm 6.5\ \mu g/m^3$ for $PM_{2.5}$ and $8.6 \pm 7.5\ \mu g/m^3$ for PM_{10}. Maximum day-to-day concentration differences are $54.7\ \mu g/m^3$ for $PM_{2.5}$ and $50.4\ \mu g/m^3$ for PM_{10}.

Different patterns are observed in data collected elsewhere in the United States. $PM_{2.5}$ concentrations obtained in Phoenix, AZ, from 1995 through 1997 (Zweidinger et al., 1998) are summarized in Figure 3-11; and frequency distributions of $PM_{2.5}$ concentrations obtained in Phoenix are shown in Figure 3-12. Mean ±SD day-to-day concentration differences in this data set are $2.9 \pm 3.0\ \mu g/m^3$; the maximum day-to-day concentration difference was $23\ \mu g/m^3$. $PM_{2.5}$ and $PM_{10\text{-}2.5}$ data were obtained with dichotomous samplers at a number of sites in California on a sampling schedule of every 6 days from 1989 through 1998. Histograms showing the frequency distribution of the entire set of $PM_{2.5}$ and $PM_{10\text{-}2.5}$ concentrations obtained by the CARB network of dichotomous samplers from 1989 to 1998 are shown in Figures 3-13 and 3-14. Also shown are log-normal distributions generated by using geometric means and standard deviations derived from the data as input. Although the data for both size fractions appear to be reasonably well simulated by the function, data obtained at individual locations may not be. Data showing the seasonal variability of $PM_{2.5}$ obtained at Riverside-Rubidoux are summarized in box plot form in Figure 3-15. The frequency distribution of $PM_{2.5}$ concentrations obtained at Riverside-Rubidoux from 1989 to 1994 is shown in Figure 3-16. It can be seen that the data are not as well fit by a log-normal distribution as are data shown in Figure 3-10, partly as the result of a significant number of days when $PM_{2.5}$ concentrations exceed $100\ \mu g/m^3$.

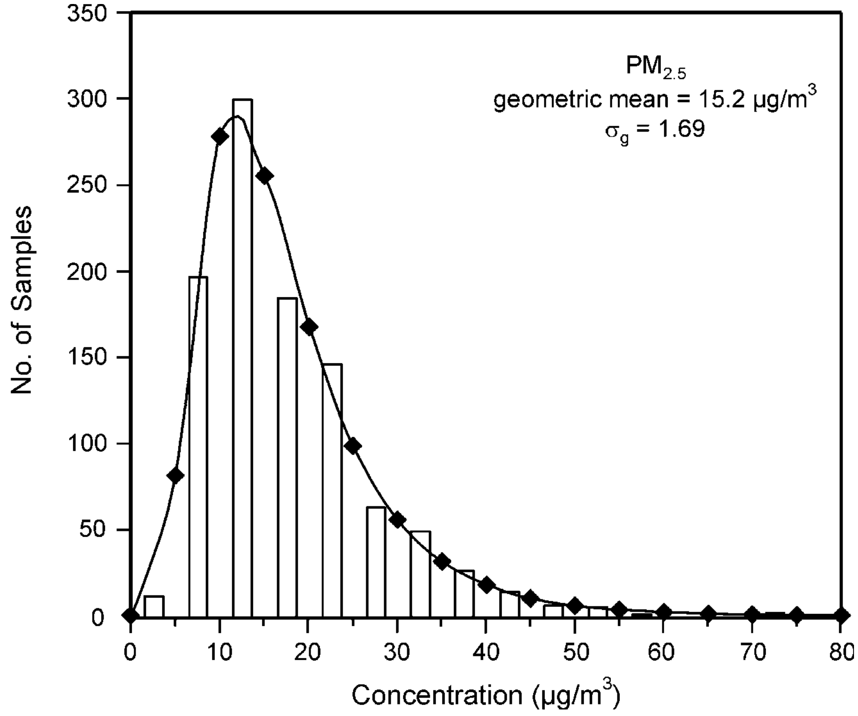


Figure 3-10. Frequency distribution of 24-h average $PM_{2.5}$ concentrations measured at the Presbyterian home (PBY) monitoring site in southwestern Philadelphia from 1992 to 1995. Log-normal distribution fit to the data shown as solid line.

Source: Bahadori et al. (2000b).

An examination of the data from the four MAACS cities, Phoenix, AZ, and Riverside, CA, indicates that substantial differences exist in aerosol properties between the eastern cities (MAACS) and the western cities (Phoenix, AZ; Riverside, CA). Fine-mode particles account for most of the PM_{10} mass observed in the MAACS cities and appear to drive the daily and seasonal variability in PM_{10} concentrations in the East; whereas coarse-mode particles represent a larger fraction of PM_{10} mass in Phoenix and Riverside and drive the seasonal variability in PM_{10} seen in the West. The average ratio of $PM_{2.5}$ to PM_{10} concentrations is much larger in the MAACS cities of Philadelphia, PA (0.72); Washington, DC (0.74); and Nashville, TN (0.63) than in either Phoenix, AZ (0.34) or Riverside, CA (0.49). Differences between median and maximum concentrations in any size fraction are much larger at the Riverside site than at either the MAACS or Phoenix sites. Many of these differences could reflect the more sporadic nature of

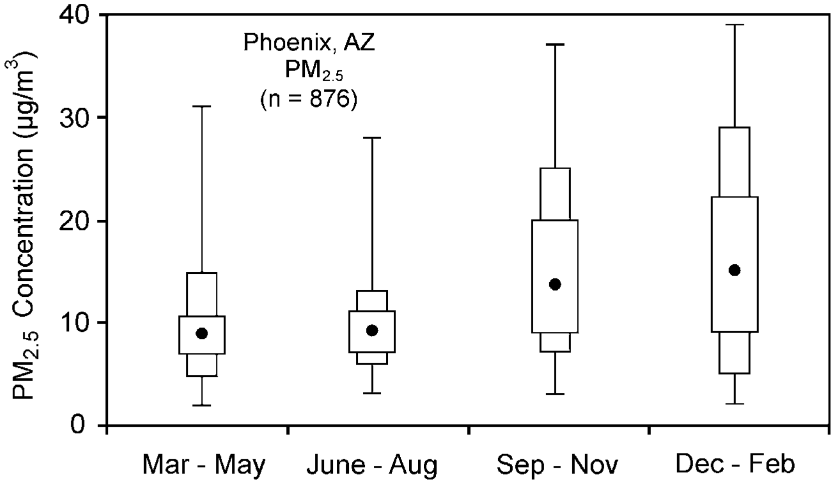


Figure 3-11. Concentrations of 24-h average $PM_{2.5}$ measured at the EPA site in Phoenix, AZ from 1995 to 1997. The data show the lowest, lowest tenth percentile, lowest quartile, median (black circles), highest quartile, highest tenth percentile, and highest $PM_{2.5}$ values.

Source: Zweidinger et al. (1998).

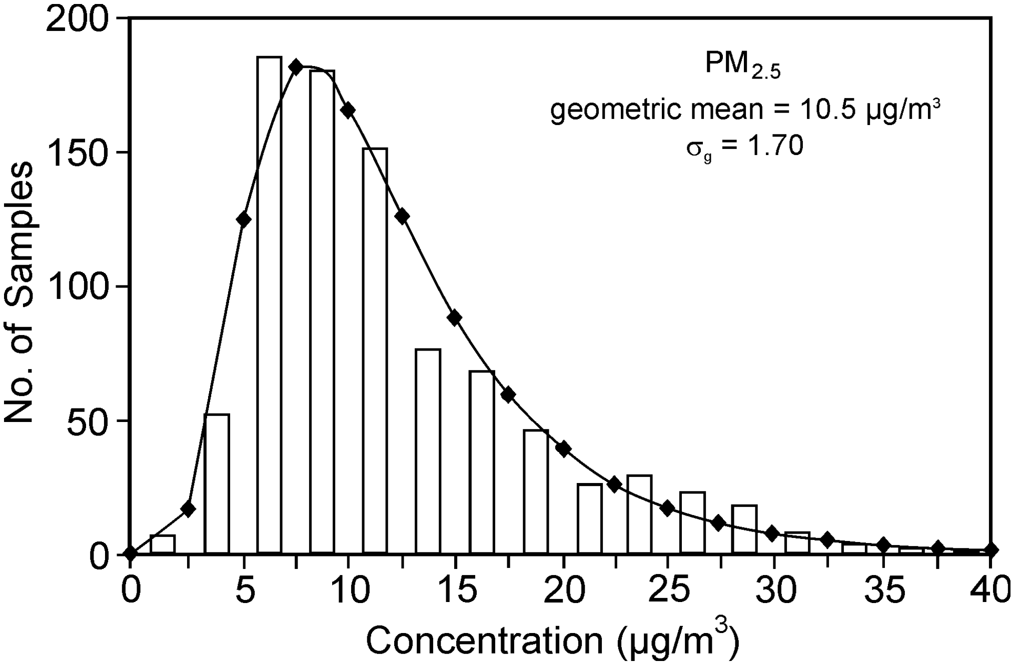


Figure 3-12. Frequency distribution of 24-h average $PM_{2.5}$ concentrations measured at the EPA site in Phoenix, AZ from 1995 to 1997.

Source: Zweidinger et al. (1998).

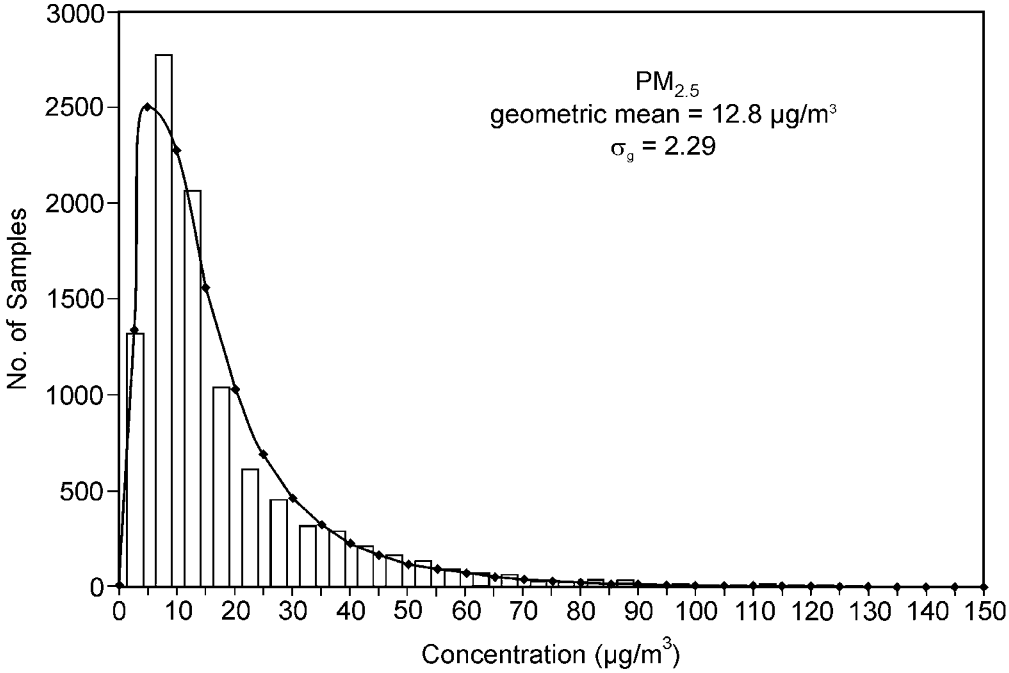


Figure 3-13. Frequency distribution of 24-h average PM$_{2.5}$ measurements obtained from all California Air Resources Board dichotomous sampler sites from 1989 to 1998.

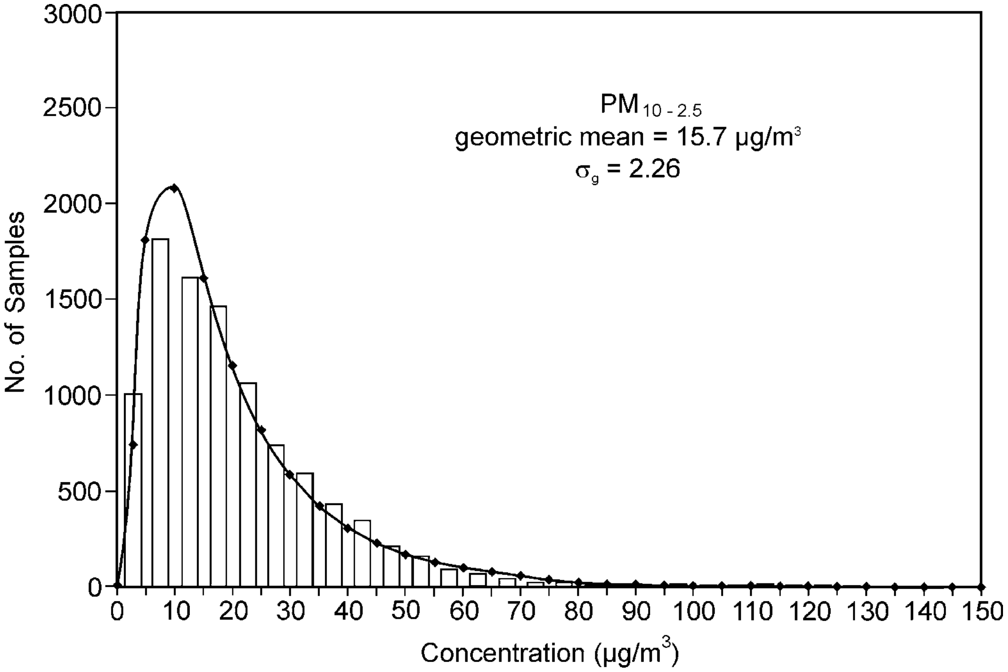


Figure 3-14. Frequency distribution of 24-h average PM$_{10-2.5}$ concentrations obtained from all California Air Resource Board Dichotomous sampler sites from 1989 to 1998.

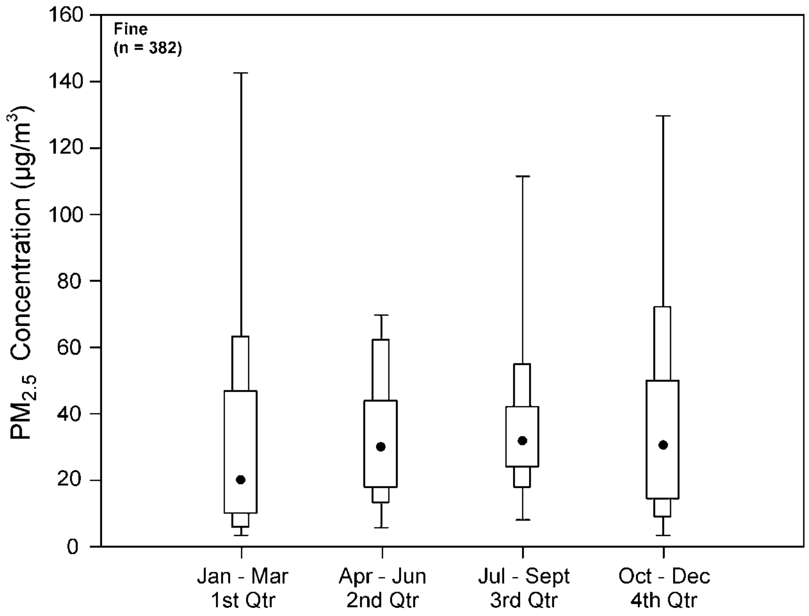


Figure 3-15. **Concentrations of 24-h average $PM_{2.5}$ measured at the Riverside-Rubidoux site from 1989 to 1998. The data show the lowest, lowest tenth percentile, lowest quartile, median (black squares), highest quartile, highest tenth percentile, and highest $PM_{2.5}$ values.**

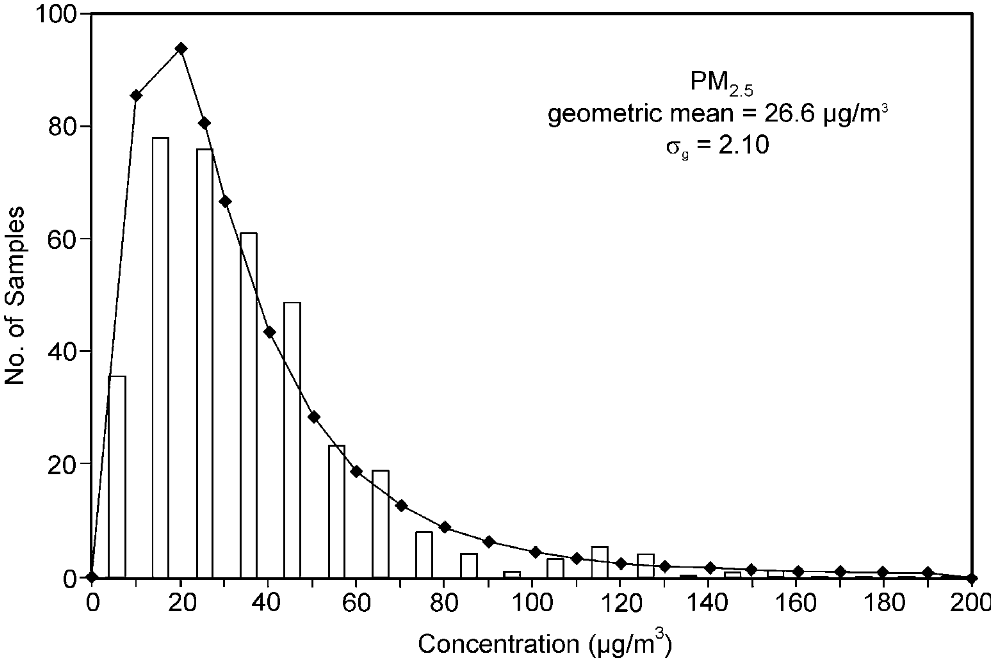


Figure 3-16. **Frequency distribution of 24-h average $PM_{2.5}$ concentrations measured at the Riverside-Rubidoux site from 1989 to 1994.**

dust suspension at Riverside. In addition, the seasonal variability of $PM_{2.5}$ concentrations observed in Phoenix and Riverside appears to be different from that observed in the MAACS cities. These considerations demonstrate the hazards in extrapolating conclusions about the nature of variability in aerosol characteristics inferred at one location to another.

3.2.2 Diurnal (Circadian) Variability in PM Concentrations

The variability of PM concentrations on time scales shorter than a day can, in principle, be characterized by measurements made by continuous samplers (e.g, TEOMs and β-gauge monitors that are currently used to provide Air Quality Index [AQI] information to the public). A description of these methods was provided in Section 2.2.9. However, as shown in Chapter 2, continuous methods are subject to artifacts in large part because of the heating of their inlets to remove water, which results in the loss of components such as ammonium nitrate and semivolatile organic compounds (Sections 2.2.2.1 and 2.2.3 for further details concerning the chemistry of volatilizable components). Consequently, caution should be used in interpreting results obtained by these techniques. It should be remembered that the Federal Reference Methods (FRMs) are also subject to artifacts; therefore, caution should also be exercised in interpreting results obtained by them.

The composite diurnal variation of $PM_{2.5}$ concentrations obtained throughout the continental United States by 31 TEOM and β-gauge monitors reporting to AIRS in 1999 is shown in Figure 3-17. As can be seen, there is a distinct pattern with maxima occurring during the morning and evening. Notable exceptions to this pattern occur in California where broad nighttime maxima and daytime minima occur which may be related to the use of β-gauges with unheated inlets there. It should be noted in examining the diurnal variations shown in Figure 3-17 that there is substantial day-to-day variability in the diurnal profile of $PM_{2.5}$ measured at the same location that is smoothed out after a suitably long averaging period is chosen. The large ratio of the interquartile range to the median values supports the view that there is substantial variability in the diurnal profiles.

The diurnal variability of PM components is determined by interactions between variations in emissions, the rates of photochemical transformations, and the vertical extent and intensity of turbulent mixing near the surface. Wilson and Stockburger (1990) characterized the diurnal variability of sulfate and lead in Philadelphia. At that time, Pb was emitted mainly by motor

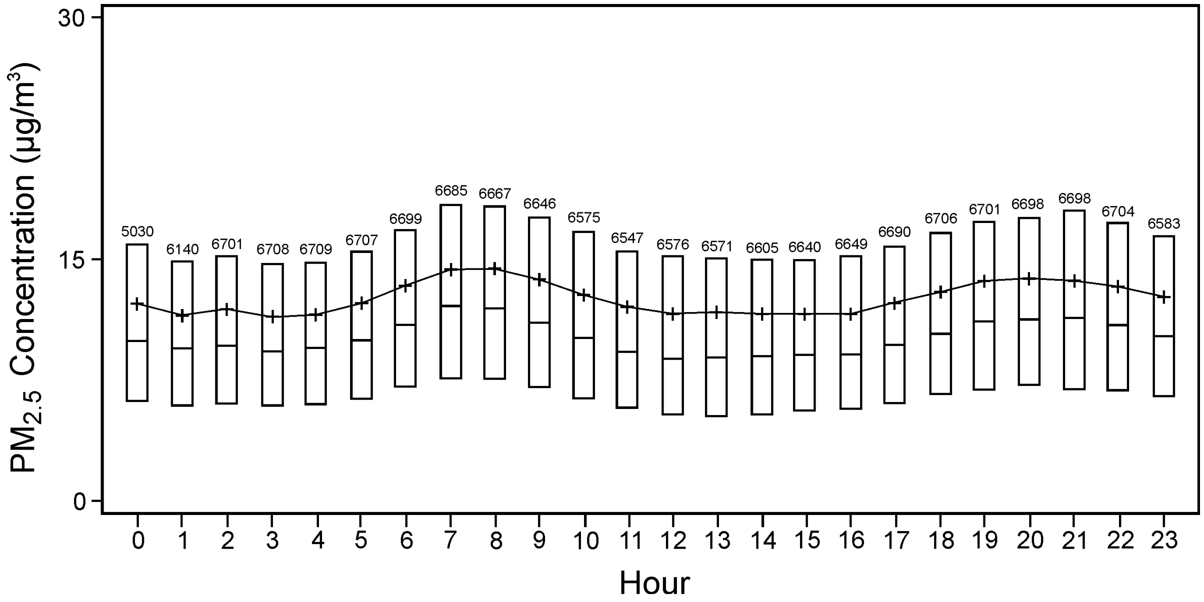


Figure 3-17. Intraday variability of hourly average $PM_{2.5}$ concentrations across the United States. Interquartile ranges, median and mean (+) values are shown. Values above the box plots refer to the number of observations during 1999.

Source: Fitz-Simons et al. (2000).

vehicles. Pollutants emitted mainly by motor vehicles, such as carbon monoxide, show two distinct peaks occurring during the morning and evening rush hours (see Chapter 3, U.S. Environmental Protection Agency, 2000b). Pollutants, such as sulfate, which are transported long distances in the free troposphere (i.e., above the planetary boundary layer), tend to be mixed downward and have their highest concentrations during the afternoon when the intensity and vertical extent of turbulent mixing (and chemical oxidation) are greatest. Secondary aerosol components (such as secondary organic compounds) that are produced by photochemical reactions may have a daily maximum in the afternoon, similar to ozone. PM produced by residential heating (e.g., from wood burning), on the other hand, reach maximum levels during the night when mixing heights are much lower than during the day.

Although the interquartile ranges for hour-to-hour changes in $PM_{2.5}$ concentrations shown in Figure 3-17 encompass several µg/m^3, extreme values for the hour-to-hour variations can be much larger (Fitz-Simons et al., 2000). The 98th percentile values for positive and negative excursions in concentration are all less than 20 μg/m^3. Maximum positive excursions were much larger, ranging from 27 μg/m^3 in the Northeast up to 220 μg/m^3 in the Southwest and with maximum excursions in other regions all less than 125 μg/m^3. It should be borne in mind that the hour-to-hour changes that are reported reflect the effects of a number of processes occurring during passage through the sampler inlets and on the TEOM measurement elements. These factors add uncertainty to the interpretation of the hour-to-hour changes that are observed, as discussed in Chapter 2. However, because of the tendency of these monitoring instruments to lose material by evaporation, the concentrations reported during excursions probably represent lower limits to the true values that were present.

3.2.3 Relations Among Particulate Matter in Different Size Fractions

Relations Among $PM_{2.5}$, $PM_{10-2.5}$, and PM_{10}

Data obtained in 1999 by collocated $PM_{2.5}$ and PM_{10} FRM monitors have been used to calculate the ratio of $PM_{2.5}$ to PM_{10} concentrations and correlations among $PM_{2.5}$, $PM_{10-2.5}$, and PM_{10} concentrations. Results are shown in Table 3-1 for each of the seven aerosol characteristic regions identified in Chapter 6 of the 1996 PM AQCD. As can be seen from the table, the ratio of $PM_{2.5}$ to PM_{10} concentrations tends to be higher in the eastern United States than in the western United States. This general pattern and the values are consistent with that found for the studies included in Appendix 6A of 1996 PM AQCD. In that compilation based on the results of studies using dichotomous samplers, the mean ratio of $PM_{2.5}$ to PM_{10} was 0.75 in the East, 0.52 in the central United States, and 0.53 in the western United States. Although a large number of paired entries have been included in Table 3-1, seasonal variations and annual averages in a number of regions could not be determined from the data set because of data sparseness mainly during the early part of 1999. It also can be seen in Table 3-1 that the ratio of $PM_{2.5}$ to PM_{10} was greater than one for a few hundred measurements. There are a number of reasons for these results, as mentioned in Section 3.2.1 in the discussion on $PM_{10-2.5}$ concentrations.

Ultrafine Particle Concentrations

Data for characterizing the concentrations of ultrafine particles (< 0.10 μm D_a) and the relations between ultrafine particles and larger particles are sparse. Although ultrafine particles

TABLE 3-1. DISTRIBUTION OF RATIOS OF $PM_{2.5}$ TO PM_{10} AND CORRELATIONS BETWEEN $PM_{2.5}$ AND PM_{10}, $PM_{2.5}$ AND $PM_{10-2.5}$, AND $PM_{10-2.5}$ AND PM_{10} FOUND AT COLLOCATED MONITORING SITES IN SEVEN AEROSOL CHARACTERISTIC (EPA/HEI) REGIONS IN 1999

				Percentiles							**Correlations**		
Region	**Mean**	**Sites**	**Values**	**95**	**90**	**75**	**50**	**25**	**10**	**5**	**$PM_{2.5}$:PM_{10}**	**$PM_{2.5}$:$PM_{10-2.5}$**	**$PM_{10-2.5}$:PM_{10}**
Northeast	0.70	45	1433	0.97	0.95	0.77	0.67	0.60	0.51	0.48	0.72[a]	0.02	0.71[a]
Southeast	0.70	76	2823	1.27	1.06	0.74	0.63	0.54	0.46	0.43	0.69[a]	−0.04[a]	0.69[a]
Industrial Midwest	0.70	92	4827	1.09	0.88	0.78	0.68	0.59	0.51	0.47	0.71[a]	0.17[a]	0.81[a]
Upper Midwest	0.53	39	1446	0.92	0.84	0.62	0.49	0.44	0.34	0.24	0.35[a]	−0.02	0.93[a]
Southwest	0.38	23	701	0.51	0.51	0.47	0.40	0.31	0.23	0.23	0.63[a]	0.49[a]	0.99[a]
Northwest	0.50	73	3300	0.67	0.65	0.56	0.49	0.44	0.39	0.36	0.69[a]	0.07[a]	0.77[a]
Southern California	0.47	36	1813	0.70	0.57	0.55	0.48	0.44	0.31	0.24	0.70[a]	0.19[a]	0.83[a]
	Total:	384	16,343										

[a] Results considered to be significantly different from zero at the $\alpha = 0.01$ level.

Source: Aerometric Information Retrieval System (AIRS; U.S. Environmental Protection Agency, 2002b).

dominate particle number concentrations, they make very minor contributions to $PM_{2.5}$ mass. For example, Cass et al. (2000) found that particles between 0.056 and 0.1 μm D_a contributed only 0.55 − 1.16 $\mu g/m^3$ at several sites in southern California. Perhaps the most extensive data set for ultrafine particle properties is that described by Woo et al. (2001) for a site located 10 km to the northwest of downtown Atlanta, GA. Size distributions from 3 to 2000 nm were measured every 12 minutes for 24 months beginning in August 1998. Approximately 89% of the total number of particles were found to be smaller than 100 nm; whereas 26% were found to be smaller than 10 nm. Concentrations tend to be lower during the summer than during the winter. No correlation was found between number concentration and either volume or surface area for particle sizes up to 2 μm. Because the total number of particles is concentrated in the smallest size ranges, these results also indicate that fine particle mass does not correlate with the number of ultrafine particles. The high time resolution of the measurements allows some inferences to be made about the possible sources of the ultrafine particles. The number of particles larger than 10 nm tends to peak during the morning rush hour (around 8 am) and then to decrease through the day and to increase again after 6 pm, consistent with a traffic-related source. Particles smaller than 10 nm tend to peak during the mid-afternoon, consistent with nucleation involving products of active photochemistry (McMurry et al., 2000). More direct relations between particle mass observed in different size ranges can be obtained using multi-stage impactors. Keywood et al. (1999) found a correlation between $PM_{2.5}$ and $PM_{0.15}$ of about 0.7; whereas they found correlations of about 0.96 between PM_1 and $PM_{2.5}$ and between $PM_{2.5}$ and PM_{10} based on samples collected by MOUDIs (Multiple Orifice Uniform Deposit Impactors) in six Australian cities.

3.2.4 Relations Between Mass and Chemical Component Concentrations

Time series of elemental composition data for $PM_{2.5}$ based on X-ray fluorescence (XRF) analyses have been obtained at a number of locations across the United States. Time series of components of the organic carbon fraction of the aerosol have not yet been obtained. The results of XRF analyses for the composition of the inorganic fraction of $PM_{2.5}$ and $PM_{10-2.5}$ are presented in Table 3-2 for Philadelphia, PA, and in Table 3-3 for Phoenix, AZ. Frequency distribution for $PM_{2.5}$ concentration data collected at these sites were shown in Figures 3-10 and 3-11. All XRF analyses were performed at the same X-ray spectrometry facility operated by the U.S.

TABLE 3-2. CONCENTRATIONS (in ng/m^3) OF $PM_{2.5}$, $PM_{10-2.5}$, AND SELECTED ELEMENTS (ng/m^3) IN THE $PM_{2.5}$ AND $PM_{10-2.5}$ SIZE RANGES WITH STANDARD DEVIATIONS (SD) AND CORRELATIONS BETWEEN ELEMENTS AND $PM_{2.5}$ MASS IN PHILADELPHIA, PA*

n = 1105	Conc (ng/m^3) ± SD (unc)	r	n = 20	Conc (ng/m^3) ± SD (unc)	r	n = 20	Conc (ng/m^3) ± SD (unc)	r
$PM_{2.5}$ [1]	17 ± 0.9 (0.8) × 10^3	1.00	$PM_{2.5}$ [2]	29.8 ± 14.7 (1.1) × 10^3	1.00	$PM_{10-2.5}$ [2]	8.4 ± 2.9 (0.4) × 10^3	1.00
Al	4.0 ± 56 (31)	0.10	Al	109 ± 61 (21)	0.15	Al	325 ± 241 (99)	0.89
Si	116 ± 107 (21)	0.51	Si	191 ± 134 (26)	0.22	Si	933 ± 652 (231)	0.90
P	8.6 ± 14 (10)	0.31	P	15 ± 4.3 (2.7)	0.72	P	28 ± 9.4 (7.1)	0.78
S	2100 ± 1610 (143)	0.92	S	3190 ± 1920 (207)	0.91	S	38 ± 45 (71)	−0.15
Cl	5.1 ± 35 (3.4)	−0.01	Cl	23 ± 28 (5.5)	0.19	Cl	47 ± 48 (5.8)	−0.11
K	60.4 ± 45 (4.7)	0.50	K	68 ± 21 (6.4)	0.31	K	100 ± 66 (10)	0.81
Ca	47 ± 33 (4.2)	0.39	Ca	63 ± 33 (9.0)	−0.02	Ca	421 ± 192 (31)	0.81
Ti	4.9 ± 5.2 (4.1)	0.44	Ti	8.7 ± 4.7 (9.0)	0.47	Ti	30 ± 17 (5.6)	0.90
V	8.8 ± 8.7 (1.8)	0.37	V	9.7 ± 7.1 (2.9)	0.38	V	3.2 ± 2.2 (1.5)	0.66
Cr	0.7 ± 1.1 (0.7)	0.15	Cr	1.4 ± 1.2 (2.9)	0.09	Cr	1.0 ± 5.0 (0.9)	0.43
Mn	3.1 ± 2.2 (0.8)	0.39	Mn	3.2 ± 1.5 (1.6)	0.43	Mn	6.3 ± 4.1 (0.6)	0.90
Fe	109 ± 71 (10.5)	0.50	Fe	134 ± 49 (0.5)	0.48	Fe	352 ± 156 (24)	0.90
Co	0.1 ± 1.8 (1.4)	0.04	Co	0.8 ± 0.7 (8.5)	0.58	Co	−0.2 ± 0.5 (0.3)	−0.10
Ni	7.3 ± 8.4 (1.4)	0.22	Ni	8.5 ± 5.6 (0.3)	0.61	Ni	2.0 ± 1.4 (0.3)	0.08
Cu	4.8 ± 4.9 (1.1)	0.25	Cu	7.7 ± 3.8 (0.7)	0.22	Cu	14 ± 12 (1.1)	−0.05
Zn	36.9 ± 44 (3.7)	0.21	Zn	56 ± 37 (4.8)	0.22	Zn	52 ± 43 (4.7)	−0.03
As	0.6 ± 1.4 (1.2)	0.18	As	0.4 ± 1.0 (1.0)	−0.02	As	0 ± 0.5 (0.5)	0.07
Se	1.5 ± 1.3 (0.6)	0.63	Se	1.3 ± 0.8 (0.4)	0.65	Se	−0.1 ± 0.2 (0.2)	−0.24
Br	5.0 ± 11.7 (0.9)	0.11	Br	14 ± 12 (1.3)	0.21	Br	3.0 ± 2.5 (0.5)	−0.10
Pb	17.6 ± 22 (2.5)	0.19	Pb	28 ± 24 (2.4)	0.26	Pb	13 ± 11 (1.3)	0.10

[1] Data obtained at the Presbyterian home (PBY) site in Philadelphia from April 1992 to April 1995 with Harvard impactors.

[2] Data obtained at the Castor Avenue Laboratory, North Central Philadelphia, from July 25 to August 14, 1994 with a modified dichotomous sampler.

*Note: Values in parentheses refer to analytical uncertainty (unc) in X-ray fluorescence determinations.

TABLE 3-3. CONCENTRATIONS (in ng/m^3) OF $PM_{2.5}$, $PM_{10-2.5}$, AND SELECTED ELEMENTS IN THE $PM_{2.5}$ AND $PM_{10-2.5}$ SIZE RANGE WITH STANDARD DEVIATIONS (SD) AND CORRELATIONS (r) BETWEEN ELEMENTS AND $PM_{2.5}$ AND $PM_{10-2.5}$ MASS IN PHOENIX, AZ*

n = 164	Conc (ng/m^3) ± SD (unc)	r	n = 164	Conc (ng/m^3) ± SD (unc)	r
$PM_{2.5}$	11.2 ± 0.6 (0.6) × 10^3	1.00	$PM_{10-2.5}$	27.6 ± 14.8 × 10^3	1.00
Al	125 ± 77 (30)	0.23	Al	1879 ± 979 (547)	0.92
Si	330 ± 191 (48)	0.35	Si	535 ± 2825 (1347)	0.92
P	11 ± 7.8 (5.7)	0.52	P	37 ± 20 (17)	0.58
S	487 ± 254 (40)	0.16	S	131 ± 47 (26)	0.77
Cl	19 ± 44 (3.0)	0.13	Cl	208 ± 204 (24)	0.28
K	110 ± 63 (9.2)	0.67	K	561 ± 298 (62)	0.92
Ca	129 ± 72 (11)	0.51	Ca	1407 ± 755 (124)	0.90
Ti	11 ± 7.1 (2.7)	0.44	Ti	130 ± 71 (20)	0.90
V	0.7 ± 2.0 (2.2)	−0.28	V	2.0 ± 2.0 (1.5)	0.51
Cr	0.6 ± 0.9 (0.7)	0.41	Cr	2.6 ± 1.7 (0.7)	0.76
Mn	5.7 ± 4.3 (0.7)	0.64	Mn	29 ± 16 (3.0)	0.91
Fe	177 ± 113 (16)	0.80	Fe	1211 ± 674 (133)	0.90
Co	−0.4 ± 1.0 (1.0)	−0.01	Co	1.2 ± 2.2 (1.9)	0.38
Ni	0.6 ± 0.9 (0.5)	0.38	Ni	1.8 ± 1.4 (0.7)	0.70
Cu	5.2 ± 6.1 (1.5)	0.69	Cu	10.3 ± 9.0 (1.5)	0.58
Zn	17 ± 14.7 (1.8)	0.64	Zn	25 ± 16 (3.2)	0.64
As	1.9 ± 3.2 (0.6)	0.50	As	0.6 ± 0.8 (0.6)	0.41
Se	0.4 ± 0.8 (0.4)	0.40	Se	−0.02 ± 0.3 (0.3)	0.21
Br	3.8 ± 2.0 (0.6)	0.57	Br	0.8 ± 0.6 (0.4)	0.48
Pb	6.6 ± 6.6 (1.0)	0.69	Pb	4.6 ± 3.8 (1.1)	0.59

* Values in parenthesis refer to analytical uncertainty (unc) in X-ray fluorescence determinations.

Source: Calculations based on data obtained by Zweidinger et al. (1998).

Environmental Protection Agency in Research Triangle Park, NC. Data shown in the first column of Table 3-2 are based on analyses of filters collected over three years (April 1992 to April 1995, labeled a) at the PBY site in southwestern Philadelphia. These data and data for

PM_{10} were collected using Harvard impactors. Data for $PM_{2.5}$ and $PM_{10-2.5}$ shown in the second and third columns were collected at the Castor Avenue Laboratory operated by the City of Philadelphia from July 25 to August 14, 1994, using a modified dichotomous sampler (VAPS). The samples at the Phoenix site were collected in 1996 and 1997 using the same type of dichotomous sampler used in the shorter term study in Philadelphia. These data are shown to give an idea of the range of concentrations found in studies conducted more recently than those shown in Appendix 6A of the 1996 PM AQCD. The speciation network will at least provide more thorough coverage of the composition of particles in the $PM_{2.5}$ size range across the United States. Results from the pilot study for the speciation network are given in Appendix 3B.

As can be seen from inspection of Tables 3-2 and 3-3, the analytical uncertainty (given in parentheses next to concentrations) as a fraction of the absolute concentration is highly variable. It exceeds the concentration for a number of trace metals whose absolute concentrations are low; whereas it is very small for abundant elements such as sulfur.

Sulfur is the major element analyzed in the $PM_{2.5}$ size fraction in the two Philadelphia studies and is highly correlated with $PM_{2.5}$; however its abundance is roughly two orders of magnitude lower in the $PM_{10-2.5}$ size range and is negatively correlated with $PM_{10-2.5}$. Concentrations of the crustal elements Al, Si, K, Ca, and Fe are much higher in the $PM_{10-2.5}$ size range than in the $PM_{2.5}$ size range and are well correlated with $PM_{10-2.5}$. A number of trace elements (e.g., Cr, Co, Ni, Cu, Zn, As, Se and Pb) are detectable in the two $PM_{2.5}$ data sets, and the concentrations of many of these elements are much greater than the uncertainty in their determination. Except for Co, As, and Se which are not detected in the $PM_{10-2.5}$ samples, the concentrations of many elements (Cr, Zn, and Pb) are comparable in the $PM_{2.5}$ and $PM_{10-2.5}$ size ranges. The concentration of Cu is significantly higher in the $PM_{10-2.5}$ size range, whereas the concentration of Ni is smaller in the $PM_{10-2.5}$ size range than in the $PM_{2.5}$ size range.

There are a number of distinct differences between the $PM_{2.5}$ sets for Philadelphia and Phoenix. For instance, sulfate and associated cations and water that would be expected to correspond to the measurement of S appear to constitute a major fraction of the composition of the PM in the Philadelphia data set; whereas they appear to constitute a much smaller fraction of the PM in the Phoenix data set. The highest $PM_{2.5}$ values were observed in Philadelphia during episodes driven by high sulfate abundances; whereas those in Phoenix were driven by raised soil dust. The concentration of S in Phoenix is much lower in the Phoenix $PM_{2.5}$ data set than in either Philadelphia $PM_{2.5}$ data set, even though it represents the most abundant element and it is only weakly correlated with $PM_{2.5}$. This is in marked contrast to the data shown for Philadelphia and also to data found at other eastern sites. It is not clear what the reasons are for this finding. As in Philadelphia, the concentration of S in Phoenix is higher in the $PM_{2.5}$ size range than in the $PM_{10-2.5}$ size range. Trace metals (e.g., Cr, Co, Ni, Cu, Zn, As, and Pb) are not well correlated ($0.04 < r < 0.25$) with $PM_{2.5}$ in the Philadelphia data set; whereas they are more variably correlated ($0.01 < r < 0.69$) with $PM_{2.5}$ in the Phoenix data set. The uncertainty in the concentration measurement most probably plays a role in determining a species' correlation with $PM_{2.5}$ especially when the analytical uncertainty is high relative to concentration as it is for a number of elements in the data shown in Tables 3-2 and 3-3. Concentrations of Al, Si, K, Ca, and Fe are again much higher in the $PM_{10-2.5}$ size range than in the $PM_{2.5}$ size range and are strongly correlated with $PM_{10-2.5}$ in both data sets.

There are also similarities in the $PM_{2.5}$ data sets for Philadelphia and Phoenix. Crustal elements are not as well correlated with $PM_{2.5}$ as they are with $PM_{10-2.5}$ in both data sets. The concentrations of trace metals (Cr, Ni, Cu, and Zn) in $PM_{2.5}$ are similar in Philadelphia and Phoenix. It can also be seen that their concentrations are of the same order of magnitude in both $PM_{2.5}$ and $PM_{10-2.5}$. Concentrations of Cu are noticeably higher in $PM_{10-2.5}$ than in $PM_{2.5}$ in both Philadelphia and Phoenix. These results are consistent with those of many monitoring studies shown in Appendix 6A of the 1996 PM AQCD, which also show that concentrations of these metals are of the same order of magnitude in both size fractions and that concentrations of Cu tend to be higher in $PM_{10-2.5}$ than in $PM_{2.5}$.

One study suggests that the partitioning of trace metals between the fine and coarse fractions varies with PM concentration. Salma et al. (2002) determined the size distribution of a number of trace elements at four sites characterizing environments ranging from the urban background to an urban traffic tunnel in Budapest, Hungary. S, K, V, Ni, Cu, Zn, As, and Pb were found mainly in the fine fraction at the urban background site; but their mass median aerodynamic diameters increased with increasing PM concentrations until they were all found mainly in the coarse fraction in the traffic tunnel. They also found that Na, Mg, Al, Si, P, Ca, Ti, Fe, Ga, Sr, Zr, Mo, and Ba were concentrated mainly in the coarse fraction at all four sites and that their mass median aerodynamic diameters increased with increasing PM concentrations.

The mean concentration of Pb observed in the methods evaluation study for the speciation network was only about 5 ng/m^3 in Philadelphia during the first half of 2000 (Appendix 3B); whereas its concentration was about three times higher during the studies conducted during the early 1990s (Table 3-3). In a study conducted in the greater Philadelphia area during the summer of 1982, Dzubay et al. (1988) found concentrations of Pb of about 250 ng/m^3, or about fifty times higher than observed in 2000. The mean Pb concentration was about 3 ng/m^3 at the Phoenix site included as part of the same methods evaluation study for the speciation network; however, the mean Pb concentration was 39 ng/m^3 during an earlier study conducted during 1989 and 1990 in Phoenix (Chow et al., 1991). These changes in Pb concentrations are consistent with those in many other urban areas for which monitoring studies have been conducted during the late 1970s and 1980s (cf., Appendix 6A of the 1996 PM AQCD) and for which there are data given in Appendix 3B. It should be remembered that the older studies were conducted while Pb was still used as a gasoline additive. The ratio of Pb in PM$_{2.5}$ to Pb in PM$_{10\text{-}2.5}$ was also much higher in the older studies than in the more recent ones, reflecting the importance of combustion as its source. Smaller decreases are apparent in the concentrations of other trace metals such as Cu, Ni, and Zn between studies conducted in the early 1980s and in the methods evaluation study for the speciation network conducted in 2000.

Some indication of the sources of metals such as Pb, Cu, Cd, and Zn in current, ambient PM$_{2.5}$ and PM$_{10\text{-}2.5}$ samples can be obtained by examining their sources in urban runoff. The sources of these elements in urban runoff were found to be the weathering of building surfaces, motor vehicle brake and tire wear, engine oil and lubricant leakage and combustion, and wet and dry atmospheric deposition (Davis et al., 2001). Once deposited on the ground, these elements can be resuspended with other material as PM$_{2.5}$ and PM$_{10\text{-}2.5}$ although research is needed into the mechanisms of how this is accomplished. Wind-abrasion on building siding and roofs (coatings such as Pb paint and building material such as brick, metal, and wood siding); brake wear (brake pads contain significant quantities of Cu and Zn); tire wear (Zn is used as a filler in tire production); and burning engine oil could all produce particles containing these metals, especially Zn.

Data for the chemical composition of ambient ultrafine particles are sparse. In a study conducted at several urban sites in Southern California, Cass et al. (2000) found that the composition of ultrafine particles ranged from 32 to 67% organic compounds, 3.5 to 17.5%

elemental carbon, 1 to 18% sulfate, 0 to 19% nitrate, 0 to 9% ammonium, 1 to 26% metal oxides, 0 to 2% sodium, and 0 to 2% chloride. Thus carbon, in various forms, was found to be the major contributor to the mass of ultrafine particles. However, ammonium was found to contribute 33% of the mass of ultrafine particles at one site in Riverside. Iron was the most abundant metal found in the ultrafine particles. Chung et al. (2001) found that carbon was the major component of the mass of ultrafine particles in a study conducted during January of 1999 in Bakersfield, CA. However, in the study of Chung et al., the contribution of carbonaceous species (OC and EC; typically 20 to 30%) was much lower than that found in the cities in Southern California. They found that calcium was the dominant cation, accounting for about 20% of the mass of ultrafine particles in their samples. Sizable contributions from silicon (0 to 4%) and aluminum (6 to 14%) were also found. Further studies, including scanning electron microscopy, may be needed to quantify the role of coarse particle bounce from the upper stages of their MOUDI impactor.

Gone et al. (2000) measured the size distribution of trace elements from 0.056 μm to 1.8 μm D_a in Pasadena, CA, and in the Great Smoky Mountains National Park, TN. They found that elements identified as being of anthropogenic origin had mass median diameters below 1 μm PM; whereas elements of crustal origin generally had a mass median diameter greater than 1 μm. Concentrations of trace metals were much higher in the accumulation mode than in the ultrafine mode in both study areas. In PM_1, 76% of Cr, 95% of Fe, 94% of Zn, 89% of As, and 79% of Cd at the Tennessee site were found in the accumulation mode; and 70% of Fe, 85% of Zn, 92% of As, and 84% of Cd were found in the accumulation mode in Pasadena. Fe was the most abundant metal found in the ultrafine particles. The abundance of crustal elements, such as Al, declined rapidly with decreasing particle size at both locations; and Al in PM_1 probably represented the lower tail of the coarse PM mode. However, on two days at Pasadena there were increases in the concentration of Al in ultrafine particles that were associated with increases in Sc and Sm. The latter two elements originate exclusively from crustal material (Gone et al., 2000).

3.2.5 Spatial Variability in Particulate Matter and its Components

PM$_{2.5}$

Aspects of the spatial variability of PM$_{2.5}$ concentrations on the urban scale are examined in this section. Intersite correlation coefficients for PM$_{2.5}$ can be calculated based on the results of FRM monitors placed at multiple sites within Metropolitan Statistical Areas (MSAs) across the United States. Pearson correlation coefficients (r) calculated for pairs of monitoring sites in the Philadelphia, PA; Cleveland, OH; Dallas, TX; and Los Angeles, CA MSAs are shown in Table 3-4. The 90th percentile value, P_{90}, of the absolute differences (in $\mu g/m^3$) between the two sites is shown in parentheses below r along with the coefficient of divergence (COD), and the number of observations used in the calculation of r, P_{90} and COD is given on the third line. The COD was used by Wongphatarakul et al. (1998) as a measure of the degree of similarity between aerosol data sets[1]. The annual mean concentrations, the number of observations used to calculate the annual average, and the standard deviation are shown directly beneath the correlation tables for each site. These analyses and those for another 23 MSAs are given along with maps in Appendix 3A. As the concentrations of PM$_{2.5}$ at two sampling sites become more alike, the COD approaches zero; as the concentrations diverge, the COD approaches one.

The four MSAs shown in Table 3-4 were chosen to illustrate different patterns of spatial variability across the United States. In addition, air-pollution health-outcome studies have been performed in a few of these MSAs. It can be seen from inspection of Table 3-4 that correlation coefficients vary over a wide range in the MSAs shown. Correlations between sites in the Philadelphia, PA; Cleveland OH; and Dallas, TX MSAs are all high and span a relatively narrow range (0.82 to 0.97). However, correlations between sites in the Los Angeles-Long Beach MSA are lower than in the three other MSAs and span a wider range of values (0.60 to 0.95). If the monitoring site in Lancaster, CA, were included, correlations would be even lower. This site was omitted because it did not meet completeness criteria for 2001. The extension of these

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[1] The COD for this purpose is defined as follows:

$$COD_{jk} = \sqrt{\frac{1}{p}\sum_{i=1}^{p}\left(\frac{x_{ij} - x_{ik}}{x_{ij} + x_{ik}}\right)^2} \qquad (3\text{-}1)$$

where x_{ij} and x_{ik} represent the 24-h average PM$_{2.5}$ concentration for day i at site j and site k and p is the number of observations.

TABLE 3-4a-d. MEASURES OF THE SPATIAL VARIABILITY OF $PM_{2.5}$ CONCENTRATIONS WITHIN SELECTED METROPOLITAN STATISTICAL AREAS

(a) Philadelphia, PA

Site I.D. #	340071007	340155001	420170012	420450002	420910013	421010004	421010136
340071007	1	0.91 (6.3, 0.14) 170	0.93 (5.2, 0.15) 167	0.87 (6.9, 0.19) 183	0.88 (5.0, 0.16) 176	0.94 (4.6, 0.15) 163	0.93 (5.1, 0.14) 166
340155001		1	0.84 (7.5, 0.19) 176	0.88 (7.4, 0.18) 194	0.83 (7.1, 0.18) 184	0.89 (7.4, 0.17) 169	0.85 (6.9, 0.18) 173
420170012			1	0.85 (7.5, 0.16) 199	0.88 (4.7, 0.13) 200	0.94 (4.9, 0.11) 177	0.89 (5.3, 0.13) 180
420450002				1	0.87 (6.1, 0.15) 208	0.94 (5.1, 0.11) 187	0.88 (4.0, 0.12) 193
420910013					1	0.90 (4.6, 0.11) 181	0.87 (4.5, 0.11) 185
421010004						1	0.96 (3.3, 0.08) 550
421010136							1
Mean	14.78	14.59	14.11	15.92	14.20	15.72	15.81
Obs	197	208	217	230	221	610	616
SD	9.20	8.65	8.47	8.65	8.93	9.18	9.26

Key
Airs Site I.D. #
Pearson r
(90th %-tile difference in concentration,
coefficient of divergence)
number of observations

(b) Cleveland, OH

Site I.D. #	390350013	390350038	390350060	390350065	390350066	390351002	390851001	390932003
390350013	1	0.91 (7.1, 0.13) 320	0.96 (3.3, 0.12) 322	0.94 (5.4, 0.10) 314	0.92 (7.2, 0.16) 300	0.88 (9.0, 0.18) 308	0.89 (10.7, 0.21) 308	0.92 (8.1, 0.17) 265
390350038		1	0.92 (6.9, 0.14) 306	0.89 (9.4, 0.15) 296	0.85 (13.1, 0.21) 290	0.84 (12.9, 0.21) 304	0.84 (14.3, 0.23) 294	0.892 (11.2, 0.18) 256
390350060			1	0.93 (5.1, 0.14) 309	0.90 (8.15, 0.19) 300	0.87 (8.6, 0.20) 310	0.88 (10.8, 0.22) 307	0.90 (8.9, 0.18) 256
390350065				1	0.96 (4.7, 0.14) 295	0.91 (5.4, 0.16) 310	0.90 (7.8, 0.20) 306	0.91 (7.7, 0.18) 264
390350066					1	0.88 (4.9, 0.16) 304	0.91 (5.8, 0.15) 295	0.91 (5.8, 0.13) 247
390351002						1	0.89 (6.0, 0.18) 303	0.87 (5.3, 0.18) 261
390851001							1	0.90 (6.6, 0.15) 275
390932003								1
Mean	18.34	20.16	18.39	17.47	14.74	15.0	14.0	15.22
Obs	368	931	353	340	332	351	342	298
SD	9.59	11.50	9.90	8.95	8.45	8.16	8.44	8.80

Key
Airs Site I.D. #
Pearson r
(90th %-tile difference in concentration,
coefficient of divergence)
number of observations

TABLE 3-4a-d (cont'd). MEASURES OF THE SPATIAL VARIABILITY OF $PM_{2.5}$ CONCENTRATIONS WITHIN SELECTED METROPOLITAN STATISTICAL AREAS.

(c) Dallas, TX

Site I.D. #	480850005	481130020	481130035	481130050	481130057	480850005	481130020
480850005	1	0.92 (3.5, 0.11) 220	0.94 (3.6, 0.11) 204	0.94 (4.3, 0.13) 213	0.89 (6.3, 0.15) 195	0.94 (3.7, 0.10) 218	0.94 (3.1, 0.10) 189
481130020		1	0.95 (3.2, 0.08) 212	0.94 (3.3, 0.09) 603	0.92 (4.1, 0.11) 205	0.95 (2.5, 0.07) 635	0.97 (2.3, 0.07) 207
481130035			1	0.97 (2.0, 0.06) 203	0.93 (3.9, 0.09) 191	0.97 (1.9, 0.06) 207	0.94 (3.6, 0.10) 185
481130050				1	0.94 (2.7, 0.08) 199	0.98 (2.2, 0.06) 608	0.94 (4.2, 0.12) 196
481130057					1	0.95 (3.1, 0.08) 198	0.91 (5.5, 0.14) 182
480850005						1	0.96 (3.0, 0.09) 198
481130020							1
Mean	11.54	12.42	12.83	13.34	13.67	12.68	11.67
Obs	234	677	222	644	215	687	216
SD	5.62	5.69	5.79	5.79	6.14	5.67	5.43

Key
Airs Site I.D. #
Pearson r
(90th %-tile difference in concentration,
coefficient of divergence)
number of observations

(d) Los Angeles, CA

Site I.D. #	060370002	060371103	060371201	060371301	060372005	060374002
060370002	1	0.87 (10.7, 0.18) 581	0.76 (14.6, 0.23) 208	0.68 (17.9, 0.25) 229	0.95 (6.2, 0.14) 212	0.60 (18.1, 0.26) 553
060371103		1	0.86 (12.8, 0.20) 205	0.89 (10.1, 0.12) 222	0.93 (7.1, 0.11) 207	0.80 (13.6, 0.17) 563
060371201			1	0.76 (18.1, 0.24) 212	0.85 (12.1, 0.18) 197	0.66 (18.2, 0.24) 197
060371301				1	0.78 (13.2, 0.18) 214	0.95 (8.1, 0.11) 216
060372005					1	0.62 (15, 0.20) 204
060374002						1
Mean	20.91	22.48	18.32	23.73	20.09	20.31
Obs	641	656	217	237	220	621
SD	13.35	13.47	11.65	13.43	11.92	12.42

Key
Airs Site I.D. #
Pearson r
(90th %-tile difference in concentration,
coefficient of divergence)
number of observations

analyses to include the relevant CMSAs (consolidated MSA) would also produce a number of sites that are even less well correlated with each other in part because sites are located outside of urban airsheds.

Correlation coefficients between pairs of sites in the other 23 MSAs given in Appendix 3A for the most part fall within the range of values given in Table 3-4. In four MSAs (Columbia, SC; Norfolk, VA; Grand Rapids, MI; and Baton Rouge, LA), intersite correlations are all greater than 0.9. In nine others (Cleveland, OH; Louisville, KY; Chicago, IL; Milwaukee, WI; Philadelphia, PA; Detroit, MI; Kansas City, KS-MO; Dallas, TX; and Salt Lake City, UT), they are all greater than 0.8. Correlations between sites in the other MSAs examined tend to be lower and span a broader range than for the MSAs mentioned above.

Seven pairs of collocated monitors in seven MSAs (Columbia, SC; Dallas, TX; Detroit, MI; Grand Rapids, MI; Louisville, KY; Steubenville, OH; Washington, DC) provide an indication of the performance of collocated monitors (see Table 3A-1). Mean values of r, P90, and COD for these seven pairs of monitors are 0.986, 1.63 $\mu g/m^3$, and 0.060 suggesting that most of the intersite variability seen is not due to sampler imprecision.

There are no strong regional patterns evident in the data given in Appendix 3A except that correlations tend to be higher between monitoring sites in MSAs in the southeastern United States than between monitoring sites in other regions.

A number of factors affect intersite correlations within MSAs. These include field measurement and laboratory analysis errors, placement of monitors close to active sources, placement of monitors in outlying areas, placement of monitors in locations that are isolated topographically from other monitors, placement of monitors in areas outside of local atmospheric circulation regimes (e.g., land-sea breezes), and transient local events (thunderstorms, sporadic emissions). In several MSAs such as Atlanta, GA; Seattle, WA; and Los Angeles-Long Beach, CA, there is at least one site that is remote from the others (by at least 100 km), is physically separated from them by mountains, and is really not part of the urban area nor the urban airshed. Correlations between concentrations at these sites and others tend to be lower than among the other sites, and concentration differences tend to be larger. It should be noted that outlying sites such as these are included in many epidemiologic time-series studies without any weighting (e.g., with respect to the exposed population, spatial differences in susceptibility) or regard to compositional differences. Although it is frequently the case that distance between sites in urban areas is largely responsible for the spatial variability that is observed, there are a few instances for which correlations are higher and differences in concentrations lower for sites that are located farthest apart. This situation may arise because these sites are influenced more by the regional background of secondary PM rather than by local sources, nor is there any set distance below which correlations and differences in concentrations tend towards some limiting values. However, it is generally the case that outlying sites are characterized by lower annual mean concentrations.

Indications of land use (commercial, industrial, residential, agricultural, forest) and location of sites (urban/city center, suburban, rural) are given in the AIRS data base. Categories such as urban/city center can refer to very different conditions in Columbia, SC, and Chicago, IL. Also, it should not be automatically assumed that concentrations measured at sites categorized as industrial are dominated by local emissions. The $PM_{2.5}$ monitoring sites are generally deployed to capture potential population exposures in a variety of environments as opposed to monitoring for compliance as it exists around local sources. It should be remembered that much of $PM_{2.5}$ is secondary in origin. The widespread formation of secondary PM coupled with the long lifetime of $PM_{2.5}$ ensures some measure of uniformity in the correlations of $PM_{2.5}$ across urban areas. Correlations between many site pairs classified as industrial can be high even though they are separated by large distances, as in the Seattle MSA.

Some indication of the variability of primary $PM_{2.5}$ produced by local sources can be obtained by examining the variability of carbon monoxide (CO), which is produced mainly by mobile sources (U.S. Environmental Protection Agency, 2000b), and by the variability in elemental carbon (EC) concentrations (Kinney et al., 2000). CO is relatively inert on the urban scale, and its distribution is governed by the spatial pattern of its emissions and the subsequent dispersion of these emissions not by photochemistry. Carbon monoxide concentrations are at least a factor of three higher near urban centers than in surrounding rural areas within the four consolidated metropolitan statistical areas examined in the EPA document, Air Quality Criteria for Carbon Monoxide (CO AQCD; U.S. Environmental Protection Agency, 2000b). The correlations of CO within the urban areas examined in that document were all low to moderate. Therefore, it might be expected that primary $PM_{2.5}$ produced by local traffic should be at least as heterogeneous as CO in a given urban area. EC is a significant component of diesel exhaust (cf., Appendix 3D). Kinney et al. (2000) measured EC and $PM_{2.5}$ concentrations at four sites located on sidewalks of streets characterized by varying exposures to diesel emissions in upper Manhattan (Harlem, NY). Whereas the mean $PM_{2.5}$ concentrations varied by about one-third from 37 to 47 μg/m^3 at the four sites, mean EC concentrations varied by a factor of four from 1.5 to 6.2 μg/m^3. The corresponding ratios of EC to $PM_{2.5}$ ranged from 0.039 to 0.14. Although EC constituted a relatively small fraction of $PM_{2.5}$ in this study, spatial variability in its sources (diesel and gasoline fueled vehicles, resuspended road dust, and cooking) contributed, on average, about one-third of the spatial variability observed in $PM_{2.5}$ concentrations. Further analyses are needed to determine whether the remaining variability could be attributed to other local and city-wide sources. Because the effects of emissions from local point sources on receptor sites depend strongly on wind direction, correlations involving contributions from local sources can be much lower than from area sources (much as motor vehicle traffic) or from regionally dispersed sources (such as the photochemical production of secondary organic PM and sulfate).

The difference in mean $PM_{2.5}$ concentrations between the site with the lowest and the site with the highest mean concentration range in all MSAs included in Appendix 3A ranges from 0.4 μg/m^3 (Baton Rouge) to about 8 μg/m^3 (Pittsburgh). Six MSAs (Chicago, Seattle, Cleveland, St. Louis, Detroit, and Pittsburgh) show maximum intersite differences in the annual mean larger than 6 μg/m^3. In the Seattle MSA, there is one monitoring site (Figure 3A-23a) that is separated from the remaining sites by topography and has much lower mean $PM_{2.5}$ concentrations, much smaller seasonal variability in concentrations, and much lower maximum concentrations than these other sites. However, the annual mean concentrations at all the other sites within the Seattle MSA are within 3 μg/m^3 of each other. Differences in annual mean concentrations are also larger between sites located in different MSAs but within the same CMSA. For example, in the consolidated MSA of Los Angeles-Riverside the range of annual mean $PM_{2.5}$ concentrations is extended from about 20 μg/m^3 in the urban area of Los Angeles county to about 29 μg/m^3 in Riverside County. Large differences in annual mean concentrations within a given area reflect differences in source or meteorological or unique topographic characteristics affecting sites; whereas very small differences found in some areas may only be the result of measurement imprecision.

Whereas high correlations of $PM_{2.5}$ provide an indication of the spatial uniformity in temporal variability (directions of changes) in $PM_{2.5}$ concentrations across urban areas, they do not imply uniformity in the $PM_{2.5}$ concentrations themselves. The 90th percentile difference in concentrations (P_{90}) and the coefficient of divergence (COD) are used here to give a more quantitative indication of the degree of spatial uniformity in $PM_{2.5}$ concentrations across urban areas. A COD of zero implies that both data sets are identical, and a COD of one indicates that two data sets are completely different. The calculation of the Pearson correlation coefficient, P_{90}, and COD allows for distinctions between pairs of sites to be made based on various combinations of these parameters. Figure 3-18 shows examples of the varying degree of heterogeneity in concentrations between pairs of sites that are highly correlated ($r > 0.9$ for all three site pairs). The increase in the spread of concentrations between the chosen site-pairs is reflected in increases in both P_{90} and COD. Pairs of sites showing high correlations and CODs < 0.1 and P_{90}'s < 4 μg/m^3 (as in Columbia, SC, Figure 3-7a) indicate homogeneity in both $PM_{2.5}$ concentrations and in their temporal variations. Presumably, sites such as these are more strongly affected by regional than local sources. Pairs of sites showing low correlations, values of P_{90} > 10 μg/m^3 and CODs > 0.2, as in Los Angeles, CA (Table 3-5), indicate heterogeneity in both $PM_{2.5}$ concentrations and in their temporal variations. Note that the extended urban area or the CMSA includes Riverside County, as well as Los Angeles County. Even lower correlations and a greater degree of heterogeneity in $PM_{2.5}$ concentrations were found in the extended CMSA. Pairs of sites showing high correlations ($r > 0.9$) and CODs > 0.2 and P_{90}'s > 10 μg/m^3 indicate heterogeneity in concentrations but homogeneity in their day to day changes. Selected pairs of sites in the Cleveland MSA show moderate to high correlations coupled with CODs > 0.2 and P_{90}'s ≥ 10 μg/m^3 (Table 3-4), suggesting moderate homogeneity in day to day changes, but significant spatial heterogeneity in concentrations.

The effect of local point sources on intersite variability can be seen at several sites among those listed in Table 3-4 and Appendix 3A. Sites 39-035-0038 (Cleveland, OH; Table 3-4 and Figure 3A-8), 18-089-0022 (Gary, IN; Figure 3A-15), 55-079-0043 (Milwaukee, WI; Figure 3A-13), and 17-119-0023 (St. Louis, MO; Figure 3A-17) are designated as “source oriented” in the AIRS data base in contrast to the “population exposure” objective associated with most of the MSA sites. $PM_{2.5}$ concentrations at these sites are weakly correlated with other sites within the MSA as evidenced by low correlation coefficients and large P_{90}s and CODs even though some of the neighboring sites may be located short distances away. Other sites designated as “source oriented” in Chicago, Milwaukee, and St. Louis do not show clear

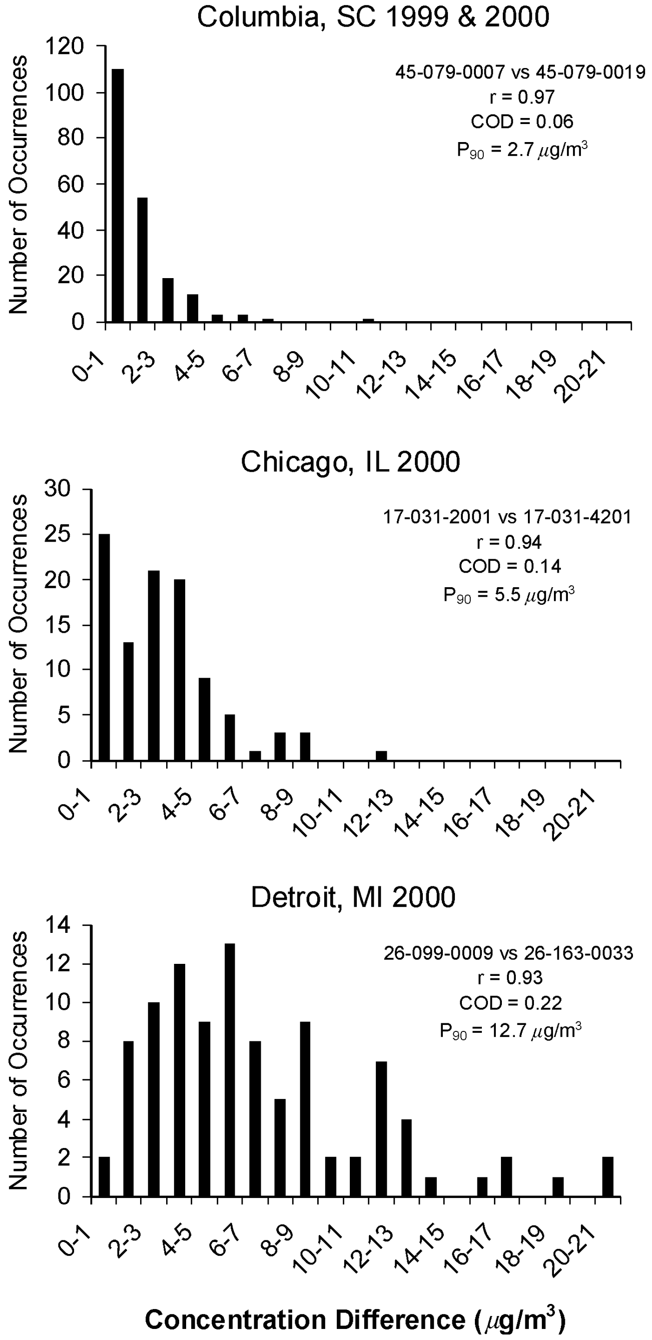

Figure 3-18. Occurrence of differences between pairs of sites in three MSAs. The absolute differences in daily average $PM_{2.5}$ concentrations between sites are shown on the x-axis and the number of occurrences on the y-axis. The MSA, years of observations, AIRS site I.D. numbers for the site pairs, Pearson correlation coefficients (r), coefficients of divergence (COD), 90th percentile (P_{90}) difference in concentration between concurrent measurements are also shown.

Source: Pinto et al. (2002).

TABLE 3-5. MEASURES OF THE SPATIAL VARIABILITY OF $PM_{10\text{-}2.5}$ CONCENTRATIONS WITHIN SELECTED METROPOLITAN STATISTICAL AREAS

(a) Cleveland, OH

Site	390350013	390350038	390350045	390350060	390350065	390851001
390350013	1	0.67 (23.2, 0.26) 182	0.67 (28.5, 0.28) 95	0.73 (17.9, 0.22) 97	0.62 (27.0, 0.31) 98	0.41 (40.0, 0.60) 94
390350038		1	0.65 (16.1, 0.22) 90	0.73 (11.7, 0.18) 93	0.69 (13.9, 0.62) 90	0.44 (24.9, 0.53) 89
390350045			1	0.66 (18.1, 0.23) 94	0.71 (10.6, 0.31) 102	0.49 (19.9, 0.50) 99
390350060				1	0.74 (15.4, 0.38) 93	0.31 (28.0, 0.59) 94
390350065					1	0.22 (20.4, 0.55) 99
390851001						1
MEAN	26.36	18.63	16.76	21.35	16.79	7.15
Obs	216	614	112	113	111	109
SD	17.38	11.60	8.96	16.39	9.49	4.94

Key
Airs Site I.D. #
Pearson r
(90th %-tile difference in concentration,
coefficient of divergence)
number of observations

(b) Dallas, TX

Site	481130020	481130035	481130050	481130057
481130020	1	0.79 (4.5, 0.17) 54	0.71 (9.3, 0.22) 55	0.66 (16.5, 0.32) 54
481130035		1	0.69 (7.8, 0.18) 50	0.60 (13.2, 0.30) 50
481130050			1	0.69 (13.5, 0.24) 50
481130057				1
MEAN	11.22	12.86	14.46	19.12
Obs	60	55	56	55
SD	5.35	6.66	6.44	10.55

Key
Airs Site I.D. #
Pearson r
(90th %-tile difference in
concentration,
coefficient of divergence)
number of observations

(c) Los Angeles, CA

Site	060370002	060371002	060371103	060374002
060370002	1	0.82 (19.0, 0.24) 49	0.63 (15.5, 0.18) 49	0.58 (17.3, 0.27) 45
060371002		1	0.74 (11.5, 0.21) 49	0.54 (11.5, 0.25) 47
060371103			1	0.57 (12.5, 0.22) 45
060374002				1
MEAN	24.10	15.33	21.44	16.08
Obs	56	56	57	53
SD	11.67	6.68	8.65	6.61

Key
Airs Site I.D. #
Pearson r
(90th %-tile difference in
concentration,
coefficient of divergence)
number of observations

evidence that local sources are contributing to intersite variability. Conversely, in the Tampa, FL MSA pairs of sites are only moderately correlated ($0.7 < r < 0.87$), but the distribution of concentrations is rather homogeneous (COD < 0.14 and $P_{90} < 5\ \mu g/m^3$; Figure 3A-7). Thus, a number of different combinations of spatial uniformity in $PM_{2.5}$ concentrations and correlations of these concentrations are found.

Values of P_{90} for absolute differences in concentrations between sites span a wide range in the data set given in Appendix 3A. In many instances they can be quite low, only about a few $\mu g/m^3$; these cases are found mainly in the eastern United States. The largest P_{90} values were associated with a single site in Pittsburgh and reached as high as 21 $\mu g/m^3$ (Figure 3A-9). Excluding this site, large P_{90} values are found mainly in the western United States. Values of P_{90} > 18 $\mu g/m^3$ are found in the Riverside and Los-Angeles-Long Beach MSAs. Maximum differences in concentrations between sites can be much larger than shown in Figure 3-18 and have been larger than 100 $\mu g/m^3$ on several occasions in the Atlanta, GA and Los Angeles-Long Beach, CA MSAs. Rizzo and Pinto (2001) and Fitz-Simons et al. (2000) examined correlations between sites located even farther apart than those examined here based on the 1999 AIRS data set for $PM_{2.5}$. They found that in a number of MSAs, $PM_{2.5}$ concentrations are still well correlated ® > 0.7) up to distances of 100 km or more. Leaderer et al. (1999) found r = 0.49 between sites outside of homes and a regional background monitor located from 1 to 175 km away in southwestern Virginia. $PM_{2.5}$ tends to be correlated over much larger areas in the East than in the West, mainly because the terrain tends to be flatter over wider areas in the East (Rizzo and Pinto, 2001). As a result, there is a greater opportunity for mixing of emissions among dispersed source regions. Many large urban areas in the West are surrounded by mountains. The presence of more rugged terrain in the West leads to greater confinement of emissions from large urban areas. Other factors such as differences in the composition and amount of emissions of precursors and in the rates of photochemical oxidation of these emissions in the atmosphere also play a role.

There is also evidence for inter-annual variability in the spatial variability in $PM_{2.5}$ concentrations. The median year-to-year changes in inter-site r (0.03), P_{90} ($-0.75\ \mu g/m^3$), and COD (-0.015) from 1999 to 2000 do not differ significantly from zero for all the site pairs considered in Appendix 3A. The year-to-year changes in the spatial variability of $PM_{2.5}$ concentrations in a number of MSAs such as the Columbia, SC; Grand Rapids, MI; Milwaukee, WI; Baton Rouge, LA; Kansas City, KS-MO; Boise, ID; and Portland, OR MSAs are similar and are smaller than those found in the Cleveland, OH; Salt Lake City, UT; and San Diego, CA MSAs. The ranges in these parameters are largest for a number of individual site-pairs, especially those involving sites that are remote from the others in their MSAs. In these MSAs (such as the Atlanta, GA; Los Angeles, CA; and Seattle, WA MSAs) there are sites that may be located in different airsheds from the remaining sites. Year-to-year changes in parameters describing spatial variability in $PM_{2.5}$ concentrations tend to be larger when sites in different counties within a given MSA are considered rather than when sites in the same county are considered. There are a number of factors that can account for inter-annual variability in these parameters, such as changes in patterns in the emissions of primary $PM_{2.5}$; in the transport and rates of transformation of secondary $PM_{2.5}$ precursors in field measurement; and analysis procedures.

Some additional data for indicating the stability with respect to year-to-year changes in spatial variability are available from earlier studies. For example, a comparison between data obtained during the summers of 1992 and 1993 (Wilson and Suh, 1997), shown in Figure 3-19, and data obtained during the summer of 1994 (Pinto et al., 1995) (cf., Table 3-8) in Philadelphia, PA, suggests that inter-site correlations of $PM_{2.5}$ have remained high and have changed very little between the two study periods.

$PM_{10\text{-}2.5}$

Intersite correlations of $PM_{10\text{-}2.5}$ concentrations obtained during the summers of 1992 and 1993 in Philadelphia, PA, (Wilson and Suh, 1997) are shown in Figure 3-19. As can be seen, correlations of $PM_{10\text{-}2.5}$ are substantially lower than those for $PM_{2.5}$.

Intersite correlation coefficients can also be calculated for $PM_{10\text{-}2.5}$ based on the AIRS data set as shown in Table 3-5 for the Cleveland, OH; Dallas, TX; and Los Angeles, CA MSAs. However, data for analyzing the spatial variability of $PM_{10\text{-}2.5}$ are more limited than for $PM_{2.5}$; therefore, fewer urban areas could be characterized in Appendix 3A (Figures 3A-28 to 3A-44). Whereas $PM_{2.5}$ concentrations were found to be highly correlated between sites in the Detroit, MI MSA (Table 3-4), estimated $PM_{10\text{-}2.5}$ concentrations are noticeably less well correlated. Likewise, correlations of $PM_{10\text{-}2.5}$ in the Chicago, IL MSA are also lower than those for $PM_{2.5}$.

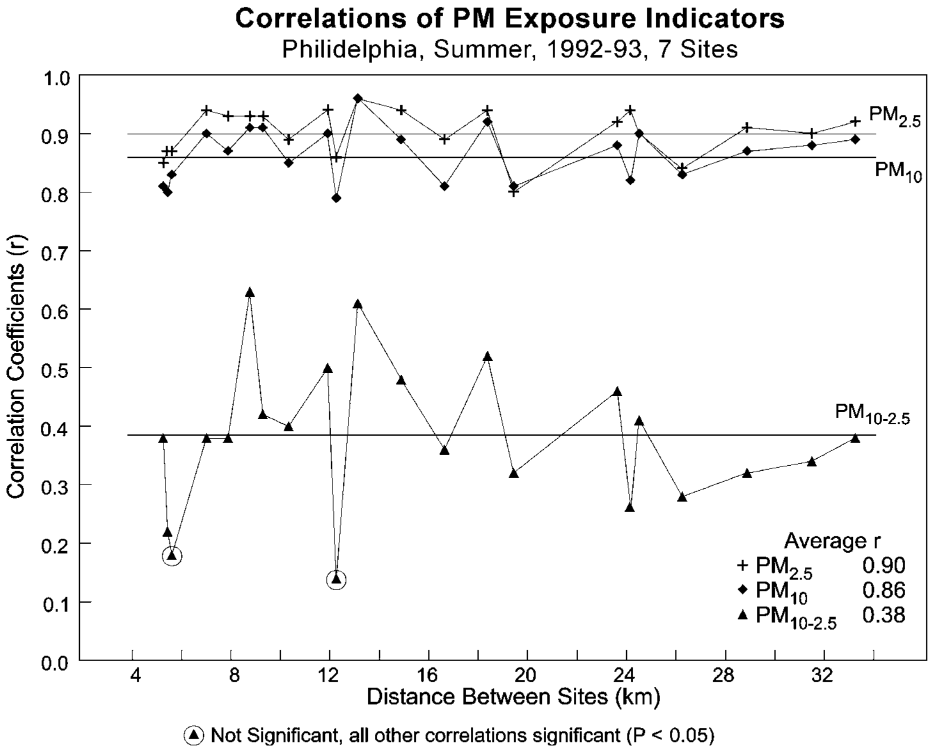

Figure 3-19. Intersite correlation coefficients for $PM_{2.5}$, PM_{10}, and $PM_{10-2.5}$.

Source: Wilson and Suh (1997).

In contrast, correlations of $PM_{10-2.5}$ concentrations between several pairs of sites in the Los Angeles-Long Beach partial MSA are higher than those for $PM_{2.5}$.

The interpretation of these results is not straightforward, as concentrations of $PM_{10-2.5}$ are generated by taking the difference between collocated $PM_{2.5}$ and PM_{10} monitors. Consequently, caution must be exercised when viewing them. Errors in the measurement of $PM_{2.5}$ and PM_{10} may play a large role in reducing apparent correlations of $PM_{10-2.5}$ such that collocated $PM_{10-2.5}$ "measurements" may be expected to be poorly correlated (White, 1998). Indeed, several estimates of concentrations are negative. Negative $PM_{10-2.5}$ concentrations also lead to artifacts in the calculation of CODs. In cases where these artifacts cause a division by zero or a very small number in the calculation of CODs, dashes are used in Table 3-5 and Figures 3A-28 through 3A-44. These results imply that negative concentrations can be almost or identically equal in absolute magnitude to positive concentrations in the same MSA. The possible causes of these errors are essentially the same as those discussed in Section 3.2.1 with regard to the occurrence of $PM_{2.5}$ to PM_{10} ratios greater than one. There are also physical bases for expecting that $PM_{10-2.5}$ concentrations may be more variable than those for $PM_{2.5}$. $PM_{10-2.5}$ is mainly primary in origin, and its emissions are spatially and temporally heterogenous. Similar considerations apply to primary $PM_{2.5}$, but much of $PM_{2.5}$ is secondary, and sources of secondary PM are much less spatially and temporally variable. Dry deposition rates of particles depend strongly on particle size. Whereas all particles may be brought to the surface by turbulent motions in the atmosphere; gravitational settling becomes more important with increasing particle size. Gravitational settling can effectively limit the horizontal distance a particle can travel. For example, 10 µm D_a particles suspended in a hypothetical 1 km deep planetary boundary layer can be removed within a few hours, but 1 µm D_a particles can remain suspended in the atmosphere for up to 100 to 1,000 times longer before being dry deposited. (Estimated atmospheric lifetimes were based on deposition velocities given in Lin et al. [1994] for typical wind speeds.) The findings of larger correlations of $PM_{10-2.5}$ between several site pairs in the Los Angeles basin (cf., Figures 3A-25/26 and Figures 3A-42/43) and one other site pair in the St. Louis, MO-IL MSA (cf., Figures 3A-17 and 3A-37) are anomalous in light of the discussion above. However, these findings could have resulted from differences between the spatial and temporal behavior of sources of $PM_{2.5}$ and $PM_{10-2.5}$ in these locations. Because of negative values, CODs were not calculated.

PM Components

Three methods for comparing the chemical composition of aerosol databases obtained at different locations and times were discussed by Wongphatarakul et al. (1998). Log-log plots of chemical concentrations obtained at pairs of sampling sites accompanied by the coefficient of divergence (COD) were examined as a way to provide an easily visualized means of comparing two data sets[2]. Examples comparing downtown Los Angeles with Burbank and with

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[2] The COD for two sampling sites is defined as follows:

$$COD_{jk} = \sqrt{\frac{1}{p}\sum_{i=1}^{p}\left(\frac{x_{ij} - x_{ik}}{x_{ij} + x_{ik}}\right)^2} \tag{3-2}$$

where x_{ij} represents the average concentration for a chemical component i at site j, j and k represent two sampling sites, and p is the number of chemical components.

Riverside-Rubidoux are shown in Figures 3-20 and 3-21. As the composition of two sampling sites become more similar, the COD approaches zero; as their compositions diverge, the COD approaches one. Correlation coefficients calculated between components can be used to show the degree of similarity between pairs of sampling sites.

In addition to calculating correlation coefficients for total mass or for individual components, correlation coefficients for characterizing the spatial variation of the contributions from given source types can also be calculated by averaging the correlation coefficients of the set of chemical components that represent the source type. Correlation coefficients showing the spatial relationships among $PM_{2.5}$ (total) and contributions from different source categories obtained at various sites in the South Coast Air Basin (SoCAB) Study are shown in Table 3-6. In Wongphatarakul et al. (1998), crustal material (crustal), motor vehicle exhaust (mv), residual oil emissions (residual oil), and secondary PM (sec) were considered as source categories. Al, Si, Fe, and Ca were used as markers for crustal material (crustal); V and Ni were used as markers for fuel oil combustion (residual oil); and Pb, Br, and Mn were used as markers for motor vehicle exhaust (mv), based on the lack of other, perhaps more suitable, tracers. NO_3^-, NH_4^+, and SO_4^{-2} represent secondary PM components. The average of the correlation coefficients of marker elements within each source category are shown in Table 3-6. Values of r_{sec} and r_{mv} are much higher than those for $r_{crustal}$ and $r_{residual\ oil}$ throughout the SoCAB, suggesting a more uniform distribution of the contributions from secondary PM formation and automobiles than from crustal material and localized stationary sources.

Correlation coefficients in Philadelphia air based on data obtained at four sites for $PM_{2.5}$ (total), crustal components (Al, Si, Ca, and Fe), the major secondary component (sulfate), organic carbon (OC), and elemental carbon (EC) are shown in Table 3-7. Because these data were obtained after Pb had been phased out of gasoline, a motor vehicle contribution could not be estimated from the data. Pb also is emitted by discrete point sources, such as the Franklin smelter. Concentrations of V and Ni were often beneath detection limits; so, the spatial variability in PM due to residual oil combustion were not estimated. Sulfate in aerosol samples collected in Philadelphia arises mainly from long-range transport from regionally dispersed sources (Dzubay et al., 1988). This conclusion is strengthened by the high correlations in sulfate between different monitoring sites and the uniformity in sulfate concentrations observed among the sites. Widespread area sources (e.g., motor vehicle traffic) also may emit pollutants that are

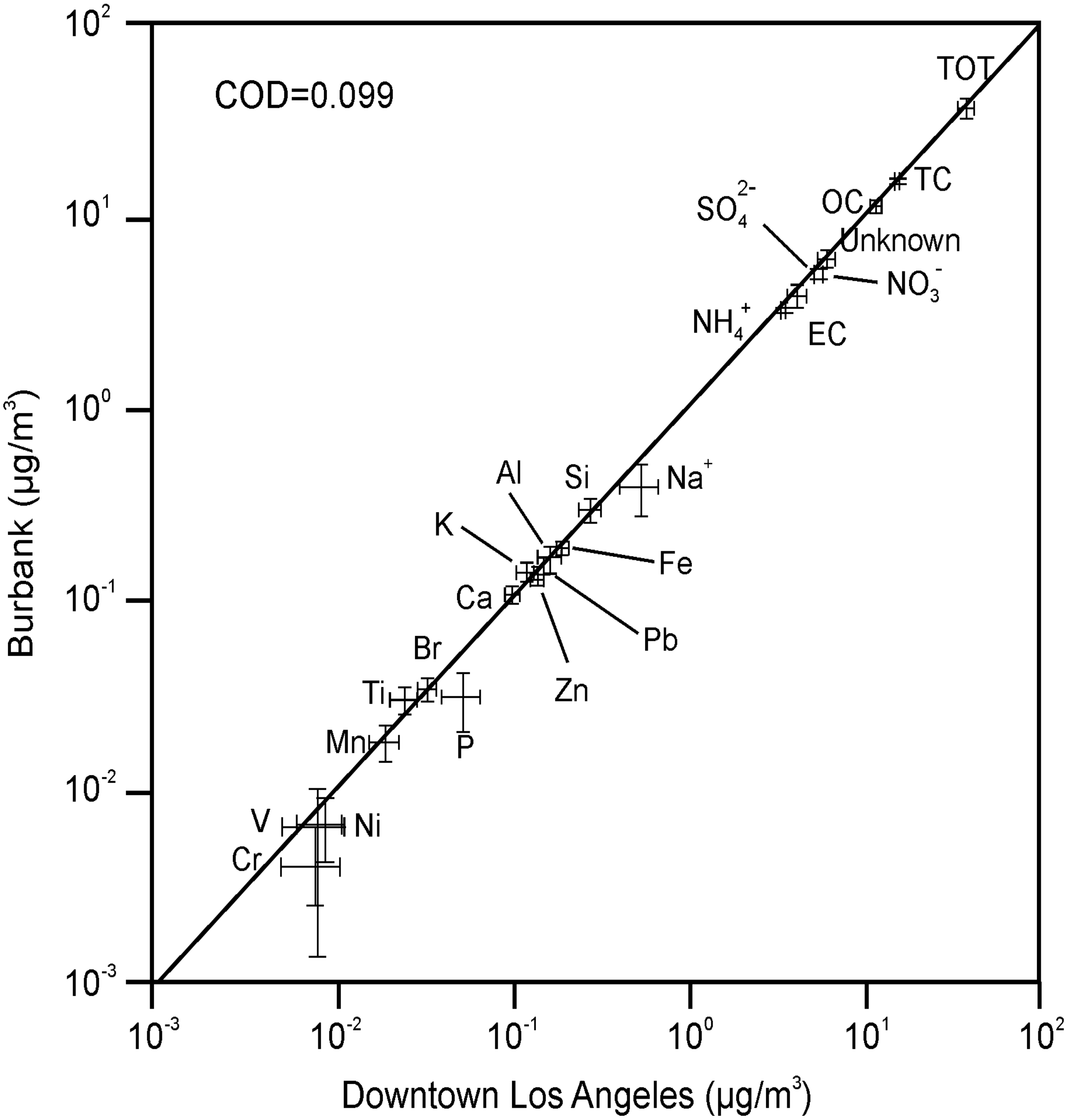

Figure 3-20. $PM_{2.5}$ chemical components in downtown Los Angeles and Burbank (1986) have similar characteristics. The spread in the data is shown by the bars.

Source: Wongphatarakul et al. (1998).

correlated between sites provided that traffic patterns and emissions are similar throughout the area under consideration.

Landis et al. (2001) found relatively high correlations between $PM_{2.5}$ (r = 0.97), sulfate (r = 0.99), OC (r = 0.97), EC (r = 0.83), NaCl (r = 0.83), and nitrate (r = 0.83) measured at two

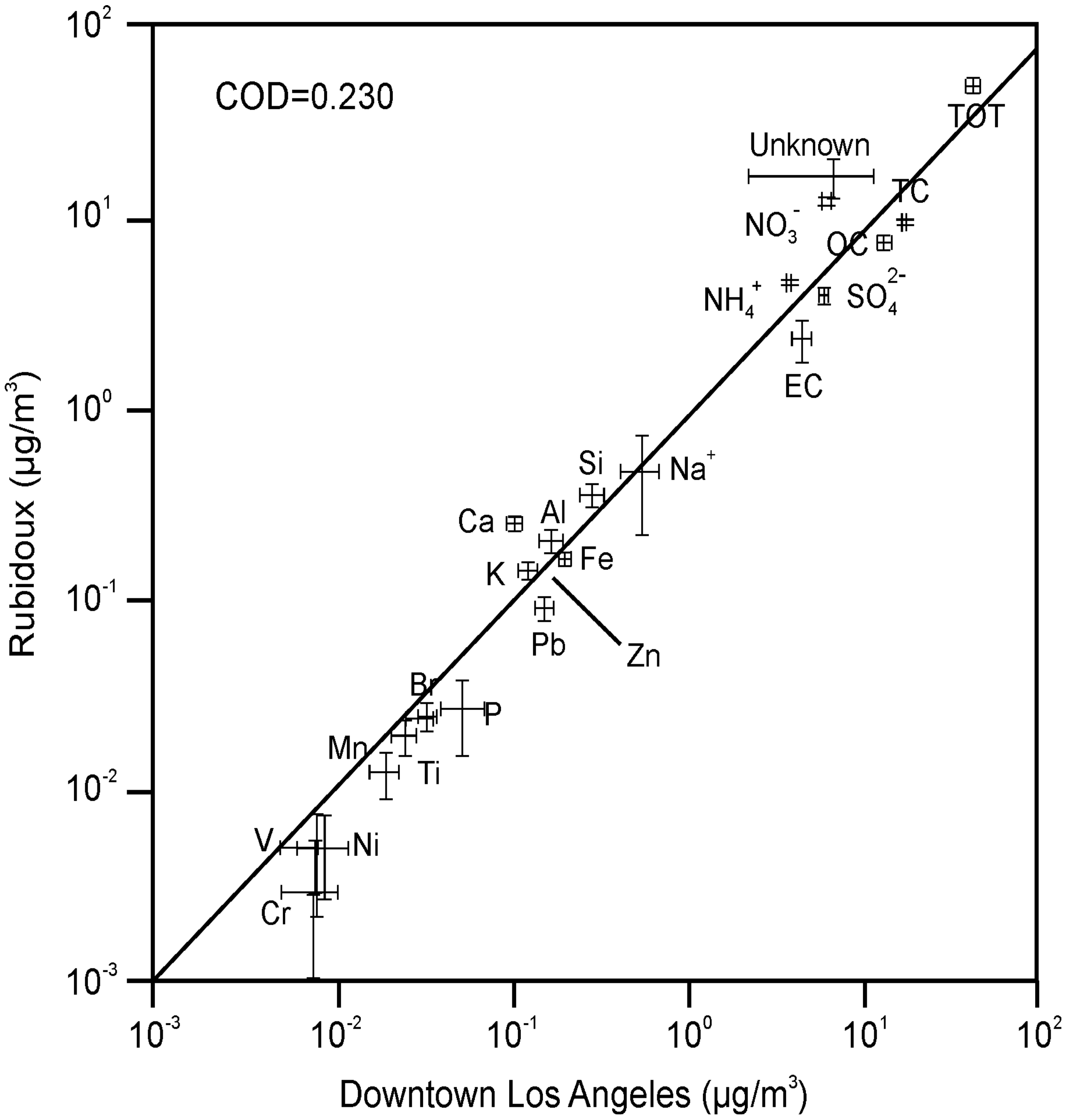

Figure 3-21. Concentrations of $PM_{2.5}$ chemical components in Rubidoux and downtown Los Angeles (1986). The diagram shows a significant spread in the concentrations for the two sites compared with downtown Los Angeles and Burbank (Figure 3-20).

Source: Wongphatarakul et al. (1998).

sites located several km apart in the Baltimore, MD area. Concentrations of crustal material ($r = 0.63$) and the sum of total metal oxides ($r = 0.76$) were not as well correlated. These results are consistent with those for another eastern city, Philadelphia, PA, given in Table 3-7.

TABLE 3-6. CORRELATION COEFFICIENTS FOR SPATIAL VARIATION OF $PM_{2.5}$ MASS AND DIFFERENT SOURCES FOR PAIRS OF SAMPLING SITES IN THE SOUTH COAST AIR BASIN (1986)

	r_{total}	$r_{crustal}$	r_{sec}	r_{mv}	$r_{residual\ oil}$
Hawthorne and Rubidoux	−0.027				
Long Beach and Rubidoux	0.051				
Anaheim and Rubidoux	0.066				
Downtown Los Angeles and Rubidoux	0.095				
Burbank and Rubidoux	0.120				
Hawthorne and Anaheim	0.760	0.034	0.768	0.492	0.170
Long Beach and Anaheim	0.852	0.075	0.888	0.504	0.150
Burbank and Anaheim	0.770	0.105	0.749	0.579	0.161
Downtown Los Angeles and Anaheim	0.827	0.143	0.804	0.556	0.233
Downtown Los Angeles and Hawthorne	0.808	0.568	0.854	0.669	0.533
Burbank and Hawthorne	0.704	0.599	0.790	0.688	0.491
Long Beach and Burbank	0.731	0.633	0.737	0.714	0.295
Long Beach and Hawthorne	0.880	0.649	0.909	0.861	0.482
Downtown Long Angeles and Long Beach	0.842	0.653	0.817	0.719	0.378
Downtown Los Angeles and Burbank	0.928	0.825	0.960	0.871	0.606

Source: Wongphatarakul et al. (1998).

TABLE 3-7. CORRELATION COEFFICIENTS FOR SPATIAL VARIATION OF $PM_{2.5}$ MASS AND DIFFERENT COMPONENTS FOR PAIRS OF SAMPLING SITES IN PHILADELPHIA (1994)

	r_{tot}	$r_{crustal}$	r_{sec}	r_{OC}	r_{EC}	r_{Pb}
Castor Ave. and Roxboro	0.92	0.52	0.98	0.88	0.84	0.43
Castor Ave. and NE Airport	0.93	0.47	0.99	0.88	0.77	−0.07
Castor Ave. and Broad St.	0.93	0.57	0.99	0.85	0.89	0.11
Roxboro and NE Airport	0.98	0.67	0.98	0.83	0.82	0.20
Roxboro and Broad St.	0.95	0.90	0.98	0.86	0.79	0.47
NE Airport and Broad St.	0.95	0.69	0.99	0.84	0.63	0.11

Source: Pinto et al. (1995).

The results presented above for Philadelphia, PA; Baltimore, MD; and Los Angeles, CA, indicate that secondary PM components are more highly correlated than primary components and may be more highly correlated than total $PM_{2.5}$. These results suggest that the correlation of PM concentrations across an urban area may depend on the relative proportions of primary and secondary components of PM at individual sites. Sampling artifacts affecting the measurement of nitrate and organic carbon can obscure these relations and may depress correlations between sites.

Kao and Friedlander (1995) examined the statistical properties of a number of PM components in the South Coast Air Basin (Los Angeles area). They found that, regardless of source type and location within their study area, the concentrations of nonreactive, primary components of PM_{10} had approximately log-normal frequency distributions with constant values of the geometric standard deviations (GSDs). However, aerosol constituents of secondary origin (e.g., SO_4^{-2}, NH_4^+, and NO_3^-) were found to have much higher GSDs. Surprisingly, the GSDs of organic (1.87) and elemental (1.74) carbon were both found to be within 1 SD (0.14) of the mean GSD (1.85) for nonreactive primary species, compared to GSD's of 2.1 for sulfate, 3.5 for nitrate, and 2.6 for ammonium. These results suggest that most of the organic carbon seen in ambient samples in the South Coast Air Basin was of primary origin. Pinto et al. (1995) found similar results for data obtained during the summer of 1994 in Philadelphia. Further studies are needed to determine if these relations are valid at other locations and to what extent the results might be influenced by sampling artifacts such as the evaporation of volatile constituents during or after sampling.

The use of correlations between OC and EC and OC to EC ratios based on a comparison between values measured in source emissions and ambient observations has also been suggested as a means to distinguish between secondary; and primary sources of OC (Turpin and Huntzicker, 1995; Strader et al., 1999). Ratios of OC to EC from combustion sources are typically three or less and may even be less than one in diesel emissions (cf., Appendix 3D). Cabada et al. (2002) concluded that secondary organic PM can contribute from 10 to 35% of total organic PM on an annual basis, with values > 50% during the summer and 0% during the winter months in Pittsburgh, PA, based on chemistry-transport model results and comparison with emissions inventory values of OC to EC ratios. All of these inferences are subject to considerable uncertainty in the methods for measuring OC (as discussed in Section 2).

Ambiguity also arises in the ratio method as the ratios may change due to chemical reactions occurring during aging of the particles. However, not much work has been done on this issue. The ratio can be greater than nine in emissions from wildfires, and transport from distant fires can skew results unless this transport is taken into account (cf., Appendix 3D). Modeling studies that rely on OC to EC ratios in emissions inventories to predict the amount of secondary OC may be biased towards higher ratios of secondary OC because emissions of primary biologic particles are not included in the inventories. Additional concerns arise from uncertainties in the mechanism of formation of secondary OC from gaseous biogenic and anthropogenic precursor emissions and the uncertainty in those emissions (Section 3.3.1). It is clear, however, that secondary organic PM is being formed in the atmosphere (Blando et al., 1998 and Appendix 3C).

Few studies have compared aerosol composition in urban areas to that in nearby rural areas. One exception is Tanner and Parkhurst (2000), which indicates that sulfate constituted a larger fraction of fine particle mass at rural sites in the Tennessee Valley $PM_{2.5}$ monitoring network than did organic carbon. For urban sites, the situation was largely reversed: organic carbon constituted a larger fraction of aerosol mass than sulfate. Future systematic comparisons of urban-rural differences in aerosol properties should be facilitated with implementation of the national speciation network and continued operation of the IMPROVE network.

3.3 SOURCES OF PRIMARY AND SECONDARY PARTICULATE MATTER

Information about the nature and relative importance of sources of ambient PM is presented in this section. Table 3-8 summarizes anthropogenic and natural sources for the major primary and secondary aerosol constituents of fine and coarse particles. Anthropogenic sources can be further divided into stationary and mobile sources. Stationary sources include those such as: fuel combustion for electrical utilities, residential space heating, and industrial processes; construction and demolition; metals, minerals, and petrochemicals; wood products processing; mills and elevators used in agriculture; erosion from tilled lands; waste disposal and recycling; and fugitive dust from paved and unpaved roads. Mobile or transportation-related sources include direct emissions of primary PM and secondary PM precursors from highway and off-highway vehicles and non-road sources. In addition to fossil fuel combustion, biomass in the form of wood is burned for fuel. Vegetation is burned to clear new land for agriculture and for

TABLE 3-8. CONSTITUENTS OF ATMOSPHERIC PARTICLES AND THEIR MAJOR SOURCES[1]

	Sources					
	Primary (PM < 2.5 µm)		Primary (PM > 2.5 µm)		Secondary PM Precursors (PM < 2.5 µm)	
Aerosol species	Natural	Anthropogenic	Natural	Anthropogenic	Natural	Anthropogenic
SO_4^{-2} Sulfate	Sea spray	Fossil fuel combustion	Sea spray	—	Oxidation of reduced sulfur gases emitted by the oceans and wetlands and SO_2 and H_2S emitted by volcanism and forest fires	Oxidation of SO_2 emitted from fossil fuel combustion
NO_3^- Nitrate	—	—	—	—	Oxidation of NO_x produced by soils, forest fires, and lighting	Oxidation of NO_x emitted from fossil fuel combustion and in motor vehicle exhaust
Minerals	Erosion and re-entrainment	Fugitive dust paved and unpaved roads, agriculture, forestry, construction, and demolition	Erosion and re-entrainment	Fugitive dust, paved and unpaved road dust, agriculture, forestry, construction, and demolition	—	—
NH_4^+ Ammonium	—	—	—	—	Emissions of NH_3 from wild animals, and undisturbed soil	Emissions of NH_3 from animal husbandry, sewage, and fertilized land
Organic carbon (OC)	Wildfires	Prescribed burning, wood burning, motor vehicle exhaust, and cooking	Soil humic matter	Tire and asphalt wear and paved road dust	Oxidation of hydrocarbons emitted by vegetation (terpenes, waxes) and wild fires	Oxidation of hydrocarbons emitted by motor vehicles, prescribed burning, and wood burning
Elemental carbon (EC)	Wildfires	Motor vehicle exhaust, wood burning, and cooking	—	Tire and asphalt wear and paved road dust	—	—
Metals	Volcanic activity	Fossil fuel combustion, smelting, and brake wear	Erosion, re-entrainment, and organic debris	—	—	—
Bioaerosols	Viruses and bacteria	—	Plant and insect fragments, pollen, fungal spores, and bacterial agglomerates	—	—	—

[1] Dash (–) indicates either very minor source or no known source of component.

building construction, to dispose of agricultural and domestic waste, to control the growth of animal or plant pests, and to manage forest resources (prescribed burning). Also shown are sources for precursor gases whose oxidation forms secondary particulate matter. The atmospheric chemical processes producing secondary PM are described in Section 3.3.1.

In general, the sources of fine PM are very different from those for coarse PM. Some of the mass in the fine size fraction forms during combustion from material that has volatilized in combustion chambers and then recondensed before emission into the atmosphere. Some ambient $PM_{2.5}$ forms in the atmosphere from photochemical reactions involving precursor gases. PM formed by the first mechanism is referred to as primary, and PM formed by the second mechanism is referred to as secondary. $PM_{10\text{-}2.5}$ is mainly primary in origin as it is produced by the abrasion of surfaces or by the suspension of biological material. Because precursor gases undergo mixing during transport from their sources, it is difficult to identify individual sources of secondary constituents of PM. Transport and transformations of precursors can occur over distances of hundreds of kilometers. The coarse PM constituents have shorter lifetimes in the atmosphere, so their effects tend to be more localized. Only major sources for each constituent within each broad category shown at the top of Table 3-8 are listed. Not all sources are equal in magnitude. Chemical characterizations of primary particulate emissions for a wide variety of natural and anthropogenic sources (as shown in Table 3-8) were given in Chapter 5 of the 1996 PM AQCD. Summary tables of the composition of source emissions presented in the 1996 PM AQCD and updates to that information are provided in Appendix 3D. The profiles of source composition were based in large measure on the results of various studies that collected signatures for use in source apportionment studies.

Natural sources of primary PM include windblown dust from undisturbed land, sea spray, and plant and insect debris. The oxidation of a fraction of terpenes emitted by vegetation and reduced sulfur species from anaerobic environments leads to secondary PM formation. Ammonium (NH_4^+) ions, which play a major role in regulating the pH of particles, are derived from emissions of ammonia (NH_3) gas. Source categories for NH_3 have been divided into emissions from undisturbed soils (natural) and emissions that are related to human activities (e.g., fertilized lands, domestic and farm animal waste). There is ongoing debate about characterizing emissions from wildfires (i.e., unwanted fire) as either natural or anthropogenic. Wildfires have been listed in Table 3-8 as natural in origin, but land management practices and other human actions affect the occurrence and scope of wildfires. For example, fire suppression practices allow the buildup of fire fuels and increase the susceptibility of forests to more severe and infrequent fires from whatever cause, including lightning strikes. Similarly, prescribed burning is listed as anthropogenic, but can be viewed as a substitute for wildfires that would otherwise occur eventually on the same land.

The transformations that gaseous precursors to secondary PM undergo after being emitted from the sources shown in Table 3-8 are described in Section 3.3.1. Aspects of the transport of primary PM and secondary PM, including the transport of material from outside the United States, are described in Section 3.3.2. A brief introduction to the deposition of particles is also given in Section 3.3.2, and a more detailed discussion of deposition processes is presented in Chapter 4. Methods to infer contributions from different source categories to ambient PM using receptor models and the results of these modeling efforts are given in Section 3.3.3. Estimates of emissions of primary PM and precursors to secondary PM from major sources are presented in Section 3.3.4. A discussion of the uncertainties associated with these emissions is given in Section 3.3.5.

3.3.1 Chemistry of Secondary PM Formation

Precursors to secondary PM have natural and anthropogenic sources, just as primary PM has natural and anthropogenic sources. The major atmospheric chemical transformations leading to the formation of particulate nitrate and sulfate are relatively well understood; whereas those involving the formation of secondary aerosol organic carbon are less so and are still subject to much current investigation. A large number of organic precursors are involved; many of the kinetic details still need to be determined; and many of the actual products of the oxidation of hydrocarbons have yet to be identified.

Formation of Sulfates and Nitrates

A substantial fraction of the fine particle mass, especially during the warmer months of the year, is secondary sulfate and nitrate formed as the result of atmospheric reactions. Such reactions involve the gas phase conversion of SO_2 to H_2SO_4 (which forms liquid particles) initiated by reaction with OH radicals and aqueous-phase reactions of SO_2 with H_2O_2, O_3, or O_2 (catalyzed by Fe and Mn). These heterogeneous reactions may occur in cloud and fog droplets or in films on atmospheric particles. NO_2 can be converted to gaseous HNO_3 by reaction with OH radicals during the day. At night, NO_2 also is oxidized to nitric acid by a sequence of reactions initiated by O_3 that produce nitrate radicals (NO_3) and dinitrogenpentoxide (N_2O_5) as intermediates. Both H_2SO_4 and HNO_3 react with atmospheric ammonia (NH_3). Gaseous NH_3 reacts with gaseous HNO_3 to form particulate NH_4NO_3. Gaseous NH_3 reacts with H_2SO_4 to form acidic HSO_4^- (in NH_4 HSO_4) as well as SO_4^{-2} in $(NH_4)_2SO_4$. In addition, acid gases such as SO_2 and HNO_3 may react with coarse alkaline particles to form coarse secondary PM containing sulfate and nitrate. Examples include reactions with basic compounds resulting in neutralization (e.g., $CaCO_3 + 2\ HNO_3 \rightarrow Ca\ (NO_3)_2 + H_2CO_3\uparrow$) or with salts of volatile acids resulting in release of the volatile acid (e.g., $SO_2 + 2NaCl + H_2O \rightarrow Na_2SO_3 + 2HCl\uparrow$).

If particulate NH_4NO_3 coagulates with an acidic sulfate particle (H_2SO_4 or HSO_4^-), gaseous HNO_3 will be released, and the NH_3 will increase the neutralization of the acidic sulfate. Thus, in the eastern United States, where PM tends to be acidic, sulfate usually constitutes a larger fraction of PM mass than nitrate. However, in the western United States, where higher NH_3 and lower SO_2 emissions permit complete neutralization of H_2SO_4, the concentration of nitrate could be higher than that of sulfate as it is in areas such as the Los Angeles Basin and the San Joaquin Valley. As SO_2 concentrations in the atmosphere in the eastern United States are reduced, the NH_3 left in the atmosphere after neutralization of H_2SO_4 will be able to react with HNO_3 to form NH_4NO_3. Therefore, a reduction in SO_2 emissions, especially without a reduction in NO_x emissions, could lead to an increase in NH_4NO_3 concentrations (West et al., 1999; Ansari and Pandis, 1998). Thus, possible environmental effects of NH_4NO_3 are of interest for both the western and eastern United States.

Chemical reactions of SO_2 and NO_x within plumes are an important source of H^+, SO_4^{-2}, and NO_3^-. These conversions can occur by gas-phase and aqueous-phase mechanisms.
In power-plant or smelter plumes containing SO_2 and NO_x, the gas-phase chemistry depends on plume dilution, sunlight, and volatile organic compounds either in the plume or in the ambient air mixing into and diluting the plume. For the conversion of SO_2 to H_2SO_4 in the gas-phase in such plumes during summer midday conditions in the eastern United States, the rate typically varies between 1 and 3% h^{-1} but in the cleaner western United States rarely exceeds 1% h^{-1}. For the conversion of NO_x to HNO_3, the gas-phase rates appear to be approximately three times

faster than the SO_2 conversion rates. Winter rates for SO_2 conversion are approximately an order of magnitude lower than summer rates.

The contribution of aqueous-phase chemistry to particle formation in point-source plumes is highly variable, depending on the availability of the aqueous phase (wetted aerosols, clouds, fog, and light rain) and the photochemically generated gas-phase oxidizing agents, especially H_2O_2 for SO_2 chemistry. The in-cloud conversion rates of SO_2 to SO_4^{-2} can be several times larger than the gas-phase rates given above. Overall, it appears that SO_2 oxidation rates to SO_4^{-2} by gas-phase and aqueous-phase mechanisms may be comparable in summer, but aqueous-phase chemistry may dominate in winter. Further details concerning the chemistry of SO_2 and NO_x in power plant plumes can be found in Hewitt (2001).

In the western United States, markedly higher SO_2 conversion rates have been reported in smelter plumes than in power plant plumes. The conversion occurs predominantly by a gas-phase mechanism. This result is attributed to the lower NO_x in smelter plumes. In power plant plumes, NO_2 depletes OH radicals and competes with SO_2 for OH radicals.

In urban plumes, the upper limit for the gas-phase SO_2 conversion rate appears to be about 5% h^{-1} under the more polluted conditions. For NO_2, the rates appear to be approximately three times faster than the SO_2 conversion rates. Conversion rates of SO_2 and NO_x in background air are comparable to the peak rates in diluted plumes. Neutralization of H_2SO_4 formed by SO_2 conversion increases with plume age and background NH_3 concentration. If the NH_3 concentrations are more than sufficient to neutralize H_2SO_4 to $(NH_4)_2SO_4$, the HNO_3 formed from NO_x conversions may be converted to NH_4NO_3.

Formation of Secondary Organic Particulate Matter (SOPM)

Atmospheric reactions involving volatile organic compounds such as alkanes, alkenes, aromatics, cyclic olefins, and terpenes (or any reactive organic gas that contains at least seven carbon atoms) yield organic compounds with low saturation vapor pressures at ambient temperature. Such reactions may occur in the gas phase, in fog or cloud droplets (Graedel and Goldberg, 1983; Faust, 1994), or possibly in aqueous aerosols (Aumont et al., 2000). Reaction products from the oxidation of reactive organic gases also may nucleate to form new particles or condense on existing particles to form secondary organic PM (SOPM). Organic compounds with two double bonds or cyclic olefins may react to form dicarboxylic acids, which, with four or more carbon atoms, also may condense. Both biogenic and anthropogenic sources contribute to primary and secondary organic particulate matter (Grosjean, 1992; Hildemann et al., 1996; Mazurek et al., 1997; Schauer et al., 1996). Oxalic acid was the most abundant organic acid found in $PM_{2.5}$ in California (Poore, 2000).

Although the mechanisms and pathways for forming inorganic secondary particulate matter are fairly well known, those for forming SOPM are not as well understood. Ozone and the OH radicals are thought to be the major initiating reactants. However, HO_2 and NO_3 radicals also may initiate reactions; and organic radicals may be nitrated by HNO_2, HNO_3, or NO_2. Pun et al. (2000) discuss formation mechanisms for highly oxidized, multifunctional organic compounds. The production of such species has been included in a photochemical model by Aumont et al. (2000), for example. Understanding the mechanisms of formation of secondary organic PM is important because SOPM can contribute in a significant way to ambient PM levels, especially during photochemical smog episodes. Experimental studies of the production of secondary organic PM in ambient air have focused on the Los Angeles Basin. Turpin and Huntzicker (1991, 1995) and Turpin et al. (1991) provided strong evidence that secondary PM formation occurs during periods of photochemical ozone formation in Los Angeles and that as much as 70% of the organic carbon in ambient PM was secondary in origin during a smog episode in 1987. Schauer et al. (1996) estimated that 20 to 30% of the total organic carbon PM in the < 2.1 µm size range in the Los Angeles airshed is secondary in origin on an annually averaged basis.

Pandis et al. (1992) identified three mechanisms for formation of SOPM: (1) condensation of oxidized end-products of photochemical reactions (e.g., ketones, aldehydes, organic acids, and hydroperoxides), (2) adsorption of semivolatile organic compounds (SVOC) onto existing solid particles (e.g., polycyclic aromatic hydrocarbons), and (3) dissolution of soluble gases that can undergo reactions in particles (e.g., aldehydes). The first and third mechanisms are expected to be of major importance during the summer when photochemistry is at its peak. The second pathway can be driven by diurnal and seasonal temperature and humidity variations at any time of the year. With regard to the first mechanism, Odum et al. (1996) suggested that the products of the photochemical oxidation of reactive organic gases are semivolatile and can partition themselves onto existing organic carbon at concentrations below their saturation concentrations.

Thus, the yield of SOPM depends not only on the identity of the precursor organic gas but also on the ambient levels of organic carbon capable of absorbing the oxidation products.

Haagen-Smit (1952) first demonstrated that hydrocarbons irradiated in the presence of NO_x produce light scattering aerosols. The aerosol-forming potentials of a wide variety of individual anthropogenic and biogenic hydrocarbons were compiled by Pandis et al. (1992) based mainly on estimates made by Grosjean and Seinfeld (1989) and on data from Pandis et al. (1991) for β-pinene and from Izumi and Fukuyama (1990) for aromatic hydrocarbons. Zhang et al. (1992) examined the oxidation of α-pinene. Pandis et al. (1991) found no aerosol products formed in the photochemical oxidation of isoprene, although they and Zhang et al. (1992) found that the addition of isoprene to reaction mixtures increased the reactivity of the systems studied. Further details about the oxidation mechanisms and secondary organic PM yields from various reactive organic gases are given in the above studies. Estimates of the production rate of secondary organic PM in the Los Angeles airshed are provided in the 1996 PM AQCD (U.S. Environmental Protection Agency, 1996).

More recently, Odum et al. (1997a,b) have found that the aerosol-formation potential of whole gasoline vapor can be accounted for solely by summing the contributions of the individual aromatic compounds in the fuel. In general, data for yields for secondary organic PM formation can be broken into two distinct categories. The oxidation of toluene and aromatic compounds containing ethyl or propyl groups (i.e., ethylbenzene, ethyltoluene, n-propylbenzene) produced higher yields of secondary organic PM than did the oxidation of aromatic compounds containing two or more methyl groups (i.e., xylenes, di-, tri-, tetra-methylbenzenes). Yields in the first group ranged from about 7 to 10%; and in the second group, they ranged from 3 to 4% for organic carbon concentrations between 13 and 100 $\mu g/m^3$. Reasons for the differences in secondary organic PM yields found between the two classes of compounds are not clear.

There have been a few recent studies that have examined the composition of secondary organic PM. Edney et al. (2001) carried out a smog chamber study to investigate the formation of multi-functional oxygenates from photooxidation of toluene. The experiments were carried out by irradiating toluene/propylene/NO_x/air mixtures in a smog chamber operated in the dynamic mode and analyzing the collected aerosol by positive chemical ionization GC-MS after derivatization of the carbonyl oxidation products. The results of the GC-MS analyses were consistent with the formation of semivolatile multi-functional oxygenates, including hydroxy diones as well as triones, tetraones, and pentaones. The authors also suggested that some of these compounds could be present in SOPM in the form of polymers.

Jang and Kamens (2001a) employed a number of analytical approaches, including GC-MS detection of volatile derivatives of carbonyl, hydroxy, and acid compounds in SOPM formed in the irradiation of toluene/NO_x mixtures. A wide range of substituted aromatics, nonaromatic ring-retaining and ring-opening products were detected. Newly identified ring-opening oxycarboxylic acids detected included glyoxylic acid; methylglyoxylic acid; 4-oxo-2-butenoic acid; oxo-C_5-alkenoic acids; dioxopentenoic acids; oxo-C_7-alkadienoic acids; dioxo-C_6-alkenoic acids; hydroxydioxo-C_7-alkenoic acids; and hydroxytrioxo-C_6-alkanoic acids. Other newly identified compounds included methylcyclohexenetriones; hydroxymethylcyclohexenetriones; 2-hydroxy-3-penten-1,5-dial, hydroxyoxo-C_6-alkenals; hydroxy-C_5-triones, hydroxydioxo-C_7-alkenals; and hydroxy-C_6-tetranones. Included among these compounds were a number of the hydroxy polyketones detected by Edney et al., (2001).

Recent laboratory and field studies support the concept that nonvolatile and semivolatile oxidation products from the photooxidation of biogenic hydrocarbons contribute significantly to ambient PM concentrations in both urban and rural environments. The oxidation of a variety of biogenic hydrocarbons emitted by trees and plants, such as terpenes (*α*-pinene, *β*-pinene, Δ^3-carene, sabinene, *α*-terpinene, *γ*-terpinene, terpinolene, myrcene, and ocimene) and sesequiterpenes (*β*-caryophyllene and *α*-humulene) could form SOPM. Vegetation also emits oxygenated organic compounds such as alcohols, acetates, aldehyde, ketones, ethers, and esters (Winer et al., 1992). However, their contribution to SOPM remains uncertain. Hoffmann et al. (1997) found SOPM yields of ≈5% for open-chain biogenic hydrocarbons such as ocimene and linalool; 5 to 25% for monounsaturated cyclic monoterpenes such as α-pinene, *Δ*-3 carene and terpinene-4-ol; and ≈40% for a cyclic monoterpene with an endocyclic and an exocyclic double bond such as d-limonene. Secondary organic PM yields of close to 100% were observed during the photochemical oxidation of one sesquiterpene, trans-caryophyllene. These results were all obtained for initial hydrocarbon mixing ratios of 100 ppb, which are much higher than found in the atmosphere.

Kamens et al. (1999) observed SOPM yields of 20 to 40% for α-pinene. Using information on the composition of secondary PM formed from α-pinene (Jang and Kamens, 1999), they were able to calculate formation rates with a kinetic model including formation mechanisms for O_3 + α-pinene reaction products.

Griffin et al. (1999) introduced the concept of incremental aerosol reactivity, the change in the secondary organic aerosol mass produced (in $\mu g/m^3$) per unit change of parent organic reacted (in ppb), as a measure of the aerosol-forming capability of a given parent organic compound in a prescribed mixture of other organic compounds. They measured the incremental aerosol reactivity for a number of aromatic and biogenic compounds for four initial mixtures. Incremental aerosol reactivity ranged from 0.133 to 10.352 $\mu g\ m^{-3}\ ppb^{-1}$ and varied by almost a factor of two depending on the initial mixture.

A number of multifunctional oxidation products produced by the oxidation of biogenic hydrocarbons have been identified in laboratory studies (Yu et al., 1998; Glasius et al., 2000; Christoffersen et al., 1998; Koch et al., 2000; and Leach et al., 1999). Many of these compounds have subsequently been identified in field investigations (Yu et al., 1999; Kavouras et al., 1998, 1999a,b; Pio et al., 2001; and Castro et al., 1999). Most studies of the formation of secondary organic aerosol formation from terpenes have focused on their reactions with ozone. There have been many fewer studies dealing with the oxidation of terpenes initiated by OH radicals. Larsen et al. (2001) found that the major aerosol products produced ultimately from the reaction of OH radicals with monoterpenes with endocyclic double bonds (α-pinene, 3-carene) were C_{10} keto-carboxylic acids (such as pinonic and caronic acids); whereas the major products from the oxidation of monoterpenes with exocyclic double bonds (β-pinene) were C_9-dicarboxylic acids (such as pinic acid), and the major product from the oxidation of limonene (which has both endo- and exocyclic double bonds) was 3-acetyl-6-oxo-heptanal (keto-limonaldehyde). A large number of related aldehydes, ketones and acids were also found in their experiments. However, the total yields of condensable products are much lower than for the corresponding reactions with ozone. For example, yields of C_9-dicarboxylic acids, C_{10}-hydroxy-keto-carboxylic acids, and C_{10}-hydroxy-keto-aldehydes from the reaction of ozone with mono-terpenes with endocyclic double bonds ranged form 3% to 9%; whereas they ranged only from 0.4 to 0.6% in the reaction with OH radicals. Likewise, the reaction of monoterpenes with exocyclic double bonds with ozone produced much higher yields (1% to 4%) of C_8- and C_9-dicarboxylic acids than did their reaction with OH radicals (0.2% to 0.3%). Apart from the complex products noted above, it should be remembered that much simpler products, such as formaldehyde and formic acid, are also formed in much larger yields from the same reactants (e.g., Winterhalter et al., 2000). Compounds such as these also contribute to the formation of secondary organic aerosol according to the mechanisms given in Pandis et al. (1992) and mentioned earlier in this section.

It is worth noting that the dicarboxylic acids and hydroxy-keto-carboxylic acids have very low vapor pressures and may act as nucleating species in OH- and O_3-terpene reactions (Larsen et al., 2001). The rate coefficient for reaction of α-pinene with OH radicals is approximately a factor of 10^6 greater than for its reaction with O_3, based on data given in Atkinson (1994). The daytime average concentration of O_3 is typically a factor of 10^6 greater than that for OH radicals in polluted boundary layers; whereas the above mentioned yields of aerosol products are roughly a factor of ten greater in the O_3-initiated reaction than in the corresponding OH radical reaction. The foregoing analysis suggests that the O_3-initiated reaction may be more important than the OH-initiated reaction for the formation of aerosol products. During the day, new particles may be generated indoors through the infiltration of ambient ozone; and, because ambient ozone is also present at night in lower concentrations, new particles may be generated under these conditions at lower rates. For example, Wainman et al. (2000) found that ozone can react with limonene released by air fresheners in indoor environments to produce substantial quantities of submicron particles. The corresponding reaction involving OH radicals outdoors at night is expected to be negligible by comparison because of the very low OH concentrations present. Sarwar et al. (2002) estimated indoor OH radical concentrations and suggested that OH in indoor environments is produced mainly by reactions of ozone transported from outdoors and terpenes emitted from indoor sources. They reported that indoor OH levels ($1\text{-}5 \times 10^5$ OH/cm^3) are usually lower than typical urban outdoor daytime OH levels ($1\text{-}5 \times 10^6$ OH/cm^3). However, they can be greater than typical urban outdoor night time OH levels ($1\text{-}5 \times 10^4$ OH/cm^3). Although much progress has been made in determining the importance of anthropogenic and biogenic hydrocarbons for the formation of secondary organic PM, further investigations are needed to accurately assess their overall contributions to $PM_{2.5}$ concentrations.

Reactions of organic compounds either in particles or on the surface of particles have only come under study during the past 20 years. Tobias and Ziemann (2000) reported evidence for the formation of relatively stable low volatility peroxy hemiacetals from reactions of hydroperoxides with aldehydes and ketones on the surface of secondary organic particles. Not long after the publication of these results, Jang and Kamens (2001a) suggested, based on results of their outdoor Teflon chamber studies of SOPM formation from irradiation of toluene/propylene/NO_x /air mixtures, that carbonyls and hydroxy compounds (either within or on the surface of aromatic SOPM) could react together to form larger and less volatile hemiacetals and acetals. They also proposed that dissolved carbonyls could undergo further reactions leading to the formation of a polymer, a mechanism that has also been suggested by Edney et al. (2001). Jang and Kamens (2001b) carried out a series of screening experiments to assess whether volatile carbonyl compounds absorbed into particles could undergo heterogeneous reactions forming low vapor pressure compounds. Experiments were carried out in which aldehydes were introduced in Teflon bags in the dark in the presence of a seed aerosol containing either ammonium sulfate or a mixture of ammonium sulfate and sulfuric acid. The increase in the aerosol volume was then measured using a scanning mobility particle sizer. The aldehydes employed for the study included glyoxal, butanal, hexanal, octanal, and decanal. Increased organic aerosol yields were found in the presence of the ammonium sulfate seed aerosol for each of the carbonyls; the highest yield was found for hexanal followed in decreasing order by glyoxal and then octanal. The presence of the acidified sulfate salt significantly increased the yields even further. In a number of other experiments, 1-decanol was added to the carbonyl-aerosol system to investigate the possible formation of hemiacetals and/or acetals. Again, the volume of aerosol increased in both the presence of ammonium sulfate aerosol and the acidified salt with a significantly larger yield found in the presence of acidity.

To explain their findings for acid-catalyzed carbonyl reactions, Jang and Kamens (2001a,b) proposed a chemical mechanism in which the dissolved carbonyl first undergoes a protonization reaction forming an adduct that can react with water to form its hydrate (1,1-dihydroxy gem-diol). The adducts can then react with OH groups of the gem-diol forming higher molecular weight and less volatile dimers that are subject to further reactions. In principal, this process, which the authors refer to as a “zipping reaction” can lead to the formation of polymers. However, because the individual reactions are reversible, the process can be reversed by an unzipping reaction. The zipping process could serve as an important mechanism for SOPM formation by converting volatile oxidation products including glyoxal and methyl glyoxal into low volatility compounds. On the other hand, the unzipping process that could take place during the workup of the aerosol samples could be responsible for the detection of highly volatile oxidation products in SOPM, including glyoxal and methyl glyoxal, that has been reported by

Edney et al. (2001), Cocker et al. (2001), and Jang and Kamens (2001a). While these processes may take place in the absence of significant acidity, the experimental results suggest that the processes are likely enhanced by acid-catalyzed reactions. Further research is needed to determine the importance of the mechanisms proposed above for the ambient atmosphere.

Sampling and characterizing PM in the ambient atmosphere and in important microenvironments is required to address important issues in exposure, toxicology, and compliance. Currently, it is not possible to fully quantify the concentration, composition, or sources of the organic components. Many of the secondary organic aerosol components are highly oxidized, difficult to measure, multifunctional compounds. Additional laboratory studies are needed to identify such compounds; strategies need to be developed to sample and measure such compounds in the atmosphere; and models of secondary organic aerosol formation need to be improved and added to air quality models in order to address issues related to human exposure.

A high degree of uncertainty is associated with all aspects of the calculation of secondary organic PM concentrations. This is compounded by the volatilization of organic carbon from filter substrates during and after sampling as well as potential positive artifact formation from the absorption of gaseous hydrocarbon on quartz filters. Significant uncertainties always arise in the interpretation of smog chamber data because of wall reactions, sampling artifacts, and the use of unrealistically high concentrations of reactants. Limitations also exist in extrapolating the results of smog chamber studies to ambient conditions found in urban airsheds and forest canopies. Concentrations of terpenes and NO_x are much lower in forest canopies (Altshuller, 1983) than the levels commonly used in smog chamber studies. The identification of aerosol products of terpene oxidation has seldom been a specific aim of field studies, making it difficult to judge the results of model calculations of secondary organic PM formation.

Uncertainties also arise because of the methods used to measure biogenic hydrocarbon emissions. Khalil and Rasmussen (1992) found much lower ratios of terpenes to other hydrocarbons (e.g., isoprene) in forest air than were expected based on their relative emissions strengths and rate coefficients for reaction with OH radicals and O_3. In many cases, reactions with these species are capable of reducing the concentrations of monoterpenes to beneath minimum detection levels as has been found by others in a wide range of North American forest ecosystems (Guenther et al., 1996, Helmig et al., 1998, Geron et al., 2000). Thus, making judgments about the importance of additional loss processes can be a highly problematic exercise given uncertainties in obtaining relevant OH radical and O_3 concentrations and in the reaction rate coefficients. The ocimenes and sesquiterpenes are estimated to have half lives of seconds to minutes in the presence of ambient ozone levels while the pinenes and isoprene have lifetimes ranging from several hours to days. Reaction with hydroxyl radicals is the major sink for isoprene. Khalil and Rasmussen offered two explanations for their findings: (1) either the terpenes were being removed rapidly by some heterogeneous process or (2) emissions were enhanced artificially by feedbacks caused by the bag enclosures they used. The isoprene emission rates observed by Khalil and Rasmussen (1992) are reasonably consistent with those found by Geron et al. (2000a and 2001) given inevitable self-shading of much of the foliage within the bag enclosures and also the lower position of the foliage within the accessible portion of the sampled tree crowns. Temperatures were sufficiently warm ($\geq$30 °C) and sunny to induce high isoprene emission although cloudiness from a passing thunderstorm could have reduced these emissions from some of the species considerably. Disturbance or elevated temperatures may also have induced elevated monoterpene emissions from several of the species sampled by Khalil and Rasmussen because emissions rates they reported are in many cases 2-20 times higher than those reported by other investigators, including those who performed enclosure studies which did not cause elevated temperatures as well as micrometeorological flux studies which did not disturb the forest canopy. Thus the somewhat reduced isoprene emissions, combined with elevated monoterpene emissions, can indeed affect the comparison of ambient isoprene versus monoterpene emissions. However, monoterpene compounds recently have been found to undergo heterogenous reactions on the surface of acid aerosol particles. Further work is needed to assess the importance of these reactions on ambient monoterpene concentrations and in the rate of production of secondary organic PM in forest ecosystems.

3.3.2 Source Contributions to Ambient PM Determined by Receptor Models

Receptor models are perhaps the primary means used to estimate the contributions of different source categories to PM concentrations at individual monitoring sites. Dispersion models (i.e., three-dimensional chemistry and transport models) are formulated in a prognostic manner (i.e., they attempt to predict species concentrations using a tendency equation that includes terms based on emissions inventories, atmospheric transport, chemical transformations, and deposition). Receptor models are diagnostic in their approach (i.e., they attempt to derive source contributions based either on ambient data alone or in combination with data from the chemical composition of sources). These methods have the advantage that they do not invoke all of the uncertainties inherent in emissions inventories or in parameterizing atmospheric transport processes in grid point models.

There are two main approaches to receptor modeling. Receptor models such as the chemical mass balance (CMB) model (Watson et al., 1990a) relate source category contributions to ambient concentrations based on analyses of the composition of ambient particulate matter and source emissions samples. This technique has been developed for apportioning source categories of primary particulate matter and was not formulated to include the processes of secondary particulate matter formation. In the second approach, various forms of factor analysis are used that rely on the analysis of time series of compositional data from ambient samples to derive both the composition of sources and the source contributions. Standard approaches such as factor analysis or Principal Component Analysis (PCA) can apportion only the variance and not the mass in an aerosol composition data set. The other techniques described below, PMF and UNMIX, do apportion mass, however. Positive matrix factorization (PMF) is a recently developed multivariate technique (Paatero and Tapper, 1993; 1994) that overcomes many of the limitations of standard techniques, such as PCA, by allowing for the treatment of missing data and data near or below detection limits. This is accomplished by weighting elements inversely according to their uncertainties. Standard methods such as PCA weight elements equally regardless of their uncertainty. Solutions also are constrained to yield non-negative factors. Both the CMB and the PMF approaches find a solution based on least squares fitting and minimize an object function. Both methods provide error estimates for the solutions based on estimates of the errors in the input parameters. It should be remembered that the error estimates often contain subjective judgments. For a complete apportionment of mass, all of the major sources affecting a monitoring site must be sampled for analysis by CMB; whereas there is no such restriction in the use of PMF.

Among other approaches, the UNMIX model takes a geometric approach that exploits the covariance of the ambient data to determine the number of sources, the composition and contributions of the sources, and the uncertainties (Henry, 1997). A simple example may help illustrate the approach taken by UNMIX. In a two-element scatter plot of ambient Al and Si, a straight line and a high correlation for Al versus Si can indicate a single source for both species (soil) while the slope of the line gives information on the composition of the soil source. In the same data set, iron may not plot on a straight line against Si, indicating other sources of Fe in addition to soil. More importantly, the Fe-Si scatter plot may reveal a lower edge. The points defining this edge represent ambient samples collected on days when the only significant source of Fe was soil. Success of the UNMIX model hinges on the ability to find these "edges" in the ambient data from which the number of source types and the source compositions are extracted. UNMIX uses principal component analysis to find edges in m-dimensional space, where m is the number of ambient species. The problem of finding edges is more properly described as finding hyperplanes that define a simplex. The vertices at which the hyperplanes intersect represent pure sources from which source compositions can be determined. However, there are measurement errors in the ambient data that "fuzz" the edges making them difficult to find. UNMIX employs an "edge-finding" algorithm to find the best edges in the presence of error. UNMIX does not make explicit use of errors or uncertainties in the ambient concentrations, unlike the methods outlined above. This is not to imply that the UNMIX approach regards data uncertainty as unimportant, but rather that the UNMIX model results implicitly incorporate error in the ambient data. The underlying philosophy is that the uncertainties are often unquantifiable, and hence it is best to make no *a priori* assumptions about what they are.

In addition to chemical speciation data, Norris et al. (1999) showed that meteorological indices could prove useful in identifying sources of particulate matter that are responsible for observed health effects (specifically asthma) associated with exposure to particulate matter. They examined meteorology associated with elevated pollution events in Spokane and Seattle, WA, and identified a "stagnation index" that was associated with low wind speeds and increases in concentrations of combustion-related pollutants. Their factor analysis also identified a meteorological index (low relative humidity and high temperatures) that was associated with increases in soil-derived particulate matter as well as a third factor (low temperatures and high relative humidity) that was associated with increases in concentrations of particulate sulfate and nitrate species (Norris, 1998).

Ondov (1996) examined the feasibility of using sensitive isotopic and elemental tracer materials to determine the contributions of petroleum-fueled sources of PM_{10} in the San Joaquin Valley, CA. Costs of these experiments are affected not only by the tracer materials cost, but also by the sensitivities of the analytical methods for each, as well as the background levels of the tracers. Suarez et al. (1996) used iridium as a tracer to tag emissions from diesel-burning sanitation trucks in Baltimore and determined the size distribution of soot from the trucks.

A number of specialty conference proceedings, review articles, and books have been published that provide greater detail about source category apportionment receptor models than described in the 1996 PM AQCD. A review of the various methods used to apportion PM in ambient samples among its source categories was given in Section 5.5.2 of the 1996 PM AQCD. The collection of the source category characterization profiles shown in Appendix 3D has been motivated in many cases by the need to use them in receptor modeling applications.

The results of several source apportionment studies are discussed in this section to provide an indication of the relative importance of different sources of particulate matter across the United States. First, results obtained mainly by using the chemical mass balance (CMB) approach for estimating contributions to $PM_{2.5}$ from different source categories at monitoring sites in the United States are discussed and presented in Table 3-9. More recent results using the PMF approach are included for Phoenix, AZ. Results obtained at a number of monitoring sites in the central and western United States by using the CMB model for PM_{10} are shown in Table 3-10. The sampling sites represent a variety of different source characteristics within different regions of Arizona, California, Colorado, Idaho, Illinois, Nevada, and Ohio. Definitions of source categories also vary from study to study. The results of the PM_{10} source apportionment studies were given in the 1996 PM AQCD and are presented here to allow easy comparison with results of $PM_{2.5}$ source apportionment studies. Chow and Watson (2002) present a detailed comparison of numerous studies using the CMB model performed mainly after 1995.

There are several differences between the broadly defined source categories shown at the tops of Tables 3-9 and 3-10. These differences reflect the nature of sources that are important for producing fine and coarse particulate matter shown in Table 3-8. They also are related to improvements in the ability to distinguish between sources of similar nature (e.g., diesel and gasoline vehicles, meat cooking, and vegetation burning). The use of organic tracers allows motor vehicle emissions to be broken down into contributions from diesel and gasoline vehicles. In studies where this distinction cannot be made, the source type is listed as ‘total motor vehicles’ in the tables. The studies that were reported to be able to distinguish gasoline- from

TABLE 3-9. RECEPTOR MODEL SOURCE CONTRIBUTIONS TO $PM_{2.5}$

	% Contribution												
Sampling Site	Measured $PM_{2.5}$ Concentration	Total Motor Vehicles	Diesel	Gasoline Vehicles	Road Dust, Soil	Vegetation Burning	Secondary Sulfate	Secondary Nitrate	Misc. Source 1	Misc. Source 2	Misc. Source 3	Misc. Source 4	Total % Allocated
Pasadena, CA 1982[1]	28.2	—	18.8	5.7	12.4	9.6	20.9	7.4	5.3[a]	9.2[b]	8.5[c]	1.1[d]	98.9
Downtown LA, CA 1982[1]	32.5	—	35.7	6.5	11.1	5.8	20.3	9.2	3.7[a]	9.2[b]	5.2[c]	0.6[d]	107.3
West LA, CA 1982[1]	24.5	—	18.0	5.7	12.2	11.0	24.1	7.8	4.1[a]	9.4[b]	8.2[c]	1.6[d]	102.1
Rubidoux, CA 1982[1]	42.1	—	12.8	0.7	13.1	1.2	13.8	24.7	4.5[a]	12.1[b]	4.5[c]	0.5[d]	87.9
Sacramento, CA Winter 1991-96[2]	39.5	24.5[e]	—	—	1.2	18.1	4.5	36.6	—	—	—	—	84.9
Bakersfield, CA Winter 1996[3]	52.0	16.0[e]	—	—	< 3	20.0	7.0	34.0	—	—	—	—	< 80
Fresno, CA Winter 1996[3]	63.0	13.0[e]	—	—	< 3	19.0	5.0	32.0	—	—	—	—	< 85
Philadelphia, PA Summer 1982[4]	27.0	8.5[e]	—	—	4.4	—	81.9[f]	—	2.2[g]	1.9[h]	0.4[i]	—	99.3
Camden, NJ Summer 1982[4]	28.3	9.2[e]	—	—	3.2	—	81.3[f]	0.4	2.5[g]	2.5[h]	0.7[i]	—	99.8
Clarksboro, NJ Summer 1982[4]	26.0	5.8[e]	—	—	2.7	—	84.6[f]	—	0.8[g]	1.5[h]	0.4[i]	—	95.8
Grover City, IL ENE[j] 1986-87[5]		—	—	—	2.3	—	83.2[f]	—	9.7[k]	3.0[l]	1.2[g]	—	99.4
Grover City, IL SSW[j] 1986-87[5]		—	—	—	—	—	59.0[f]	—	11.6[k]	11.9[l]	4.1[g]	4.6[m]	91.2
Grover City, IL WNW[j] 1986-87[5]		2.4[e]		—	5.1	—	88.5[f]	—	2.8[k]	—	—	—	98.8
Grover City, IL NNW[j] 1986-87[5]		—	—	—	3.1	—	86.6[f]	—	3.4[l]	3.0[n]	—	—	96.0
Reno, NV Summer 1998[6]	7.8	68.0[e]	—	—	14.5	4.0	11.0	2.0	0.6[q]	—	—	—	100.1
Phoenix, AZ Summer 1995-98[7]	8.3	—	10.9	36.2	1.8	15.0	—	—	20.8[n]	4.9[r]	6.7[s]	3.6[q]	99.9
Phoenix, AZ Winter 1995-98[7]	13.8	—	14.5	38.9	1.1	8.9	—	—	9.5[n]	4.5[r]	18.7[s]	4.1[q]	100.2

[1] Schauer et al. (1996)
[2] Motallebi (1999)
[3] Magliano et al. (1998)
[4] Dzubay et al (1988)
[5] Glover et al. (1991)
[6] Gillies et al. (2000)
[7] Ramadan et al. (2000)

[a] Secondary and other organic compounds
[b] Secondary ammonium
[c] Meat cooking
[d] Vegetative detritus
[e] Value represents sum of diesel and gasoline vehicle exhaust
[f] Including associated cations and water
[g] Incinerators
[h] Oil fly ash
[i] Fluidized catalyst cracker
[j] Wind direction
[k] Lead smelter
[l] Iron works
[m] Copper smelter
[n] Coal power plant
[o] As ammonium sulfate
[p] As ammonium nitrate
[q] Sea salt
[r] Wood burning
[s] Nonferrous smelting

TABLE 3-10. RECEPTOR MODEL SOURCE CONTRIBUTIONS TO PM_{10}

		% Contribution										
Sampling Site	Measured PM_{10} Concentration	Primary Geological	Primary Construction	Primary Motor Vehicle Exhaust	Primary Vegetative Burning	Secondary Ammonium Sulfate	Secondary Ammonium Nitrate	Misc. Source 1	Misc. Source 2	Misc. Source 3	Misc. Source 4	Total % Allocated
Craycroft, AZ Winter 1989-1990[1]	23.4	55.6	0.0	35.5	0.0	3.0	2.6	5.1[a]	0.0	0.0	0.0	101.8
Hayden 1, AZ 1986[1]	105.0	4.8	1.9[b]	0.0	0.0	3.8	0.0	70.5[c]	4.8[d]	1.0[e]	0.0	86.6
Hayden 2, AZ 1986[1]	59.0	35.6	6.8[b]	0.0	0.0	6.8	0.0	47.5[c]	0.0	1.7[e]	0.0	98.4
Rillito, AZ 1988[2]	79.5	53.7	17.4[b]	1.5[f]	0.0	0.0	0.0	14.6[g]	0.0	0.0	0.0	87.2
Bakerfield, CA 1988-1989[3]	79.6	53.9	2.0	9.7	8.2	6.9	16.0	1.3[m]	1.9[n]	0.8[k]	0.0	100.7
Crows Landing, CA 1988-1989[3]	52.5	61.3	0.0	4.2	6.5	5.3	12.4	1.0[m]	1.9[n]	2.3[k]	0.0	94.9
Fellows, CA 1988-1989[3]	54.6	53.1	2.6	3.8	6.2	9.3	13.7	12.8[m]	2.6[n]	2.6[k]	0.0	106.7
Fresno, CA 1988-1989[3]	71.5	44.5	0.0	9.5	7.1	5.0	14.5	0.4[m]	1.9[n]	0.1[k]	0.0	83
Indio, CA[4]	58.0	56.9	5.2	7.6	12.2	6.2	7.1	0.3[j]	1.7[h]	0.0	0.0	97.2
Kern Wildlife Refuge, CA 1988-1989[3]	47.8	31.6	4.2	4.6	8.4	6.9	3.1	1.0[m]	3.1[n]	1.5[k]	0.0	64.4
Long Beach, CA 1986[5]	51.9	39.9	0.0	9.8[i]	0.0	15.4	17.7	0.2[j]	3.9[h]	12.3[k]	0.0	63.2
Long Beach, CA Summer 1987[6]	46.1	24.1	0.0	13.7	0.0	23.6	1.7	0.2[j]	4.8[h]	0.0	0.0	68.1
Long Beach, CA Fall 1987[6]	96.1	11.8	0.0	44.5	0.0	4.0	24.1	0.0[j]	2.8[h]	0.0	0.0	87.2
Riverside, CA 1988[7]	64.0	50.9	0.0	10.9	0.0	7.5	33.4	0.5[j]	2.0[h]	1.7[o]	0.0	106.9
Rubidoux, CA 1986[5]	87.4	49.3	4.6	6.4[i]	0.0	7.3	24.4	0.3[j]	1.1[h]	6.8[k]	0.0	100.2
Rubidoux, CA Summer 1987[6]	114.8	30.4	3.9	15.1	0.0	8.3	23.9	0.0[j]	4.4[h]	0.0	0.0	86

TABLE 3-10 (cont'd). RECEPTOR MODEL SOURCE CONTRIBUTIONS TO PM_{10}

		% Contribution										
Sampling Site	Measured PM_{10} Concentration	Primary Geological	Primary Construction	Primary Motor Vehicle Exhaust	Primary Vegetative Burning	Secondary Ammonium Sulfate	Secondary Ammonium Nitrate	Misc. Source 1	Misc. Source 2	Misc. Source 3	Misc. Source 4	Total % Allocated
Rubidoux, CA Fall 1987[6]	112.0	17.1	14.4	27.1	0.0	1.9	28.2	0.0[j]	1.0[h]	0.0	0.0	89.7
Rubidoux, CA 1988[7]	87.0	55.2	0.0	11.7	0.0	6.1	24.9	0.6[j]	1.7[h]	6.6[o]	0.0	106.8
San Nicolas Island, CA Summer 1987[6]	17.4	9.2	0.0	5.2	0.0	21.3	2.9	0.0[j]	24.7[h]	0.0	0.0	63.3
Stockton, CA 1989[3]	62.4	55.1	0.8	8.3	7.7	5.0	11.2	1.1[m]	2.9[n]	0.0[k]	0.0	92.1
Pocatello, ID 1990[8]	100.0	8.3	7.5[q]	0.1	0.0	0.0	0.0	0.0	0.0	84.1[r]	0.0	100
S. Chicago, IL 1986[9]	80.1	34.0	3.0	3.5	0.0	19.2[s]	—	18.9[t]	2.7[u]	0.0	0.0	81.3
S.E. Chicago, IL 1988[10]	41.0	35.9[v]	0.0	2.2[f]	0.0	18.8	—	2.0[t]	0.7[h]	2.7[w]	18.8[g]	81.1
Reno, NV 1986-87[11]	30.0	49.7	0.0	33.3	6.3	4.3	2.0	0.0	0.0	0.0	0.0	95.6
Sparks, NV 1986-87[11]	41.0	36.8	0.0	28.3	32.7	6.6	2.2	0.0	0.0	0.5[k]	0.0	107.1
Follansbee, WV 1991[12]	66.0	15.2	0.0	53.0	0.0	24.2	—	14.1[t]	0.0	0.0	0.0	106.5
Mingo, OH 1991[12]	60.0	20.0	0.0	23.3	6.8	25.0	—	5.7[t]	18.3[x]	0.0	0.0	99.1
Steubenville, OH 1991[12]	46.0	18.0	0.0	30.4	1.7	30.4	—	8.3[t]	10.9[x]	0.0	0.0	99.7

[1] Chow et al. (1992a)
[2] Garfield; Ryan et al. (1988)
[3] Jail; Ryan et al. (1988)
[4] Thanukos et al. (1992)
[5] Chow et al. (1992b)
[6] Kim et al. (1992)
[7] Gray et al. (1988)
[8] Watson et al. (1994)
[9] Chow et al. (1992c)
[10] Houck et al. (1992)
[11] Hopke et al. (1988)
[12] Vermette et al. (1992)
[13] Chow et al. (1988)
[14] Skidmore et al. (1992)
[a] Smelter background aerosol
[b] Cement plant sources, including kiln stacks, gypsum pile, and kiln area
[c] Copper ore
[d] Copper tailings
[e] Copper smelter building
[f] Heavy-duty diesel exhaust emission
[g] Background aerosol
[h] Marine aerosol, road salt, and sea salt plus sodium nitrate
[i] Motor vehicle exhaust from diesel and leaded gasoline
[j] Residual oil combustion
[k] Secondary organic carbon
[l] Biomass burning
[m] Primary crude oil
[n] $NaCl + NaNO_3$
[o] Lime
[p] Road sanding material
[q] Asphalt industry
[r] Phosphorus/phosphate industry
[s] Regional sulfate
[t] Steel mills
[u] Refuse incinerator
[v] Local road dust, coal yard road dust, and steel haul road dust
[w] Incineration
[x] Unexplained mass

diesel-fueled vehicles found that gasoline vehicles make significant, and sometimes the dominant, contributions to ambient $PM_{2.5}$ concentrations. Meat cooking is also distinguished from vegetation burning in more recent studies although both are considered to be part of biomass burning. Vegetation burning consists of contributions from residential fuel wood burning, wildfires, prescribed burning, and burning of agricultural and other biomass waste. Miscellaneous sources of fine particles include contributions from combustion sources; whereas miscellaneous sources of coarse particles consist of contributions from soil and sea spray and industrial processing of geological material (e.g., cement manufacturing). Although a large number of elements and chemical components are used to differentiate among source categories and although there can be a large number of source types affecting a given site, only a few broadly defined source types are needed to account for most of the mass of $PM_{2.5}$ and PM_{10}. At any given site, $\leq$ 5 source types account for > 65% of the mass of $PM_{2.5}$ (Table 3-9); and $\leq$5 source types account for > 65% of the mass of PM_{10} (Table 3-10).

Secondary sulfate is the dominant component of $PM_{2.5}$ samples collected in the studies of Dzubay et al. (1988) and Glover et al. (1991). Both studies found that sulfate at their monitoring site arose from regionally dispersed sources. Sulfate also represents the major component of $PM_{2.5}$ found in monitoring studies in the eastern United States shown in Appendix 6A of the 1996 PM AQCD. Primary and secondary organic components also make major contributions to $PM_{2.5}$. Contributions from road dust and soils are relatively minor, typically constituting less than 10% of $PM_{2.5}$ in the studies shown in Table 3-9. Studies in the western United States shown in Table 3-9 have found larger contributions from motor vehicles, fugitive dust, and ammonium nitrate. The most notable difference in the relative importance of major source categories of $PM_{2.5}$ shown in Table 3-9 and PM_{10} shown in Table 3-10 involves crustal material, (e.g., soil, road dust), which represents about 40% on average of the total mass of PM_{10} in the studies shown in Table 3-10. The fraction is higher at sites located away from specific sources such as sea spray or smelters. Emissions of crustal material are concentrated mainly in the $PM_{10-2.5}$ size range.

In Table 3-10, primary motor vehicle exhaust contributions are highly variable and can account for over 40% of average PM_{10} at a few of the sampling sites. Vehicle exhaust contributions are also variable at different sites within the same study area. The mean value and the variability of motor vehicle exhaust contributions reflects the proximity of sampling sites to roadways and traffic conditions during the time of sampling. Many studies were conducted during the late 1980s when a portion of the vehicle fleet still used leaded gasoline. Pb and Br in motor vehicle emissions facilitated the distinction of motor vehicle contributions from other sources. Vehicles using leaded fuels have higher emission rates than vehicles using unleaded fuels. Pb also poisons automobile exhaust catalysts and produces adverse human health effects. As a result, Pb has been eliminated from vehicle fuels. Organic species such as n-pentacosane through n-nonacosene, cholestanes, ergostanes, sitostanes, and hopanes have replaced Pb as a source marker for motor vehicle emissions (e.g., Schauer and Cass, 2000). In their comprehensive review of CMB modeling studies undertaken since 1995, Chow and Watson (2002) note that in twenty-two studies fossil fuel combustion was found to be a large contributor to $PM_{2.5}$ and PM_{10} concentrations, with most of the contributions to primary PM originating from the exhaust of diesel and gasoline vehicles.

Marine aerosol is found, as expected, at coastal sites such as Long Beach (average 3.8% of total mass) and San Nicolas Island (25%). These contributions to PM_{10} are relatively variable and are larger at the more remote sites. Individual values reflect proximity to local sources. Of great importance are the contributions from secondary ammonium sulfate in the eastern United States and ammonium nitrate in the western United States. Secondary ammonium sulfate is especially noticeable at sites in California's San Joaquin Valley (Bakersfield, Crows Landing, Fellows, Fresno, and Stockton) and in the Los Angeles area.

Because many source apportionment studies address problems in compliance with the National Ambient Air Quality Standards and other air quality standards, samples selected for chemical analysis are often biased toward the highest PM_{10} mass concentrations in the studies shown in Table 3-10. Thus, the average source contribution estimates shown in Table 3-10 are probably not representative of annual averages and may not be representative of a large spatial area for some source-dominated studies. For example, the study by Motallebi (1999) considered only days when the PM_{10} concentration was greater than 40 $\mu g/m^3$. Quoted uncertainties in the estimated contributions of the individual sources shown in Tables 3-9 and 3-10 range from 10 to 50%. Errors can be much higher when the chemical source profiles for different sources are highly uncertain or are too similar to distinguish one source from another.

Very few source apportionment studies using the CMB modeling technique have examined the spatial variability of source contributions at different sites within an urban area. As can be seen from Table 3-9, Dzubay et al. (1988) found a uniform distribution of sulfate at the NE Airport in Philadelphia, PA; downtown Camden, NJ; and Clarksboro, NJ, during the summer of 1982. The farthest distance between two monitoring sites (NE Airport and Clarksboro) was approximately 40 km. Magliano et al. (1998) examined the spatial variability of PM_{10} source contributions at a number of sites in Fresno and Bakersfield, CA, during the winter of 1995-1996 and reported values for 1 day, December 27, 1995. During that day, mobile sources contributed from 13.0 to15.8 $\mu g/m^3$, vegetation burning contributed from 5.1 to 11.1 $\mu g/m^3$, ammonium sulfate contributed 2.4 to 3.4 $\mu g/m^3$, and ammonium nitrate contributed 19.3 to 24.6 $\mu g/m^3$ to PM_{10} at the sites in Bakersfield. Mobile sources contributed 13.9 to 22.5 $\mu g/m^3$, vegetation burning contributed 8.2 to 15.7 $\mu g/m^3$, ammonium sulfate contributed 1.8 to 2.3 $\mu g/m^3$, and ammonium nitrate contributed 14.5 to 18.9 $\mu g/m^3$ at the sites in Fresno. All of these components are expected to be found mainly in the $PM_{2.5}$ size fraction. As can be seen, source contributions at different sites varied by factors of 1.2 to 2.2 in Bakersfield and by factors of 1.3 to 1.9 in Fresno on that day.

The receptor modeling methods outlined above do not explicitly include consideration of the distances between PM sources and the receptor site. Information about the relative importance of sources as a function of distance may be available from examination of data obtained by continuous monitoring methods. For example, concentration spikes are expected to be the result of transport from nearby sources because turbulent mixing in the atmosphere would not allow them to persist for very long. Short duration spikes in the time series of concentrations are assumed to result from emissions from local sources (0.1 to 1 km away) in this method. Contributions from sources located further away are determined by comparisons between baselines measured at different sites. Details such as these are also lost in integrated 24-h samples. Watson and Chow (2001) used time series of black carbon (BC) obtained by aetholometers over five minute intervals to estimate the contributions from sources located < 1 km away, 1 to 5 km away, and > 5 km away from a monitoring site in downtown Mexico City. They found that most of the BC was produced by sources scattered throughout the city and that sources located less than 1 km away from the site contributed only about 10% to BC concentrations even in the presence of local sources such as buses and trucks.

3.3.3 Background Concentrations of PM in the United States

This section contains information about the concentrations of "background" PM that are relevant for policy setting. For the purposes of this document (and consistent with the 1996 PM AQCD), background concentrations are those that would result in the United States from emissions from natural sources worldwide plus anthropogenic sources outside of North America. In other words, they are the concentrations that would exist if anthropogenic emissions in North America were zero. Concentrations defined this way will be referred to here as policy relevant background (PRB) concentrations. It is impossible to obtain estimates of PRB concentrations solely by examining measurements of $PM_{2.5}$, $PM_{10-2.5}$, or PM_{10} concentrations because of long-range transport from anthropogenic source regions within North America. Other additional information must be used.

Annual average natural background concentrations of PM_{10} have been estimated to range from 4 to 8 $\mu g/m^3$ in the western United States and 5 to 11 $\mu g/m^3$ in the eastern United States. Corresponding $PM_{2.5}$ levels have been estimated to range from 1 to 4 $\mu g/m^3$ in the western United States and from 2 to 5 $\mu g/m^3$ in the eastern United States; $PM_{10-2.5}$ levels have been very roughly estimated at 3 $\mu g/m^3$ in both the East and the West, with a range of 0 to 9 $\mu g/m^3$ in the East and 0 to 7 $\mu g/m^3$ in the West (U.S. Environmental Protection Agency, 1996). The estimated natural background concentrations given above do not include contributions from long-range transport from sources outside North America. Values in the lowest 5th percentile annual mean $PM_{2.5}$ concentrations for specific sites in the AIRS data base range from 2.8 $\mu g/m^3$ to 6.9 $\mu g/m^3$. This range is consistent with the range of annual mean $PM_{2.5}$ concentrations at IMPROVE network sites in the western United States (cf., Appendix E). However, $PM_{2.5}$ concentrations are much higher at sites in the eastern United States than at sites in the western United States. At most IMPROVE sites in the western United States, the annual mean concentration of $PM_{10-2.5}$ is higher than that of $PM_{2.5}$, and daily average $PM_{2.5}$ concentrations are moderately correlated ($r = 0.72$) with $PM_{10-2.5}$ concentrations. In contrast, $PM_{2.5}$ concentrations are higher than those of $PM_{10-2.5}$ at IMPROVE sites in the eastern United States, and $PM_{2.5}$ concentrations are only weakly correlated ($r = 0.26$) with those of $PM_{10-2.5}$. Peak 24-h average natural background concentrations may be substantially higher than the annual or seasonal average natural background concentrations, especially within areas affected by wildfires and dust storms.

Sources of PM that fit under the definition of PRB are located either within or outside of North America.

Long-Range Transport from Outside North America

Windblown dust from dust storms in the Sahara desert has been observed in satellite images as plumes crossing the Atlantic Ocean and reaching the southeast coast of the United States (e.g., Ott et al., 1991). Dust transport from the deserts of Asia across the Pacific Ocean also occurs (Prospero, 1996). Most dust storms in the deserts of China occur in the spring following the passage of strong cold fronts after the snow has melted and before a surface vegetation cover has been established. Strong winds and unstable conditions result in the rapid transport of dust to altitudes of several kilometers where it is transported by strong westerly winds out over the Pacific Ocean (Duce, 1995). Satellite images were used to track the progress of a dust cloud from the Gobi desert to the northwestern United States during the spring of 1998 (Husar et al., 2000).

Satellite images obtained at visible wavelengths cannot track mineral dust across the continents because of a lack of contrast between the plume and the underlying surface. Other means must be used to track the spread of North African dust through the eastern United States. Perry et al. (1997) used two criteria ($PM_{2.5}$ soil concentration > 3 $\mu g\ m^{-3}$ and Al/Ca > 3.8) to distinguish between soil of local origin from soil originating in North Africa in characterizing the sources of PM in aerosol samples collected in the IMPROVE network. North African dust has been tracked as far north as Illinois (Gatz and Prospero, 1996) and Maine (Perry et al., 1997). The analysis of Perry et al. (1997) indicates that incursions of Saharan dust into the continental United States have occurred, on average, about three times per year from 1992 to 1995. These events persist for about 10 days on average, principally during the summer. Large scale dust events typically cover from 15 to 30% of the area of the continental United States and result in increases of $PM_{2.5}$ levels of $8.7 \pm 2.3\ \mu g\ m^{-3}$ throughout the affected areas during these events, with mean maximum dust contributions of $19.7 \pm 8.4\ \mu g\ m^{-3}$ and a peak contribution of 32 $\mu g\ m^{-3}$ to 24-h average $PM_{2.5}$ levels.

As can be expected, the frequency of dust events is highest in the southeastern United States. About half of these events are observed only within the state of Florida and are associated with dense hazes in Miami (Figure 3-22) during the summer (Prospero et al., 1987).

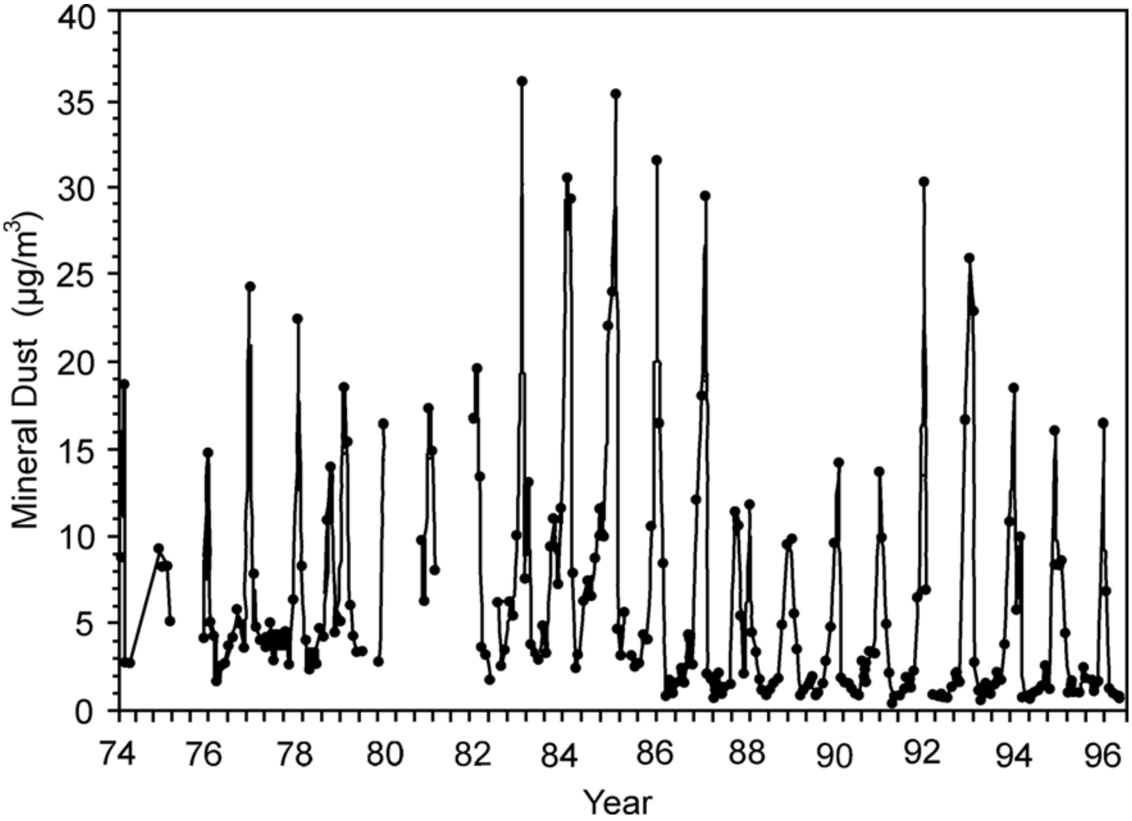

Figure 3-22. Monthly average Saharan dust components of the aerosol sampled in Miami, FL, from 1974 to 1996. Approximately one-third to one-half of Saharan dust is in the $PM_{2.5}$ size range.

Source: Prospero (1999).

North African dust is the dominant aerosol constituent in southern Florida during the summer; whereas soil dust constitutes only a minor fraction of PM during the remainder of the year (Prospero, 1999). Approximately one-third to one-half of the mass of the particles reaching southern Florida have aerodynamic diameters less than 2.5 micrometers (Prospero et al., 2001). During episodes when daily total dust concentrations ranged up to 100 $\mu g/m^3$, it can be seen that daily $PM_{2.5}$ concentrations of up to 50 $\mu g/m^3$ could have resulted in Miami, FL.

Husar et al. (2000) documented the transport of dust from the Gobi and Taklimakan deserts to North America during April 1998. The PM_{10} concentration averaged over 150 stations in Washington, Oregon, California, Nevada, and Idaho reporting data to AIRS was 65 $\mu g/m^3$

between April 26 and May 1, compared to about 20 µg/m^3 during the rest of April and May. Data from several networks indicated that PM$_{10}$ concentrations were over 100 µg/m^3 in central British Columbia, Washington State, and Oregon. The highest PM concentrations observed were 120 µg/m^3 for PM$_{10}$ and 50 µg/m^3 for PM$_{2.5}$ at Chilliwack Airport in northwestern Washington State (Figure 3-23). Aircraft measurements made over the northwestern United States were consistent with a mass median diameter of the dust being between 2 and 3 µm.

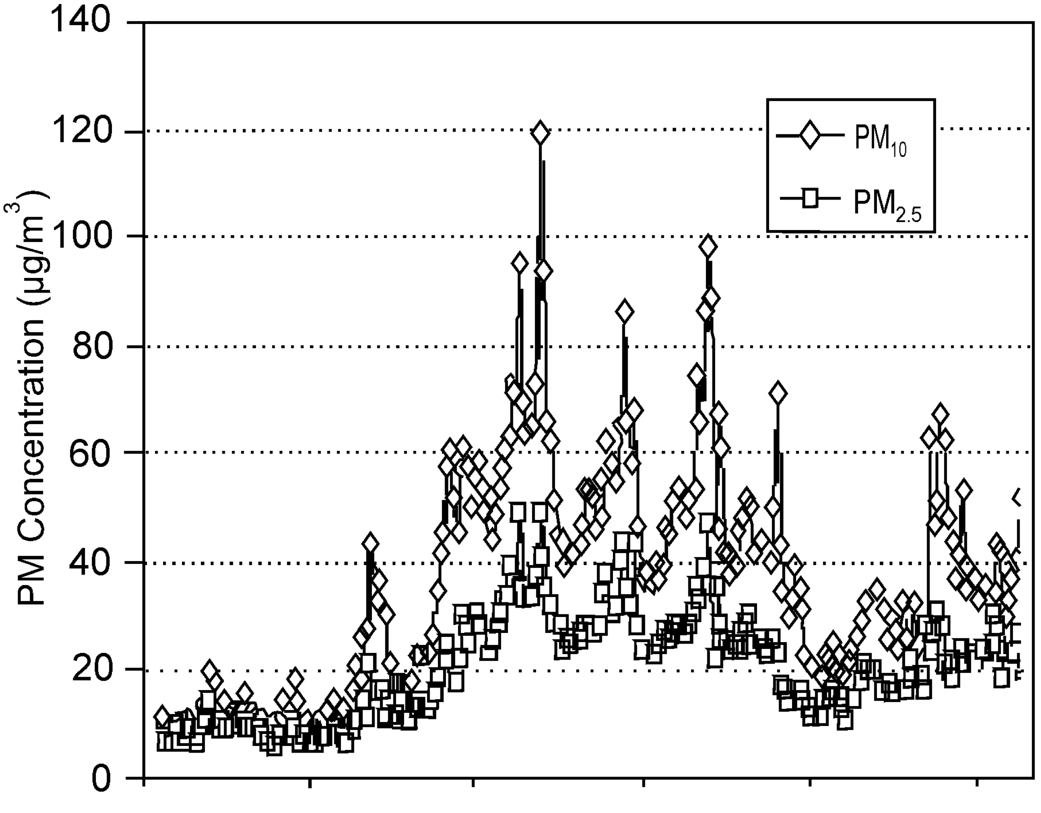

Figure 3-23. PM$_{2.5}$ and PM$_{10}$ concentrations measured at Chilliwack Airport, located in northwestern Washington State, just before and during the Asian desert dust episode of April and May 1998.

Source: Aerometric Information Retrieval System (AIRS; U.S. Environmental Protection Agency, 2002b).

Desert dust deposited over oceans provides nutrients to marine ecosystems (Savoie and Prospero, 1980). Desert dust deposited on nutrient depleted soils also provides nutrients, as in Hawaiian rain forests (Chadwick et al., 1999). Microorganisms, including fungi and bacteria, have been found attached to African dust particles in the U.S. Virgin Islands (Griffin et al., 2001). The fungus, *Aspergillus sydowii*, which has been connected to the death of coral reefs, has been identified in air samples collected in the Caribbean during African dust transport events (Smith et al., 1996; Shinn et al., 2000). Measurements of the composition of Saharan dust in Miami indicate enhancements of nitrate, non-sea-salt sulfate, ammonium, and trace metals over concentrations expected for clean marine air, suggesting pollution emitted in Europe and North Africa as sources (Prospero, 1999). It is likely that many other constituents will be found associated with dust from outside North America as more measurements are made. It should be noted that, as North African dust and associated material are transported northward through the United States during the summer, they are added to the mixture of primary and secondary PM generated domestically.

The transport of PM from uncontrolled biomass burning in Central America and southern Mexico resulted in anomalously high PM levels observed in southern Texas and generally elevated PM concentrations throughout the entire central and southeastern United States during the spring and early summer of 1998. Biomass burning for agricultural purposes occurs normally during the spring of each year in Central America and southern Mexico. During the spring of 1998, fires burned uncontrollably because of abnormally hot and dry conditions associated with the intense El Niño of 1997 to 1998. PM_{10} concentrations observed in the southern Rio Grande Valley were elevated substantially during the passage northward of the biomass burning plume produced by these fires as shown in Figure 3-24. Elevated PM_{10} concentrations also were found as far north as St. Louis, MO (Figure 3-25). As can be seen from Figure 3-24 and Figure 3-25, the elevations in PM concentrations were limited in duration. Uncontrolled wildfires occur in the United States every year, but their effects on air quality throughout the United States still need to be evaluated systematically. These fires can be widespread, and the frequency of their occurrence can vary markedly from year to year. For example, approximately 26,000 km^2 of forested land were consumed during 2000, but only a small fraction of this area was burnt during 2001 in the western United States. Wildfires also occur throughout the boreal forests of Canada. Wotawa and Trainer (2000) suggested that the

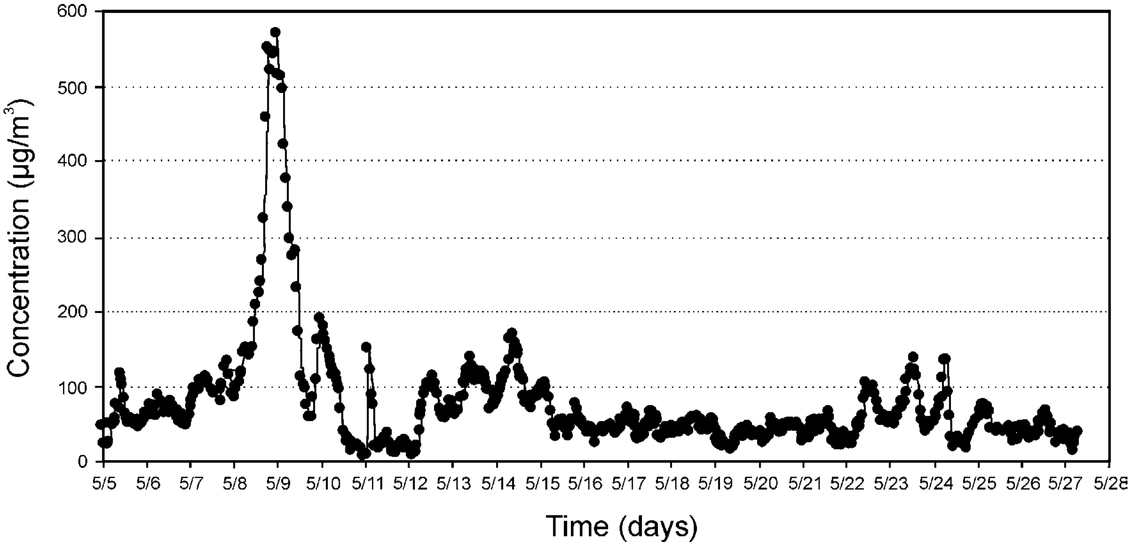

Figure 3-24. Time series of 24-h average PM_{10} concentrations observed in the Rio Grande Valley during May 1998.

Source: Aerometric Information Retrieval System (AIRS; U.S. Environmental Protection Agency, 2002b).

plume from fires occurring in the Northwest Territories of Canada in early July 1995 may have extended throughout most of the eastern United States, resulting in elevated levels of CO and ozone. Simple scaling of their calculated excess CO concentrations because of the fires, by the ratio of emission factors of $PM_{2.5}$ to CO, indicates that the excess $PM_{2.5}$ concentrations in the plume may have ranged from about 5 µg/m^3 in the Southeast and to close to 100 µg/m^3 in the northern Plains States.

Sources Within North America

It is much more difficult to determine 24-h PRB concentrations in the absence of specific events such as those given above because contributions from anthropogenic sources located either nearby or elsewhere within North America can contribute substantially to observed values and perhaps overwhelm the contributions from PRB sources. Source-apportionment modeling techniques (described in Section 5.5 of the 1996 PM AQCD and updated in Section 3.3.2 of this document) can be helpful for this purpose. Western sites are most useful because contributions from pollution sources can overwhelm those from background sources in the East, and

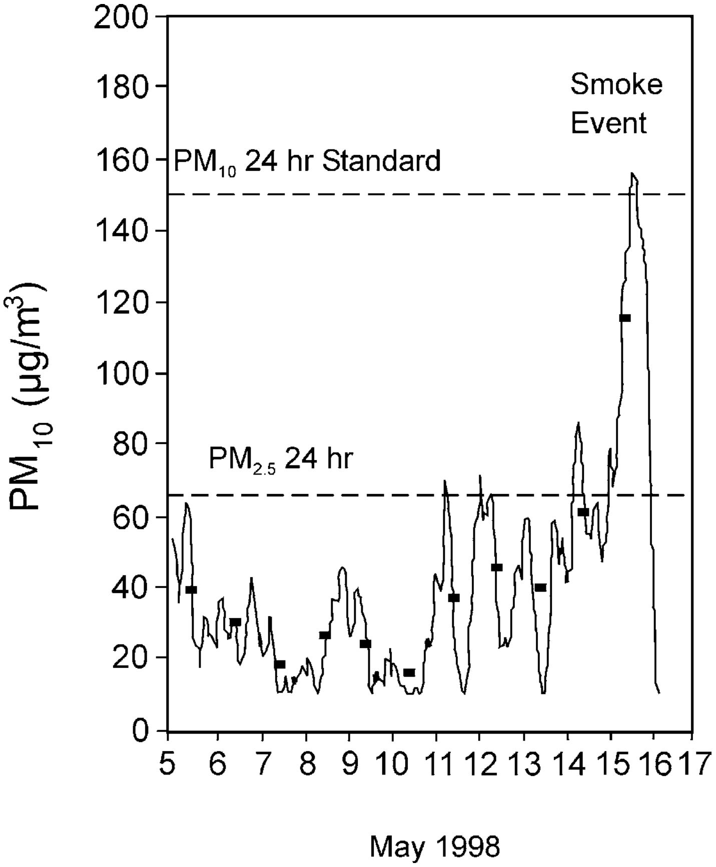

Figure 3-25. PM_{10} concentrations observed in St. Louis, MO, during May 1998.

Source: Aerometric Information Retrieval System (AIRS; U.S. Environmental Protection Agency, 2002b).

background source contributions can be lost within the errors of their source contributions. However, it should be noted that source apportionment techniques such as PMF are not able to distinguish between bioaerosol and organic PM from whatever source, mainly because of analytical limitations. In addition, background PM source contributions are contaminated by contributions from pollution sources during transport from source to receptor monitoring site. Thus, background source contributions derived by these methods should be regarded as upper limits on the true values; however, the daily time series can provide more stringent limits about what the day to day variability in these contributions might be than by examining ambient $PM_{2.5}$ data alone.

Song et al. (2001) derived source contributions to $PM_{2.5}$ concentrations measured at Washington, DC, Brigantine, NJ, and Underhill, VT, using PMF. They found that wildfires could contribute 0.93 ± 0.97 $\mu g/m^3$; soil could contribute 0.11 ± 0.22 $\mu g/m^3$; and sea spray could contribute 0.90 ± 1.0 $\mu g/m^3$ on an annual basis at Brigantine, NJ throughout the sampling period from 1989 to 1999. They also derived contributions of 1.2 ± 0.9 $\mu g/m^3$ from wildfires; 0.32 ± 0.61 $\mu g/m^3$ from soil; and 0.05 ± 0.05 $\mu g/m^3$ from sea spray at Underhill, VT from 1989 through 1999. The "background" sources contribute about 7% to annual average $PM_{2.5}$ concentrations at Brigantine and about 12% at Underhill. The daily time series at the NJ and VT sites show striking variability in background components, characterized by spikes. Maximum daily values during these spikes are in the range of several $\mu g/m^3$. Song et al. concluded these spikes in concentrations are likely caused by transient meteorological events such as storms or transport of dust from remote regions such as northern Africa and by events such as wild fires. Contributions from all of these sources should be regarded as upper limits because of entrainment of pollutant emissions during transport from source to receptor of the background source emissions.

Pun et al. (2002) used a regional scale chemistry-transport model (CMAQ) to simulate O_3 and $PM_{2.5}$ concentrations arising from natural sources alone in model domains centered over Tennessee and over the mid-Atlantic region for several days in July 1995. These calculations were performed for meteorological conditions that resulted in high ambient ozone concentrations in the eastern United States. They found that natural sources contributed about 1.7 $\mu g/m^3$ to Washington, DC, (ranging from about 0.6 to 3.1 $\mu g/m^3$ in the mid-Atlantic domain) and about 1.2 $\mu g/m^3$ to Nashville, TN, on a 24 h average basis. The formation of secondary organic PM from biogenic precursors may be expected to be maximized for these conditions; however, their contribution was estimated to be at most 15% of natural $PM_{2.5}$ or less than 1 $\mu g/m^3$. The largest contributions in both cases came from natural $PM_{2.5}$ that was advected in from other regions of the United States. In addition to the sources considered above, contributions to both primary and secondary PM from events such as volcanic eruptions or geothermal activity are highly sporadic. The spatial and temporal distributions of secondary PM produced by background sources shown in Table 3-8 still remain to be investigated.

It can be concluded from the above that 24-h policy relevant background concentrations are highly variable both spatially and temporally. Contributions to PRB concentrations from external sources (e.g., Asian and North African dust storms and Central American wildfires) can be significant on an episodic, but probably not on an annual basis. More local sources of primary PRB PM are also likely to be episodic, reflecting the occurrence of volcanic eruptions, wildfires, and storms that raise dust and sea spray. The influence from events such as these can be felt over thousands of square kilometers. Very little work has been done to quantify the magnitude and variability of contributions from the production of secondary PM. However, the one modeling study cited above found values < 1 $\mu g/m^3$ as secondary PM. Perhaps the greatest possibility for estimating these concentrations comes from the application of source apportionment techniques such as PMF (positive matrix factorization) to time series of species compositional data obtained at relatively remote monitoring sites (RRMS) to minimize interference from anthropogenic sources. In the absence of such results, some useful estimates may be obtained by examining the time series of PM concentrations at RRMS with screening to eliminate days when concentrations are influenced by anthropogenic sources.

It is instructive in this regard to examine the variability observed at RRMS. Data from eighteen IMPROVE sites are examined in Appendix 3E and analyzed in greater detail in Lefohn et al. (2004). The ranges of annual average $PM_{2.5}$, $PM_{10\text{-}2.5}$, and PM_{10} concentrations are shown in Table 3-E1 and the corresponding ranges for the 90th percentile concentrations are summarized in Table 3-E2. Information about the range of 24-h average $PM_{2.5}$ and $PM_{10\text{-}2.5}$ concentrations observed at selected sites in the IMPROVE network on a calendar quarter basis are shown in Figures 3-E2a-d and Figures 3-E3a-d.

As mentioned earlier, it is impossible to obtain estimates of PRB concentrations solely on the basis of measurements of $PM_{2.5}$, $PM_{10\text{-}2.5}$, or PM_{10}. It is preferable to quantify contributions from both background and non-background sources by using compositional data in techniques such as source apportionment modeling. However, of those measured throughout the United States, the concentrations observed at several RRMS in the western United States probably come closest to what PRB concentrations might be in the West. It must be recognized at the outset that these concentrations will only provide upper limits. However, at some sites in the western United States (e.g., Bridger, WY, and Yellowstone Park, WY) annual mean concentrations are within the range of PRB values estimated in 1996 PM AQCD and given earlier in this section. At other RRMS in the western United States, they are consistent with, although slightly above, the annual average values defined earlier in the 1996 PM AQCD. Some screening should be performed to rule out transport from urban areas or other sources of anthropogenic PM on a day by day basis. Such a procedure is impractical in the eastern United States as concentrations there are heavily affected by anthropogenic emissions. Mean concentrations observed there are often several times those defined in the 1996 PM AQCD. It is important to note that there is much smaller relative variability in $PM_{2.5}$ concentrations (from the minimum to the P_{90} level) on a year-to-year basis at the western IMPROVE sites than at the eastern IMPROVE sites (cf., Figure 3E-4a-d). This may be related to a lack of discrete transport events affecting most samples at the western sites compared to the eastern sites and does not rule out the possibility that the western sites are receiving highly diluted contributions from many distant urban sources. Further inquiry is needed to address these issues. Likewise, data for $PM_{10-2.5}$ concentrations at RRMS can be used for similar purposes.

The above discussions do not explicitly consider the contributions from primary biological particles (PBP). As mentioned earlier, one extensive study conducted in Mainz, Germany, (Mathias-Maser, 1998) found that PBP could contribute from about 17 to 20% of total aerosol volume and from 9 to 30% of total particle number in the size range from 0.35 μm to 50 μm, depending on season. Pollen can at times represent the dominant contributors to PM in particles larger than 10 μm. These pollen grains can then fracture and appear as fragments in the smaller size ranges.

3.3.4 Emissions Estimates for Primary Particulate Matter, and Precursors to Secondary Particulate Matter (SO_2, NO_x, VOCs, and NH_3) in the United States

In principle, source contributions to ambient PM also could be estimated on the basis of predictions made by chemistry-transport models (CTM) or even on the basis of emissions inventories alone. Uncertainties in emissions inventories have arguably been regarded as representing the largest source of uncertainty in CTMs (Calvert et al., 1993). Apart from uncertainties in emission inventories, a number of other factors limit the ability of an emissions inventory-driven CTM to determine the effects of various sources on particle samples obtained at a particular location. CTM predictions represent averages over the area of a grid cell, which in the case of CMAQ (Community Model for Air Quality) and MAQSIP (Multiscale Air Quality Simulation Platform), ranges from 16 km^2 (4 km × 4 km) to 1296 km^2 (36 km × 36 km). CMAQ and MAQSIP constitute the CTMs within the overall Models3 framework, which also includes emissions processors, the meteorological model, and modules for decision support. The contributions of sources to pollutant concentrations at a monitoring site are controlled strongly by local conditions that cannot be resolved by an Eulerian grid-cell model. Examples would be the downward mixing of tall-stack emissions and deviations from the mean flow caused by buildings. The effect of local sources at a particular point in the model domain may not be predicted accurately because their emissions would be smeared over the area of a grid cell or if the local wind fields at the sampling point deviated significantly from the mean wind fields calculated by the model. CTMs also have problems in predicting pollutant concentrations because of uncertainties in vertical mixing and in predicting concentrations of pollutants from stationary combustion sources resulting from uncertainties in estimates of plume rise. CTMs are an integral part of air quality management programs and are reviewed in the NARSTO Fine Particle Assessment (NARSTO, 2002).

Estimated emissions of primary $PM_{2.5}$ from different sources in the United States are summarized in Table 3-11, and estimated emissions of precursors to the formation of secondary $PM_{2.5}$ (SO_2, NO_x, VOCs, and NH_3) are summarized in Table 3-12. These estimates are given to provide a rough overview of the relative importance of major PM sources in the United States. The emissions estimates are based on information presented in the EPA National Air Pollutant Emission Trends Report, 1990-1999 (U.S. Environmental Protection Agency, 2001), to which the reader is referred for detailed tables showing trends in $PM_{2.5}$ emissions from a number of source categories from 1990 to 1999. Detailed descriptions of the methodology for constructing emissions inventories for criteria pollutants, quality assurance procedures, and examples of calculations of emissions can be found in U. S. Environmental Protection Agency (1999). Although uncertainties associated with the estimates in the National Air Pollutant Emission Trends Report are not given therein, a discussion of uncertainties in emissions estimates is given in Section 3.3.5.

For the sake of completeness, an attempt was made to supplement the information given in the emissions tables in the Trends Report, which concentrates mainly on anthropogenic emissions, with information about emissions from natural sources. Details regarding the composition of the emissions of primary $PM_{2.5}$ from the source categories shown in Table 3-11 are summarized in Appendix 3D, where available. Fugitive dust emissions are estimated to constitute over 50 percent of nationwide primary $PM_{2.5}$ emissions according to Table 3-11. However, there are a number of issues concerning the methods for obtaining relevant emissions factor data for fugitive dust in field studies as discussed in Section 3.3.5. An estimate of the production of $PM_{2.5}$ from wind erosion on natural surfaces was not included in Table 3-11

TABLE 3-11. EMISSIONS OF PRIMARY $PM_{2.5}$ BY VARIOUS SOURCES IN 1999

Source	Emissions (10^9 kg/y)	Major PM Components	Notes
On-road vehicle exhaust	0.21	Organic compounds, elemental carbon	Exhaust emissions from diesel (72%) and gasoline vehicles (28%).
Non-road vehicle exhaust	0.37	Organic compounds, elemental carbon	Exhaust emissions from off-road diesel (57%) and gasoline vehicles (20%); ships and boats (10%); aircraft (7%); railroads (6%).
Fossil fuel combustion	0.36	Crustal elements, trace metals	Fuel burning in stationary sources such as power plants (33%); industries (39%); businesses and institutions (25%); residences (3%).
Industrial processes	0.35	Metals, crustal material, organic compounds	Metals processing (29%); mineral products (27%); chemical mfg. (11%); other industries (33%).
Biomass burning	1.2	Organic compounds, elemental carbon	Managed burning (47%); residential wood burning (28%); agricultural burning (7%); wildfires (18%).
Waste disposal	0.48	Organic compounds, trace metals	Open burning (91%); incineration (9%).
Fugitive dust	3.3	Crustal elements	Dust raised by vehicles on paved (19%) and unpaved roads (40%); construction (15%), dust from raising crops (24%) and livestock (2%).
Windblown dust	NA[1]	Crustal elements	Dust raised by wind on bare land.
Other	0.02	Organic compounds, elemental carbon	Structural fires.
Total	6.2		

[1] NA = not available.

Source: Adapted from U. S. Environmental Protection Agency (2001).

because this source is highly sporadic, occurs during periods of high winds, thus, the resulting emissions are too highly uncertain to be included. As can be seen from a comparison of entries in Tables 3-11 and 3-12, estimates of emissions of potential precursors to secondary PM formation are considerably larger than those for estimates of primary $PM_{2.5}$ emissions in the United States. The emissions of SO_2, NO_x, and NH_3 should be multiplied by factors of 1.5, 1.35, and 1.07, respectively, to account for their chemical form in the aerosol phase. Estimating a factor for VOCs is somewhat less straight forward. Turpin and Lim (2001) recommends a factor of 2 to account for the conversion of VOC precursors to oxygen- and nitrogen-containing compounds in the aerosol phase. These factors are all greater than 1 and further underscore the potential importance of secondary PM precursor emissions relative to primary PM emissions. However, the emissions of precursors cannot be translated directly into rates of PM formation.

TABLE 3-12. EMISSIONS OF PRECURSORS TO SECONDARY $PM_{2.5}$ FORMATION BY VARIOUS SOURCES IN 1999

Precursor	Emissions (10^9 kg/y)	Secondary PM Component	Notes
SO_2	17	Sulfate	Exhaust from on-road (2%) and non-road (5%) engines and vehicles; fossil fuel combustion by electrical utilities, industries, other sources (85%); various industrial processes (7%); and other minor sources (1%).
NO_x[1,2]	26	Nitrate	Exhaust from on-road (34%) and non-road (22%) engines and vehicles; fossil fuel combustion by electrical utilities, industries, other sources (39%); lightning (4%); soils (4%); and other minor sources (5%).
Anthropogenic VOCs	16	Various mainly unidentified compounds of 'OC'	Evaporative and exhaust emissions from on-road (29%) and non-road (18%) vehicles; evaporation of solvents and surface coatings (27%); biomass burning (9%); storage and transport of petroleum and volatile compounds (7%); chemical and petroleum industrial processes (5%); other sources (5%).
Biogenic VOCs[1]	44	Various mainly unidentified compounds of 'OC'	Approximately 98% emitted by vegetation. Isoprene (35%); monoterpenes (25%); all other reactive and non-reactive compounds (40%).
NH_3	45	Ammonium	Exhaust from on-road and non-road engines and vehicles (5%); chemical manufacturing (3%); waste disposal, recycling, and other minor sources (5%); livestock (82%); and fertilizer application (18%).

[1] Includes estimates of natural sources from Guenther et al. (2000).
[2] Emissions expressed in terms of NO_2.

Source: Adapted from U. S. Environmental Protection Agency (2001).

Dry deposition and precipitation scavenging of some of these gaseous precursors and their intermediate oxidation products occur before they are converted to PM in the atmosphere. In addition, some fraction of these gases are transported outside of the domain of the continental United States before being oxidized. Likewise, emissions of these gases from areas outside the United States can result in the transport of their oxidation products into the United States.

As discussed in Section 3.3.1, the photochemical oxidation of sulfur dioxide leads to the production of sulfate; whereas that of nitrogen oxide leads ultimately to particulate-phase nitrite and nitrate. Due to uncertainties it is difficult to calculate the rates of formation of secondary organic particulate matter (SOPM) from the emissions of VOC precursors. Smog chamber and laboratory studies discussed in Section 3.3.1 indicate that anthropogenic aromatic compounds and biogenic terpenoid compounds have the highest potential for forming secondary organic particulate matter; and as can be seen from Table 3C-1, the dominant compounds tend to be those derived from these categories. Each of the source categories capable of emitting VOCs shown in Table 3-12 has components capable of forming SOPM, although in small yields (ranging typically up to several per cent, cf., Section 3.3.1). The oxidation of lighter organic compounds leads ultimately to the formation of CO and CO_2. As discussed by Pandis et al. (1991) and in Section 3.3.1, soluble gas phase compounds, such as formaldehyde (CH_2O), other aldehydes, organic acids, etc., formed during the oxidation of a wide variety of hydrocarbons, can be incorporated into suspended particles. Although isoprene is a major component of biogenic emissions, its oxidation has not been found to result in the formation of new particles; whereas the oxidation of monoterpenes has. However, it should be remembered that soluble gas phase species such as CH_2O are formed during the oxidation of isoprene.

The emissions estimates shown in this section are based on annual totals. However, annual averages do not reflect the variability of a number of emissions categories on shorter time scales. Residential wood burning in fireplaces and stoves, for example, is a seasonal practice that reaches its peak during cold weather. Cold weather also affects motor vehicle exhaust particulate matter emissions, both in terms of chemical composition and emission rates (e.g., Watson et al., 1990b; Huang et al., 1994). Agricultural activities such as planting, fertilizing, and harvesting are also seasonal. Forest fires occur mainly during the local dry season and during periods of drought. Maximum dust production by wind erosion in the United States occurs during the spring; whereas the minimum occurs during the summer (Gillette and Hanson, 1989). Efforts are being made to account for the seasonal variations of emissions in the nationwide emissions inventories. Techniques for calculating emissions of criteria pollutants on a seasonal basis are given in U. S. Environmental Protection Agency (1999).

Trends in nationwide, annual average concentrations of PM_{10}, and precursor gases (SO_2, NO_2, and VOC) over the 10 years from 1992 to 2001 are shown in Table 3-13. As can be seen from Table 3-13, there have been substantial decreases in the ambient concentrations of PM_{10}, SO_2, and NO_2. Not enough data are available to define trends in concentrations of VOCs. There also have been substantial decreases in the emissions of all the species shown in Table 3-13, except for NO_2, although its average ambient concentration has decreased by 11%. These entries suggest that decreases in the average ambient concentration of PM_{10} could have been produced

TABLE 3-13. NATIONWIDE CHANGES IN AMBIENT CONCENTRATIONS AND EMISSIONS OF PM_{10} AND GASEOUS PRECURSORS TO SECONDARY PARTICULATE MATTER FROM 1992 TO 2001

	% Change 1992-2001	
	Ambient Concentration	Emissions
PM_{10}	−14%	−13%*
$PM_{2.5}$	—	−10%*
SO_2	−35% (SO_2)	−24% (SO_2)
NO_x	−11% (NO_2)	−3% (NO_x)
VOC	—	−8%

*Includes only primary PM.

Source: U.S. Environmental Protection Agency (2002).

by both decreases in emissions of primary PM_{10} and the formation of secondary PM_{10}. The large reductions in ambient SO_2 concentrations have resulted in reductions in sulfate formation that would have been manifest in $PM_{2.5}$ concentrations on the regional scale in the East and Midwest where sulfate has constituted a larger fraction of $PM_{2.5}$ than in the West. Likewise, reductions in NO_2 concentrations would have had a more noticeable effect on $PM_{2.5}$ concentrations in the West than in the East because nitrate is a larger component of the aerosol in the West.

Trends in aerosol components (i.e., nitrate, sulfate, carbon, etc.) are needed for a more quantitative assessment of the effects of changes in emissions of precursors. Aerosol nitrate and sulfate concentrations obtained at North Long Beach and Riverside, CA, tracked downward trends in NO_x concentrations. SO_2 and sulfate concentrations have both decreased; however, the rate of decline of sulfate has been smaller than that of SO_2, indicating the long range transport of sulfate from outside the airshed may be an important source in addition to the oxidation of locally generated SO_2. There are a number of reasons why pollutant concentrations do not track estimated reductions in emissions. Some of these reasons are related to atmospheric effects such as meteorological variability and secular changes in the rates of photochemical transformations and deposition (U.S. Environmental Protection Agency, 2000c). Other reasons are related to uncertainties in ambient measurements and in emissions inventories.

3.3.5 Uncertainties of Emissions Inventories

As described in the 1996 PM AQCD, it is difficult to quantitatively assign uncertainties to entries in emissions inventories. Methods that can be used to verify or place constraints on emissions inventories are sparse. In general, the overall uncertainty in the emissions of a given pollutant includes contributions from all of the terms used to calculate emissions (i.e., activity rates, emissions factors, and control device efficiencies). Additional uncertainties arise during the compilation of an emissions inventory because of missing sources and computational errors. The variability of emissions can cause errors when annual average emissions are applied to applications involving shorter time scales.

Activity rates for well-defined point sources (e.g., power plants) should have the smallest uncertainty associated with their use because emissions are monitored continuously in many cases and accurate production records need to be kept. On the other hand, activity rates for a number of very disperse fugitive sources are difficult to quantify. Emissions factors for easily measured fuel components that are released quantitatively during combustion (e.g., CO_2, SO_2) should be the most reliable. Emissions of components formed during combustion are more difficult to characterize, as the emissions rates are dependent on factors specific to individual combustion units and on combustion stage (i.e., smoldering or active). Although the AP-42 emissions factors (U.S. Environmental Protection Agency, 1995) contain extensive information for a large number of source types, these data are very limited in the number of sources sampled. The efficiency of control devices is determined by their design, age, maintenance history, and operating conditions. It is virtually impossible to assign uncertainties in control device performance because of these factors. It should be noted that the largest uncertainties occur for those devices that have the highest efficiencies (> 90%). This occurs because the efficiencies are subtracted from one, and small errors in assigning efficiencies can lead to large errors in emissions.

Ideally, an emissions inventory should include all major sources of a given pollutant. This may be an easy task for major point sources. However, area sources of both primary PM and precursors to secondary PM formation are more difficult to characterize than point sources; and, thus, they require special emphasis when preparing emission inventories. Further research is needed to better characterize the sources of pollutants to reduce this source of uncertainty. Errors also can arise from the misreporting of data, and arithmetic errors can occur in the course of compiling entries from thousands of individual sources. A quality assurance program is required to check for outliers and arithmetic errors. Because of the variability in emissions rates, there can be errors in the application of inventories developed on an annually averaged basis (as are the inventories shown in Tables 3-11 and 3-12) to episodes occurring on much shorter time scales. As an example, most modeling studies of air pollution episodes are carried out for periods of a few days.

Uncertainties in annual emissions were estimated to range from 4 to 9% for SO_2 and from 6 to 11% for NO_x in the 1985 NAPAP inventories for the United States (Placet et al., 1991). Uncertainties in these estimates increase as the emissions are disaggregated both spatially and temporally. The uncertainties quoted above are minimum estimates and refer only to random variability about the mean, assuming that the variability in emissions factors was adequately characterized and that extrapolation of emissions factors to sources other than those for which they were measured is valid. The estimates do not consider the effects of weather or variations in operating and maintenance procedures.

Fugitive dust sources, as mentioned above, are extremely difficult to quantify; and stated emission rates may represent only order-of-magnitude estimates. Although crustal dust emissions constitute about 50% of the total primary $PM_{2.5}$ inventory, they constitute less than about 15% of the source strengths inferred from the receptor modeling studies shown in Table 3-9. However, it should be remembered that secondary components (sulfate, nitrate, and some fractions of organic carbon) often account for most of the mass of ambient $PM_{2.5}$ samples.

Although mineral dust sources represent the major category in Table 3-11, their contributions are distributed much more widely than are those from combustion sources. Watson and Chow (2000) reexamined the methodology used to determine emissions of fugitive dust. The standard methods use data obtained by particle monitors stacked at several elevations from 1 to 2 m up to 7 to 10 m above the surface. However, small-scale turbulent motions and variable winds characterize atmospheric flow patterns immediately adjacent to the surface in this height range (Garratt, 1994). The depth of this turbulent layer is determined by surface roughness elements, and there is a high probability of particles being entrained in turbulent eddies and redepositing on the ground within a very short distance. In addition to the source-sampling problem referred to above, it should be remembered that dust often is raised in remote areas far removed from population centers. Precipitation or scavenging by cloud droplets and dry deposition removes particles during transport from the source area. In addition, gravitational settling can be an important loss mechanism for particles larger than a few micrometers in aerodynamic diameter.

As rough estimates, uncertainties in emissions estimates could be as low as 10% for the best characterized source categories; whereas emissions figures for windblown dust should be regarded as order-of-magnitude estimates. The application of emissions inventories to the estimation of source contributions at monitoring sites is also limited by the effects of local topography and meteorology. For example, Pinto et al. (1998) found that the contribution of power plants and residential space heating to $PM_{2.5}$ concentrations in northwestern Bohemia are comparable on the basis of CMB receptor modeling. However, according to the emissions inventories, the contribution from power plants should have been roughly an order of magnitude larger than that from residential space heating. The difference between the two methods can be explained by noting that mixing of the emissions from the power plants downward to the surface is inhibited by strong surface inversions that develop during the winter season in this area.

There have been few field studies designed to test emissions inventories observationally. The most direct approach would be to use aircraft to obtain cross-sections of pollutants upwind and downwind of major urban areas. The computed mass flux through a cross section of the urban plume can then be equated to emissions from the city chosen. This approach has been attempted on a few occasions, but results have been ambiguous because of contributions from fugitive sources, variable wind flows, and logistic difficulties.

3.4 SUMMARY AND KEY CONCLUSIONS

The recently deployed $PM_{2.5}$ FRM network has returned data for a large number of sites across the United States. Annual mean $PM_{2.5}$ concentrations range from about 5 $\mu g/m^3$ to about 30 $\mu g/m^3$. In the eastern United States, the data from 1999 to 2001 indicate that highest quarterly mean concentrations and maximum concentrations most often occur during the summer. In the western United States, highest quarterly mean values and maximum values occur mainly during the winter at a number of sites although there were exceptions to these general patterns. Sites affected strongly by sources of primary PM are expected to show winter maxima. These findings are generally consistent with those based on longer term data sets such as MAAQS in the eastern United States and the CARB network of dichotomous samplers in California. $PM_{2.5}$ and PM_{10} concentrations in a number of urban areas have generally declined over the past few decades. However, they appear to have leveled off in the past few years.

Differences in annual mean $PM_{2.5}$ concentrations between monitoring sites in urban areas examined are typically less than 6 or 7 $\mu g/m^3$. However, on individual days, differences in 24-h average $PM_{2.5}$ concentrations can be much larger. Some sites in metropolitan areas are highly correlated with each other but not to others due to the presence of local sources, topographic barriers, etc. Although $PM_{2.5}$ concentrations at sites within an MSA can be highly correlated, there still can be significant differences in their concentrations on any given day. Consequently, additional measures should be used to characterize the spatial variability of $PM_{2.5}$ concentrations. The degree of spatial uniformity in $PM_{2.5}$ concentrations in urban areas varies across the country. These factors should be considered in using data obtained by the $PM_{2.5}$ FRM network to approximate community-scale human exposure, and caution should be exercised in extrapolating conclusions obtained in one urban area to another. $PM_{2.5}$ to PM_{10} ratios were generally higher in the East than in the West, and values for this ratio are consistent with those found in numerous earlier studies presented in the 1996 PM AQCD.

Data for $PM_{10\text{-}2.5}$ are not as abundant as they are for $PM_{2.5}$, and their interpretation is complicated by the difference method used to determine their concentrations. The more sporadic nature of sources of $PM_{10\text{-}2.5}$ and its shorter atmospheric lifetime tend to result in lower spatial correlations for $PM_{10\text{-}2.5}$ than for $PM_{2.5}$ concentrations. Errors in measurement of $PM_{2.5}$ and PM_{10} also result in calculations of lower spatial correlations of $PM_{10\text{-}2.5}$. Calculated concentrations of $PM_{10\text{-}2.5}$ are occasionally negative as reflected by $PM_{2.5}$ to PM_{10} ratios greater than one. Because analytical errors are generally larger for individual species than for total mass, similar problems arise in their determination in $PM_{10\text{-}2.5}$ samples by the difference approach. Some, but not all of these problems could be resolved by the use of dichotomous samplers that also provide a direct sample of $PM_{10\text{-}2.5}$ for compositional analyses.

Estimates of concentrations of individual species in $PM_{10\text{-}2.5}$ samples used in this chapter were limited to those obtained by dichotomous samplers. Generally, concentrations of most elements differ for $PM_{2.5}$ and $PM_{10\text{-}2.5}$. However, the available data suggest that concentrations of many metals are of the same order of magnitude in both size fractions. This is in marked contrast to the situation twenty years ago when uncontrolled combustion sources were prevalent.

At that time, concentrations of many metals, especially lead, were much higher than today in fine-mode particles, and their concentrations were much higher in the fine-mode than in the coarse-mode. No substantive conclusions about contemporary concentrations and composition of ultrafine particles (0.1 µm < D_a) can be drawn for the nation as a whole because of a lack of data.

Ambient PM contains both primary and secondary components. The results of ambient monitoring studies and receptor modeling studies indicate that $PM_{2.5}$ is dominated by secondary components in the eastern United States. General statements about the origin of OC in ambient $PM_{2.5}$ samples cannot yet be made and so the contribution of secondary components throughout the rest of the United States is still highly uncertain. Primary constituents represent smaller but still important component of $PM_{2.5}$. Crustal materials, which are primary constituents, constitute the largest measured fraction of $PM_{10-2.5}$ throughout the United States. Data for the concentration of bioaerosols in both the $PM_{2.5}$ and $PM_{10-2.5}$ size ranges are sparse. Data collected in several airsheds, including the Los Angeles Basin, Bakersfield and Fresno, CA; and Philadelphia, PA, suggest that secondary PM components are more uniformly distributed than are primary PM components. Compositional data obtained at multiple sites in other urban areas are sparse.

Because of the complexity of the composition of ambient $PM_{2.5}$ and $PM_{10-2.5}$, sources are best discussed in terms of individual constituents of both primary and secondary $PM_{2.5}$ and $PM_{10-2.5}$. Each of these constituents can have anthropogenic and natural sources as shown in Table 3-8. The distinction between natural and anthropogenic sources is not always obvious. Although windblown dust might seem to be the result of natural processes, highest emission rates are associated with agricultural activities in areas that are susceptible to periodic drought. Examples include the dust bowl region of the midwestern United States and the Sahel of Africa. There is also ongoing debate about characterizing wildfires as either natural or anthropogenic. Land management practices and other human actions affect the occurrence and scope of wildfires. Similarly, prescribed burning can be viewed as anthropogenic or as a substitute for wildfires that would otherwise eventually occur on the same land.

Over the past decade, a significant amount of research has been carried out to improve the understanding of the atmospheric chemistry of secondary organic PM formation. Although additional sources of SOPM might still be identified, there appears to be a general consensus that biogenic compounds (monoterpenes, sesquiterpenes) and aromatic compounds (toluene, ethylbenzene) are the most significant SOPM precursors. A large number of compounds have been detected in biogenic and aromatic SOPM although the chemical composition of these two categories has not been fully established, especially for aromatic SOPM. Transformations that occur during the aging of particles are still inadequately understood. There are still large gaps in the current understanding of a number of key processes related to the partitioning of semivolatile compounds between the gas phase and ambient particles containing organic compounds, liquid water, and inorganic salts and acids. In addition, there is a general lack of reliable analytical methods for measuring multifunctional oxygenated compounds in the gas and aerosol phases.

The results of receptor modeling studies throughout the United States indicate that the combustion of fossil and biomass fuels is the major source of measured ambient $PM_{2.5}$. Fugitive dust, found mainly in the $PM_{10-2.5}$ range size, represents the largest source of measured ambient PM_{10} in many locations in the western United States. Quoted uncertainties in the source apportionment of constituents in ambient aerosol samples typically range from 10 to 50%. It is apparent that a relatively small number of source categories, compared to the total number of chemical species that typically are measured in ambient monitoring-source receptor model studies, are needed to account for the majority of the observed mass of PM in these studies.

The application of any of the source apportionment techniques is still limited by the availability of source profile data. Whereas the CMB approach relies directly on source profile data, solutions from the PMF technique yield profiles for the factors that contribute to PM. However, there is some rotational ambiguity present in the solutions. Source profile data obtained by PMF must still be verified by comparison with data and these data can be used in techniques such as PMF to improve the solutions. Serious limitations still exist with regard to source profiles for organic compounds. The complexity of reactions involving organic compounds in particles adds to the difficulties of finding stable species that could be used as tracers.

As seen in Table 3-8, emissions of mineral dust, organic debris, and sea spray are concentrated mainly in the coarse fraction of PM_{10} (> 2.5 µm aerodynamic diameter). A small fraction of this material is in the $PM_{2.5}$ size range (< 2.5 µm aerodynamic diameter). Still, $PM_{2.5}$ concentrations of crustal material can be appreciable, especially during dust events. It also should be remembered that from one-third to one-half of the Saharan dust reaching the United

States is in the $PM_{2.5}$ size range. Emissions from combustion sources (mobile and stationary sources and biomass burning) are also predominantly in the $PM_{2.5}$ size range.

A number of sources contribute to policy relevant background (PRB) concentrations. Data obtained at relatively remote monitoring sites (RRMS) in the western United States could be used to place reasonable upper limits on policy relevant background concentrations. More definitive results for both annual average and daily average concentrations could potentially be obtained from the application of source-receptor models and/or the application of large-scale chemistry transport models. Many areas in the East are affected by dust transported from northern Africa, and it has recently become apparent that many areas, especially, but not limited to the Northwest, are affected by dust transported from the deserts of Asia. In addition to crustal material, pollutants and primary biological aerosol particles (PBP) are also transported during intercontinental transport events. Many areas are also affected by smoke from wildfires either within the United States or in Canada, Mexico and Central America. Storms, in which the winds can suspend material from the surface of the land or seas, contribute soil, sea spray and PBP. Contributions of primary PM from natural sources and sources outside Northern America as given above are all episodic. Because the concentration of PBP is so poorly quantified, even though it can constitute a significant fraction of the organic fraction of the atmospheric aerosol, estimates of policy relevant background concentrations will remain highly uncertain. Estimates of annually averaged PRB concentrations or their range have not changed from the previous PM assessment document.

Key points derived from the findings summarized above can be highlighted as follows:

- Spatial Variability in $PM_{2.5}$ Concentrations. Although $PM_{2.5}$ concentrations within an MSA can be highly correlated between sites, there can still be significant differences in their concentrations. The degree of spatial uniformity in $PM_{2.5}$ concentrations and the strength of site to site correlations in urban areas varies across the country. These factors should be considered in using data obtained by the $PM_{2.5}$ FRM network to approximate community-scale human exposures, and caution should be exercised in extrapolating conclusions as to spatial uniformity or correlations obtained in one urban area to another. Limited information also suggests that the spatial variability in urban source contributions is likely to be larger than for regional source contributions to $PM_{2.5}$ and for $PM_{2.5}$, itself.

1 - PM$_{10-2.5}$ Concentrations. Data for PM$_{10-2.5}$ concentrations are not as abundant as they are for PM$_{2.5}$. The difference method used in their derivation is subject to the effects of uncertainties in both PM$_{10}$ and PM$_{2.5}$. As a result, estimates of PM$_{10-2.5}$ concentrations, at times, come out as negative values, based on currently available data (e.g., in the EPA AIRS Database).

2 - Evaluating Source Contributions. The use of organic compounds in source apportionment studies could potentially result in the attribution of PM to many more source categories than is possible using only trace elements. However, in the relatively few studies of the composition of the organic fraction of ambient particles that have been performed, typically only about 10 to 20 % of organic compounds have been quantified. The separation of contributions from diesel- and gasoline-fueled vehicles using organic marker compounds is still somewhat problematic. Additional efforts to develop protocols for extraction and analysis of organic markers are needed to fully realize their potential.

3 - Policy Relevant Background (PRB) Concentrations. Recent but limited information about PRB concentrations have not provided sufficient evidence to warrant any changes in estimates of the annual average background concentrations given in the 1996 PM AQCD. These are: 1 to 4 μg/m^3 in the West and 2 to 5 μg/m^3 in the East for PM$_{2.5}$; and approximately 3 μg/m^3 in both the East and the West for PM$_{10-2.5}$, with a range of 0 to 9 μg/m^3 in the West and 0 to 7 μg/m^3 in the East. PRB concentration are likely to be highly variable both spatially and temporally. Further information regarding the frequency distribution of 24-hour concentrations based on analyses of observations at relatively remote monitoring sites and on source apportionment analyses has become available and can be used for selected sites.

4

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APPENDIX 3A

Spatial and Temporal Variability of the Nationwide AIRS $PM_{2.5}$ and $PM_{10-2.5}$ Data Sets

Aspects of the spatial and temporal variability of 24-h average $PM_{2.5}$ concentrations for 1999, 2000, and 2001 in a number of metropolitan statistical areas (MSAs) across the United States are presented in this Appendix. $PM_{2.5}$ data for multiple sites in 27 urban areas have been obtained from the AIRS data base and analyzed for their seasonal variations, for their spatial correlations, and for their spatial uniformity. A number of aspects of the spatial and temporal variability of the $PM_{2.5}$ data set from 1999 were presented in Rizzo and Pinto (2001) based in part on analyses given in Fitz-Simons et al. (2000). An analysis of the data obtained during the first two years of operation of the Federal Reference Method $PM_{2.5}$ network can be found in Pinto et al. (2003).

Information about seasonal and spatial variability in $PM_{2.5}$ concentrations within 27 MSAs across the United States are provided in the accompanying figures (Figures 3A-1 to 3A-27). Underneath the value for r, the 90th percentile values of the absolute difference in $PM_{2.5}$ concentrations (in $\mu g/m^3$) and the coefficient of divergence (COD) are given in parentheses. Beneath these two measures of spatial variability, the number of observations used in the calculations of the statistics in part *c* of each figure is given.

Quality assured measurements for at least fifteen days during each calendar quarter for 1999, 2000, and 2001 (preferably) or for 2000 and 2001 at a minimum of four monitoring sites in a given MSA were required for their inclusion in the analyses given in this appendix. The Columbia, SC and Baton Rouge, LA MSAs, which had only three sites meeting this criterion, are exceptions. Typically, at least 200 measurements were available for each monitoring site chosen. Monitoring sites were chosen without consideration of the land use type used to characterize their locations.

Because of changes in monitoring strategies, funding levels etc., there were year to year changes in monitoring sites meeting the above criteria in a number of MSAs. Data for the Philadelphia, PA; Norfolk, VA; Pittsburgh, PA; Detroit, MI; Chicago, IL; Louisville, KY;

St. Louis, MO; and the Dallas, TX MSAs have been analyzed only for 2000 and 2001 because of a lack of consistent coverage in 1999.

Information about seasonal and spatial variability in $PM_{10-2.5}$ concentrations within 17 MSAs across the United States are provided in the accompanying figures (Figures 3A-28 to 3A-44). Underneath the value for r, the 90th percentile values of the absolute difference in $PM_{2.5}$ concentrations (in $\mu g/m^3$) and the coefficient of divergence (COD) are given in parentheses. Beneath these two measures of spatial variability, the number of observations used in the calculations of the statistics in part *c* of each figure is given. In order to maximize coverage, data were calculated for a number of sampling periods. Only Milwaukee, WI, and Salt Lake City, UT, had enough data for a 3 year average (1999 to 2001). Tampa, FL; Cleveland, OH; Steubenville, OH; Baton Rouge, LA; Portland, OR; and Riverside, CA had data for a 2 year average (2000 to 2001), as did Chicago, IL and Pittsburgh, PA (1999 to 2000). Other MSAs had only one year data (2000 or 2001).

The COD was defined mathematically and used earlier in Chapter 3 as a measure of the degree of similarity between two data sets. A COD of zero implies that values in both data sets are identical, and a COD of one indicates that two data sets are completely different. Values of P_{90} provide a measure in absolute terms of differences in concentrations between sites, and CODs provide a relative measure of these differences. The maximum number of days of coincident data from paired sites were used to calculate correlation coefficients, values for P_{90}, and CODs. The correlation coefficients were also calculated by using only concurrent measurements obtained at all of the monitoring sites within urban areas meeting the above selection criteria. The correlation coefficients that were calculated differed only in the third significant figure between the two methods.

Metrics used above for characterizing differences between separated monitors are applied to collocated monitors in Table 3A-1.

Information about the spatial and temporal variability of 24-h average $PM_{10-2.5}$ concentrations is summarized in Figures 3A-28 to 3A-44. Data are shown for a subset of MSAs included in the analyses for $PM_{2.5}$. Not all MSAs could be included because of a lack of data. A schematic map showing locations of sampling sites within each MSA is given in part *a*, at the top of each figure. Also included in the map are major highways and a distance scale. A key giving the AIRS site ID #'s is shown alongside each map. Box plots showing lowest, lower quartile, median, upper quartile and highest $PM_{2.5}$ concentrations for each calendar quarter are shown in part *b* of each figure. AIRS site ID #'s, annual mean concentrations, the number of observations, and the standard deviation of the data are shown above the box plots. Finally, in part *c* of each figure, statistics characterizing the spatial variability in $PM_{2.5}$ concentrations are given. For each site-pair, the Pearson correlation coefficient (r) is provided. Underneath each value for r, the 90th percentile of the absolute difference in $PM_{10-2.5}$ concentrations, the COD, and number of observations is given. In some cases, because of negative concentration values, the COD may not be calculated. Dashes are shown for these cases.

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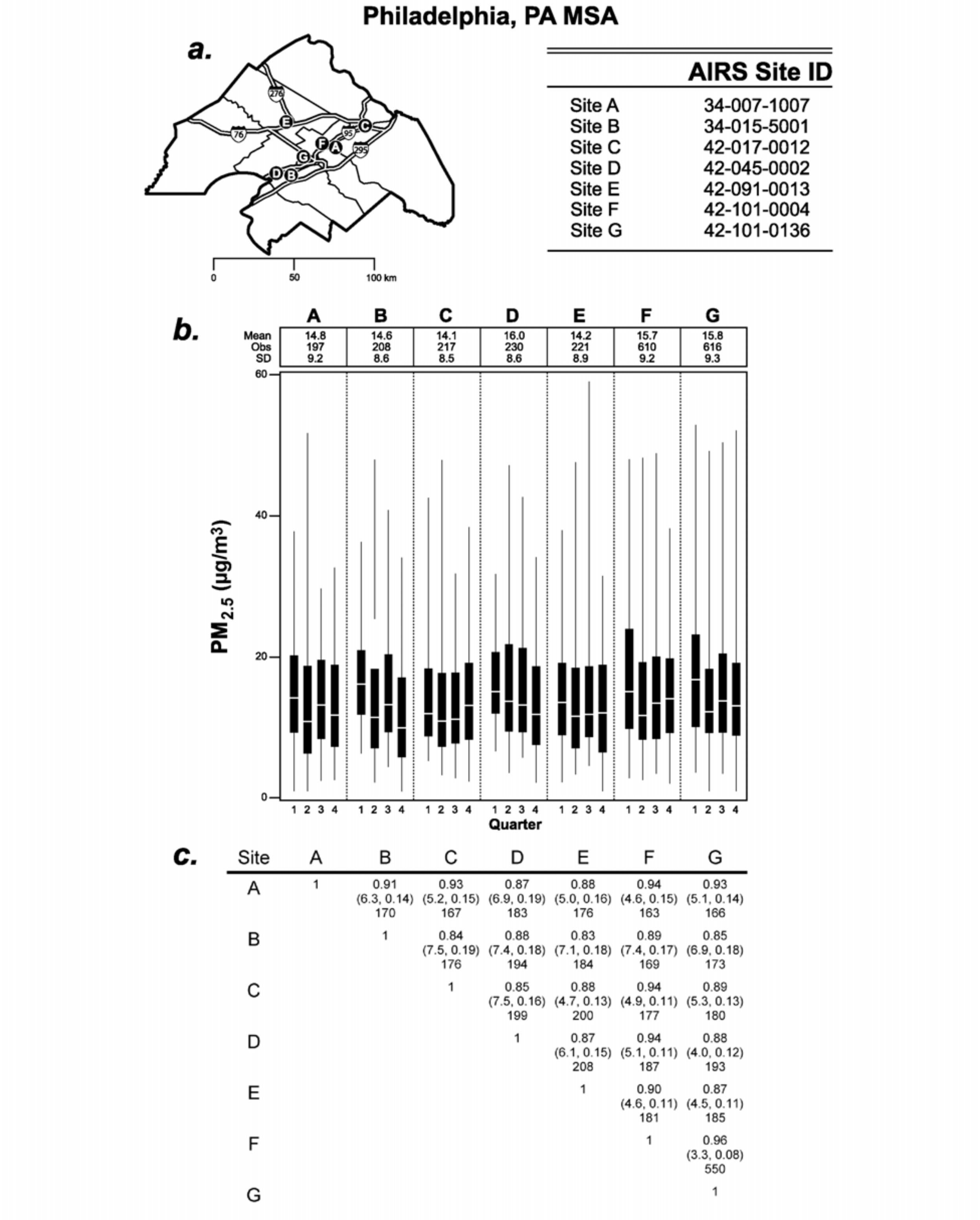


	AIRS Site ID
Site A	34-007-1007
Site B	34-015-5001
Site C	42-017-0012
Site D	42-045-0002
Site E	42-091-0013
Site F	42-101-0004
Site G	42-101-0136

	A	B	C	D	E	F	G
Mean	14.8	14.6	14.1	16.0	14.2	15.7	15.8
Obs	197	208	217	230	221	610	616
SD	9.2	8.6	8.5	8.6	8.9	9.2	9.3

Site	A	B	C	D	E	F	G
A	1	0.91 (6.3, 0.14) 170	0.93 (5.2, 0.15) 167	0.87 (6.9, 0.19) 183	0.88 (5.0, 0.16) 176	0.94 (4.6, 0.15) 163	0.93 (5.1, 0.14) 166
B		1	0.84 (7.5, 0.19) 176	0.88 (7.4, 0.18) 194	0.83 (7.1, 0.18) 184	0.89 (7.4, 0.17) 169	0.85 (6.9, 0.18) 173
C			1	0.85 (7.5, 0.16) 199	0.88 (4.7, 0.13) 200	0.94 (4.9, 0.11) 177	0.89 (5.3, 0.13) 180
D				1	0.87 (6.1, 0.15) 208	0.94 (5.1, 0.11) 187	0.88 (4.0, 0.12) 193
E					1	0.90 (4.6, 0.11) 181	0.87 (4.5, 0.11) 185
F						1	0.96 (3.3, 0.08) 550
G							1

Figure 3A-1. Philadelphia, PA-NJ MSA. (*a*) Locations of sampling sites by AIRS ID#; (*b*) Quarterly distribution of 24-h average PM$_{2.5}$ concentrations for 2000-2001; *(c)* Intersite correlation statistics, for each data pair, the correlation coefficient, (P$_{90}$, COD) and number of measurements are given.

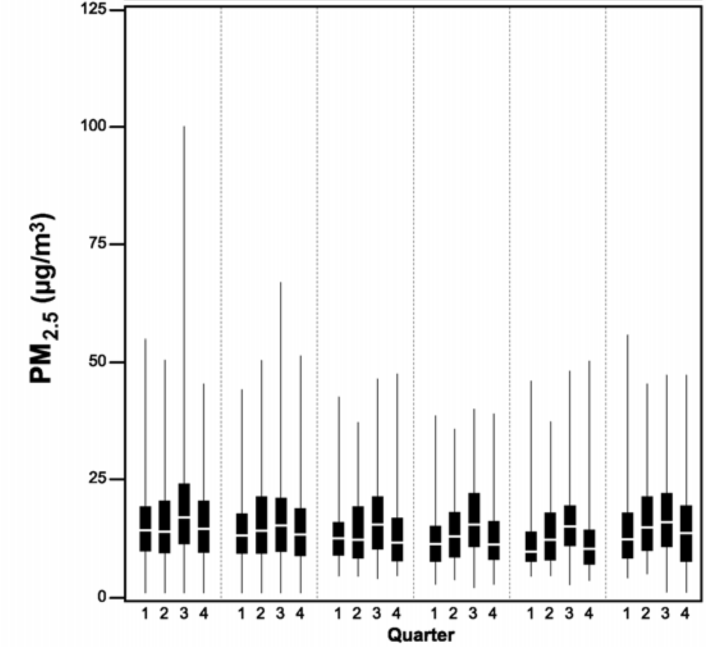
Washington, DC MSA

a.

	AIRS Site ID
Site A	11-001-0041
Site B	11-001-0043
Site C	51-013-0020
Site D	51-059-0030
Site E	51-107-1005
Site F	54-003-0003

b.

	A	B	C	D	E	F
Mean	16.7	15.5	14.7	14.1	13.8	16.1
Obs	859	926	337	848	324	314
SD	9.8	8.7	8.0	7.4	8.2	9.3



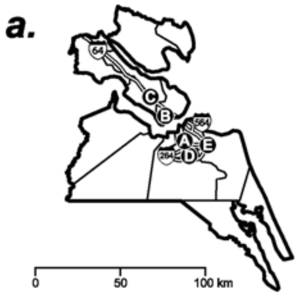
c.

Site	A	B	C	D	E	F
A	1	0.83 (5.1, 0.18) 784	0.91 (5.7, 0.15) 273	0.82 (7.4, 0.17) 691	0.84 (7.7, 0.19) 267	0.77 (8.6, 0.20) 262
B		1	0.84 (5.1, 0.16) 297	0.87 (6.2, 0.16) 731	0.79 (7.5, 0.20) 284	0.77 (7.6, 0.19) 281
C			1	0.96 (3.5, 0.08) 276	0.94 (4.9, 0.11) 312	0.85 (8.3, 0.16) 289
D				1	0.91 (4.5, 0.11) 266	0.82 (9.1, 0.18) 246
E					1	0.87 (8.5, 0.17) 284
F						1

Figure 3A-2. Washington, DC MSA. *(a)* Locations of sampling sites by AIRS ID#; *(b)* Quarterly distribution of 24-h average $PM_{2.5}$ concentrations for 1999-2001; *(c)* Intersite correlation statistics, for each data pair, the correlation coefficient, (P_{90}, COD) and number of measurements are given.

Norfolk, VA MSA

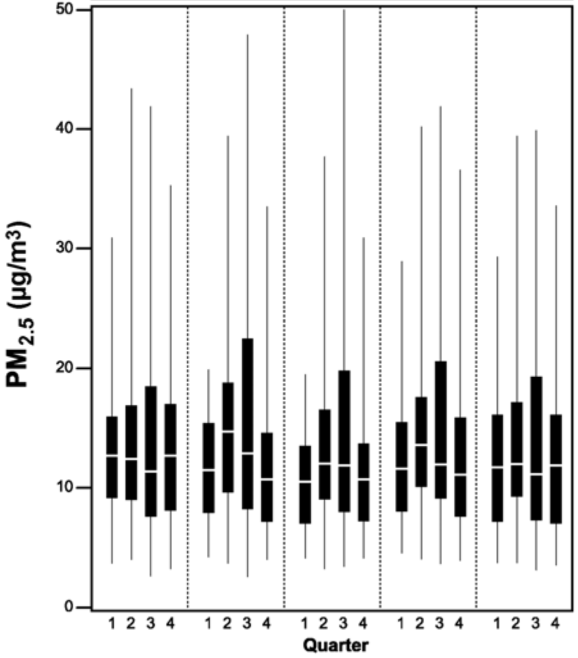
a.



	AIRS Site ID
Site A	51-550-0012
Site B	51-650-0004
Site C	51-700-0013
Site D	51-710-0024
Site E	51-810-0008

b.

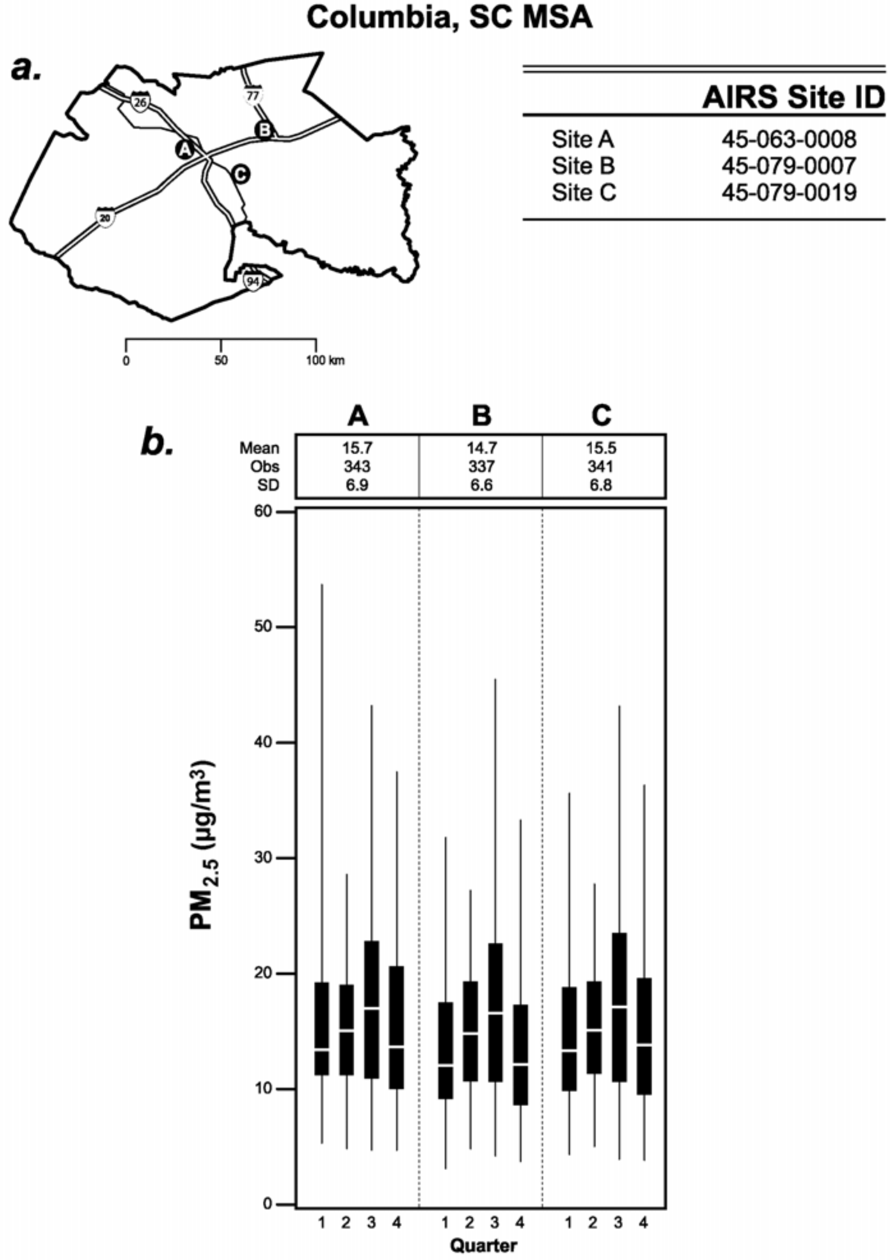
	A	B	C	D	E
Mean	13.6	13.5	12.6	13.7	13.0
Obs	598	208	222	227	232
SD	6.9	7.2	6.7	7.0	7.0



c.

Site	A	B	C	D	E
A	1	0.94 (3.7, 0.09) 167	0.91 (5.0, 0.11) 180	0.96 (3.0, 0.08) 182	0.94 (3.5, 0.08) 184
B		1	0.96 (2.6, 0.09) 191	0.96 (3.1, 0.07) 194	0.93 (4.0, 0.09) 198
C			1	0.96 (3.6, 0.09) 206	0.92 (4.3, 0.11) 212
D				1	0.93 (3.6, 0.10) 217
E					1

Figure 3A-3. Norfolk, VA MSA. *(a)* Locations of sampling sites by AIRS ID#; *(b)* Quarterly distribution of 24-h average $PM_{2.5}$ concentrations for 2000-2001; *(c)* Intersite correlation statistics, for each data pair, the correlation coefficient, (P_{90}, coefficient of divergence) and number of measurements are given.

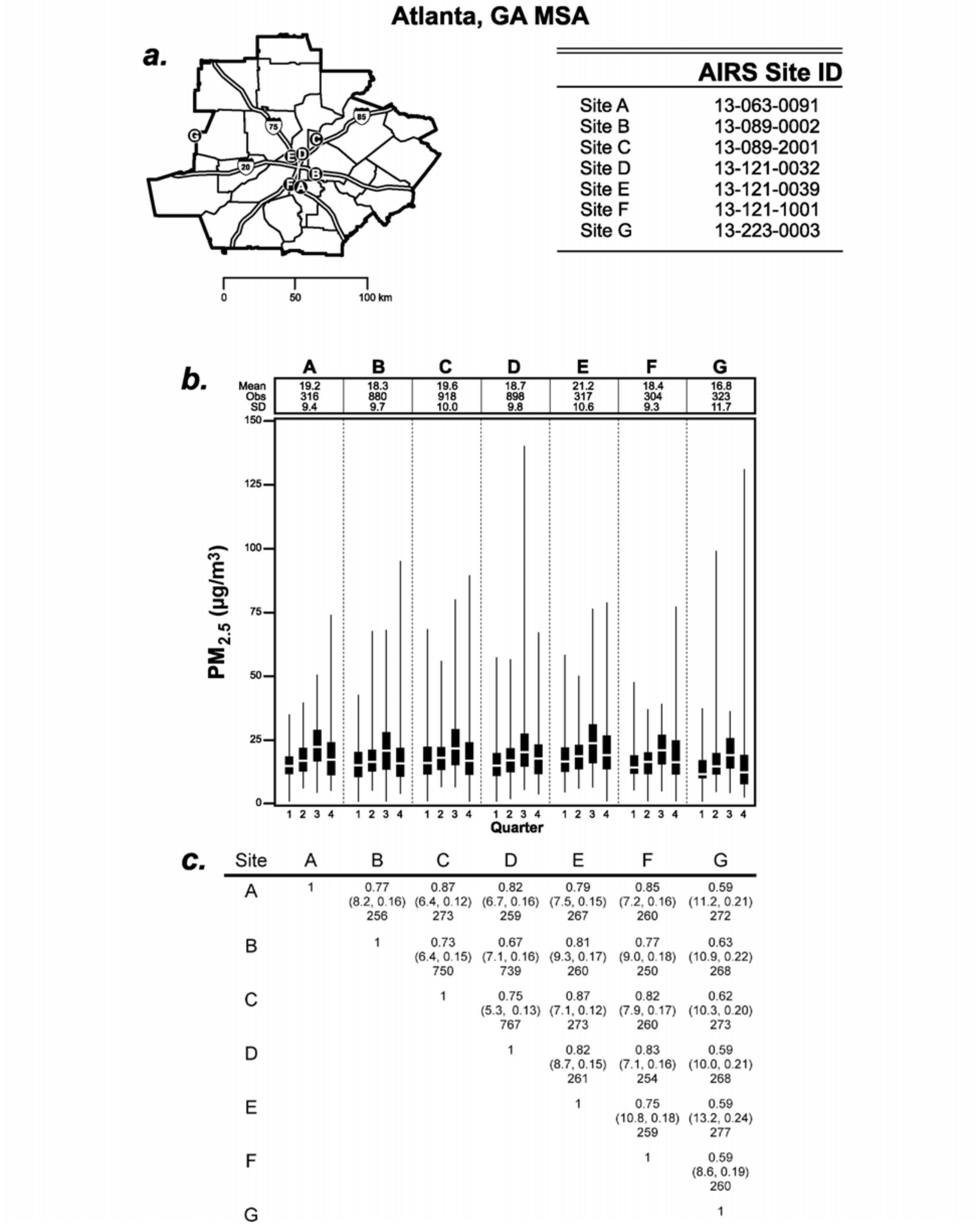


	AIRS Site ID
Site A	45-063-0008
Site B	45-079-0007
Site C	45-079-0019

c.

Site	A	B	C
A	1	0.93 (3.3, 0.08) 316	0.95 (3.2, 0.07) 319
B		1	0.97 (2.8, 0.06) 313
C			1

Figure 3A-4. Columbia, SC MSA. *(a)* Locations of sampling sites by AIRS ID#; (*b*) Quarterly distribution of 24-h average PM$_{2.5}$ concentrations for 1999-2001; *(c)* Intersite correlation statistics, for each data pair, the correlation coefficient, (P$_{90}$, COD) and number of measurements are given.



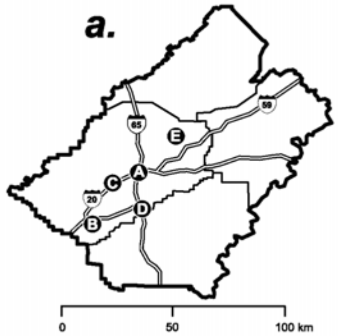
	AIRS Site ID
Site A	13-063-0091
Site B	13-089-0002
Site C	13-089-2001
Site D	13-121-0032
Site E	13-121-0039
Site F	13-121-1001
Site G	13-223-0003

	A	B	C	D	E	F	G
Mean	19.2	18.3	19.6	18.7	21.2	18.4	16.8
Obs	316	880	918	898	317	304	323
SD	9.4	9.7	10.0	9.8	10.6	9.3	11.7

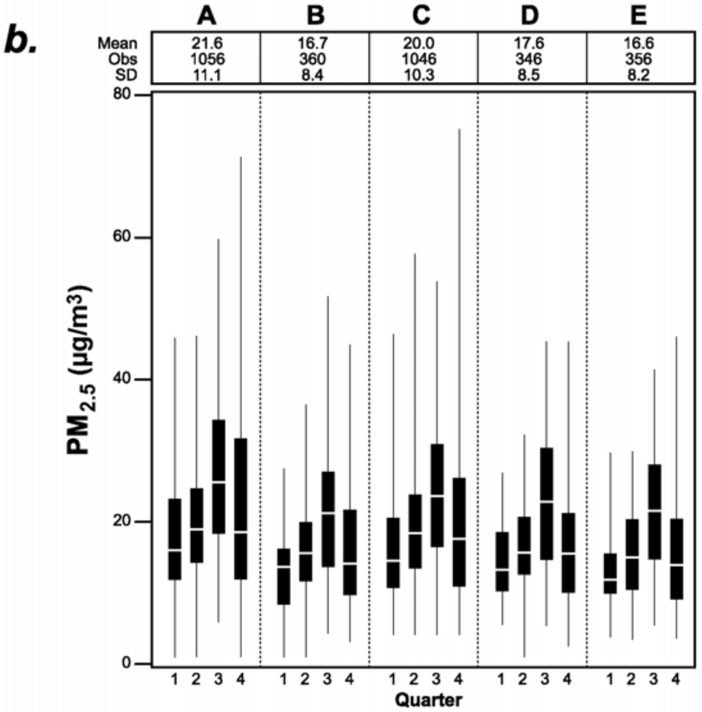
Site	A	B	C	D	E	F	G
A	1	0.77 (8.2, 0.16) 256	0.87 (6.4, 0.12) 273	0.82 (6.7, 0.16) 259	0.79 (7.5, 0.15) 267	0.85 (7.2, 0.16) 260	0.59 (11.2, 0.21) 272
B		1	0.73 (6.4, 0.15) 750	0.67 (7.1, 0.16) 739	0.81 (9.3, 0.17) 260	0.77 (9.0, 0.18) 250	0.63 (10.9, 0.22) 268
C			1	0.75 (5.3, 0.13) 767	0.87 (7.1, 0.12) 273	0.82 (7.9, 0.17) 260	0.62 (10.3, 0.20) 273
D				1	0.82 (8.7, 0.15) 261	0.83 (7.1, 0.16) 254	0.59 (10.0, 0.21) 268
E					1	0.75 (10.8, 0.18) 259	0.59 (13.2, 0.24) 277
F						1	0.59 (8.6, 0.19) 260
G							1

Figure 3A-5. Atlanta, GA MSA. *(a)* Locations of sampling sites by AIRS ID#; *(b)* Quarterly distribution of 24-h average PM$_{2.5}$ concentrations for 1999-2001; *(c)* Intersite correlation statistics, for each data pair, the correlation coefficient, (P$_{90}$, COD) and number of measurements are given.

Birmingham, AL MSA



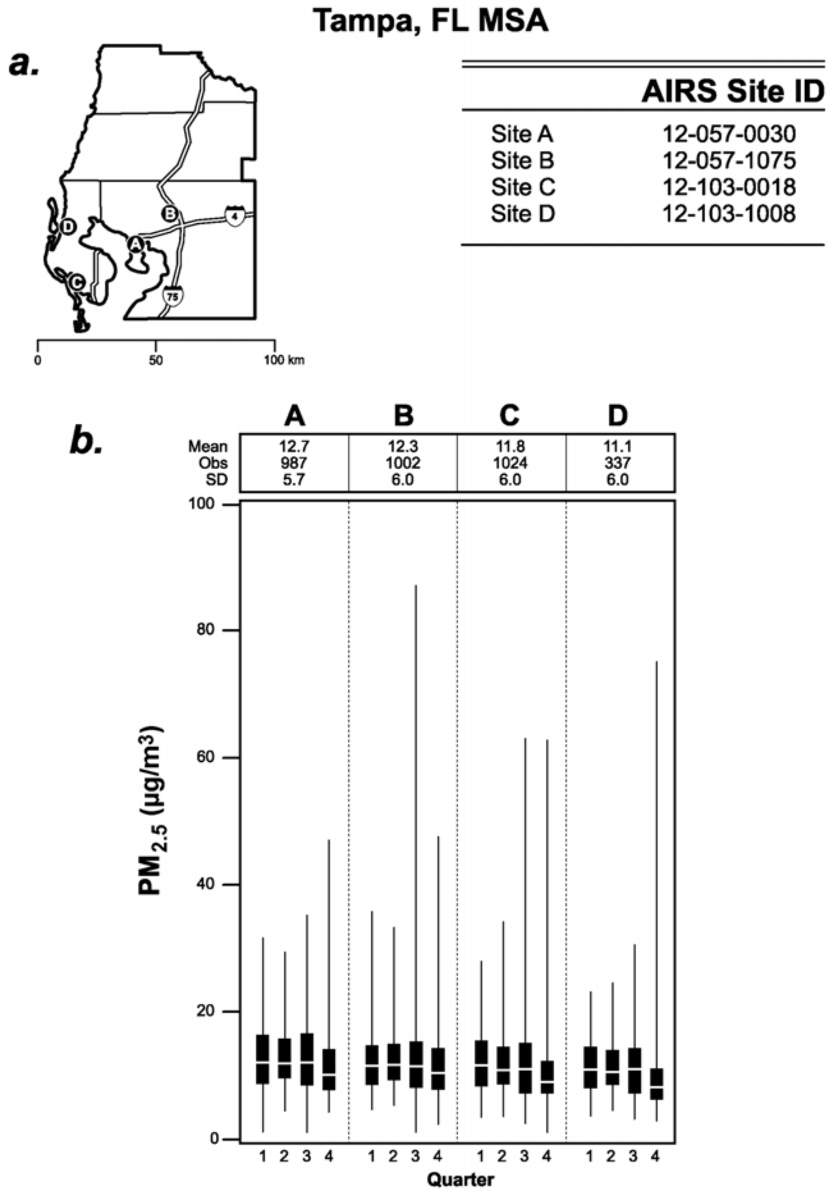
	AIRS Site ID
Site A	01-073-0023
Site B	01-073-1005
Site C	01-073-2003
Site D	01-073-2006
Site E	01-073-5002



c.

Site	A	B	C	D	E
A	1	0.80 (14.5, 0.20) 356	0.86 (9.8, 0.15) 1011	0.79 (13.7, 0.20) 342	0.80 (15.2, 0.21) 353
B		1	0.79 (10.2, 0.18) 348	0.86 (7.8, 0.16) 334	0.86 (6.7, 0.15) 345
C			1	0.78 (9.9, 0.18) 335	0.78 (10.3, 0.18) 344
D				1	0.86 (7.6, 0.15) 329
E					1

Figure 3A-6. Birmingham, AL MSA. *(a)* Locations of sampling sites by AIRS ID#; *(b)* Quarterly distribution of 24-h average $PM_{2.5}$ concentrations for 1999-2001; *(c)* Intersite correlation statistics, for each data pair, the correlation coefficient, (P_{90}, COD) and number of measurements are given.



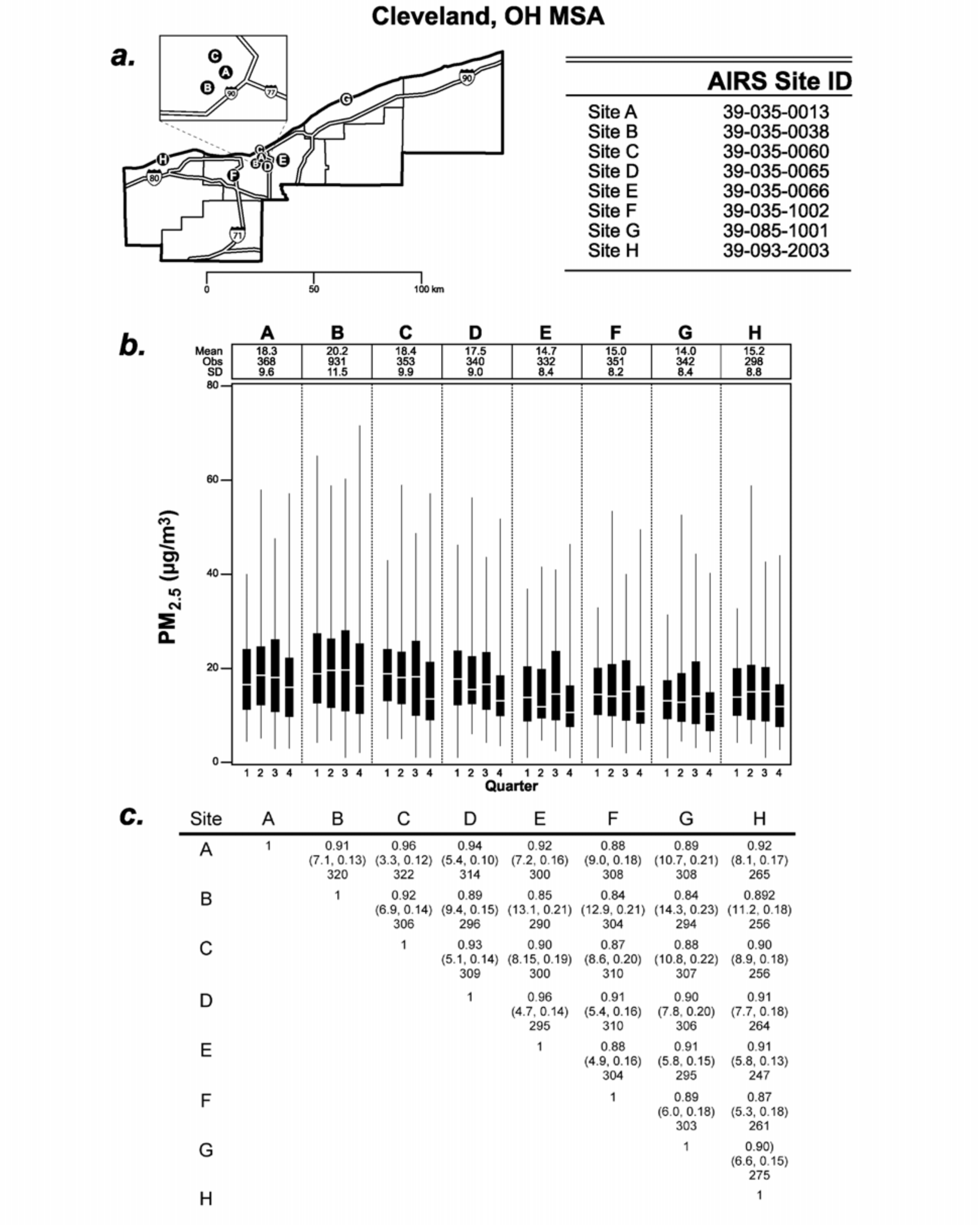
	AIRS Site ID
Site A	12-057-0030
Site B	12-057-1075
Site C	12-103-0018
Site D	12-103-1008

	A	B	C	D
Mean	12.7	12.3	11.8	11.1
Obs	987	1002	1024	337
SD	5.7	6.0	6.0	6.0

c.

Site	A	B	C	D
A	1	0.79 (3.6, 0.10) 919	0.87 (4.0, 0.11) 920	0.87 (4.3, 0.12) 308
B		1	0.70 (4.6, 0.14) 939	0.71 (5.0, 0.13) 314
C			1	0.82 (3.1, 0.10) 325
D				1

Figure 3A-7. Tampa, FL MSA. *(a)* Locations of sampling sites by AIRS ID#; *(b)* Quarterly distribution of 24-h average PM$_{2.5}$ concentrations for 1999-2001; *(c)* Intersite correlation statistics, for each data pair, the correlation coefficient, (P$_{90}$, COD) and number of measurements are given.



	AIRS Site ID
Site A	39-035-0013
Site B	39-035-0038
Site C	39-035-0060
Site D	39-035-0065
Site E	39-035-0066
Site F	39-035-1002
Site G	39-085-1001
Site H	39-093-2003

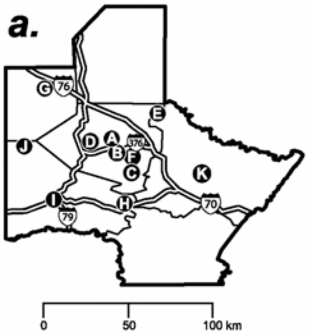
	A	B	C	D	E	F	G	H
Mean	18.3	20.2	18.4	17.5	14.7	15.0	14.0	15.2
Obs	368	931	353	340	332	351	342	298
SD	9.6	11.5	9.9	9.0	8.4	8.2	8.4	8.8

Site	A	B	C	D	E	F	G	H
A	1	0.91 (7.1, 0.13) 320	0.96 (3.3, 0.12) 322	0.94 (5.4, 0.10) 314	0.92 (7.2, 0.16) 300	0.88 (9.0, 0.18) 308	0.89 (10.7, 0.21) 308	0.92 (8.1, 0.17) 265
B		1	0.92 (6.9, 0.14) 306	0.89 (9.4, 0.15) 296	0.85 (13.1, 0.21) 290	0.84 (12.9, 0.21) 304	0.84 (14.3, 0.23) 294	0.892 (11.2, 0.18) 256
C			1	0.93 (5.1, 0.14) 309	0.90 (8.15, 0.19) 300	0.87 (8.6, 0.20) 310	0.88 (10.8, 0.22) 307	0.90 (8.9, 0.18) 256
D				1	0.96 (4.7, 0.14) 295	0.91 (5.4, 0.16) 310	0.90 (7.8, 0.20) 306	0.91 (7.7, 0.18) 264
E					1	0.88 (4.9, 0.16) 304	0.91 (5.8, 0.15) 295	0.91 (5.8, 0.13) 247
F						1	0.89 (6.0, 0.18) 303	0.87 (5.3, 0.18) 261
G							1	0.90) (6.6, 0.15) 275
H								1

Figure 3A-8. Cleveland, OH MSA. *(a)* Locations of sampling sites by AIRS ID#; (*b*) Quarterly distribution of 24-h average PM$_{2.5}$ concentrations for 1999-2001; *(c)* Intersite correlation statistics, for each data pair, the correlation coefficient, (P$_{90}$, COD) and number of measurements are given.

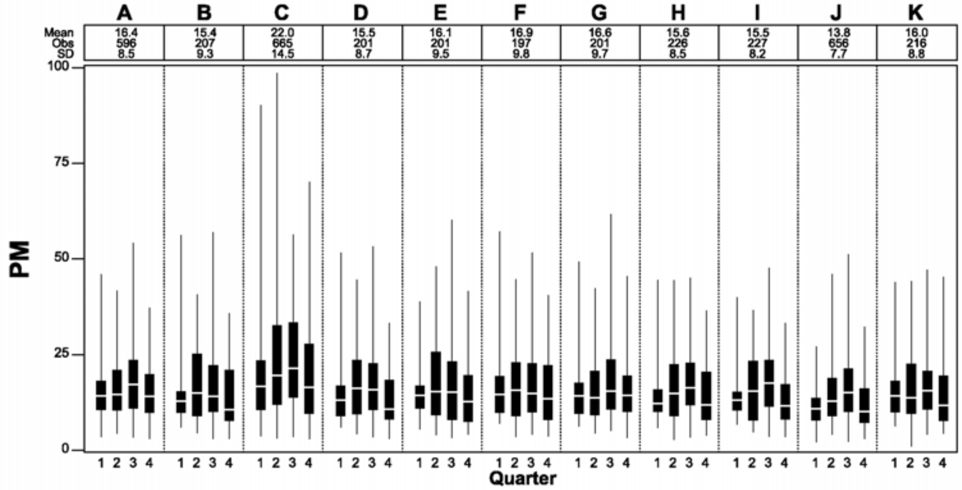
Pittsburgh, PA MSA

a.



	AIRS Site ID
Site A	42-003-0008
Site B	42-003-0021
Site C	42-003-0064
Site D	42-003-0116
Site E	42-003-1008
Site F	42-003-1301
Site G	42-007-0014
Site H	42-125-0005
Site I	42-125-0200
Site J	42-125-5001
Site K	42-129-0008

b.



	A	B	C	D	E	F	G	H	I	J	K
Mean	16.4	15.4	22.0	15.5	16.1	16.9	16.6	15.6	15.5	13.8	16.0
Obs	596	207	665	201	201	197	201	226	227	656	216
SD	8.5	9.3	14.5	8.7	9.5	9.8	9.7	8.5	8.2	7.7	8.8

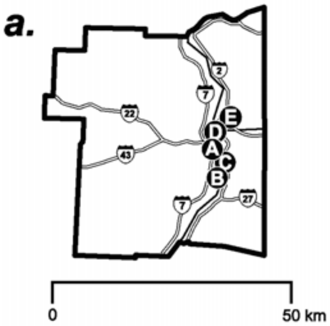
c.

Site	A	B	C	D	E	F	G	H	I	J	K
A	1	0.96 (2.6, 0.07) 171	0.79 (15.9, 0.19) 572	0.97 (3.0, 0.07) 168	0.94 (4.7, 0.09) 167	0.93 (5.2, 0.10) 173	0.94 (5.9, 0.09) 164	0.92 (5.1, 0.11) 183	0.93 (5.1, 0.10) 185	0.91 (6.6, 0.14) 531	0.87 (5.4, 0.11) 174
B		1	0.77 (18.0, 0.21) 193	0.95 (3.4, 0.08) 180	0.92 (6.1, 0.10) 173	0.91 (7.0, 0.13) 179	0.93 (6.1, 0.10) 132	0.93 (4.2, 0.09) 149	0.94 (4.8, 0.09) 151	0.91 (6.4, 0.13) 189	0.87 (4.9, 0.13) 144
C			1	0.80 (16.5, 0.20) 188	0.81 (17.1, 0.20) 188	0.86 (12.6, 0.15) 186	0.72 (19.1, 0.21) 182	0.74 (18.1, 0.22) 203	0.67 (20.3, 0.22) 203	0.69 (21.0, 0.26) 601	0.66 (18.1, 0.23) 194
D				1	0.92 (5.8, 0.11) 169	0.91 (6.0, 0.12) 172	0.94 (5.7, 0.11) 131	0.94 (4.9, 0.10) 143	0.94 (4.9, 0.10) 143	0.91 (6.6, 0.14) 181	0.87 (5.5, 0.13) 142
E					1	0.91 (6.2, 0.13) 165	0.94 (5.3, 0.11) 126	0.90 (7.0, 0.13) 147	0.89 (7.0, 0.14) 147	0.89 (8.7, 0.16) 190	0.83 (6.6, 0.15) 137
F						1	0.91 (7.1, 0.13) 126	0.89 (6.7, 0.14) 144	0.86 (7.6, 0.16) 144	0.86 (10.3, 0.19) 177	0.86 (7.2, 0.15) 139
G							1	0.89 (8.0, 0.13) 186	0.89 (8.1, 0.13) 184	0.90 (8.3, 0.16) 179	0.81 (9.5, 0.16) 175
H								1	0.94 (4.7, 0.09) 219	0.89 (4.7, 0.14) 201	0.88 (5.7, 0.12) 200
I									1	0.94 (5.6, 0.12) 202	0.88 (6.3, 0.12) 202
J										1	0.84 (7.3, 0.16) 195
K											1

Figure 3A-9. Pittsburgh, PA MSA. ***(a)*** **Locations of sampling sites by AIRS ID#;** ***(b)*** **Quarterly distribution of 24-h average $PM_{2.5}$ concentrations for 2000-2001;** ***(c)*** **Intersite correlation statistics, for each data pair, the correlation coefficient, (P_{90}, COD) and number of measurements are given.**

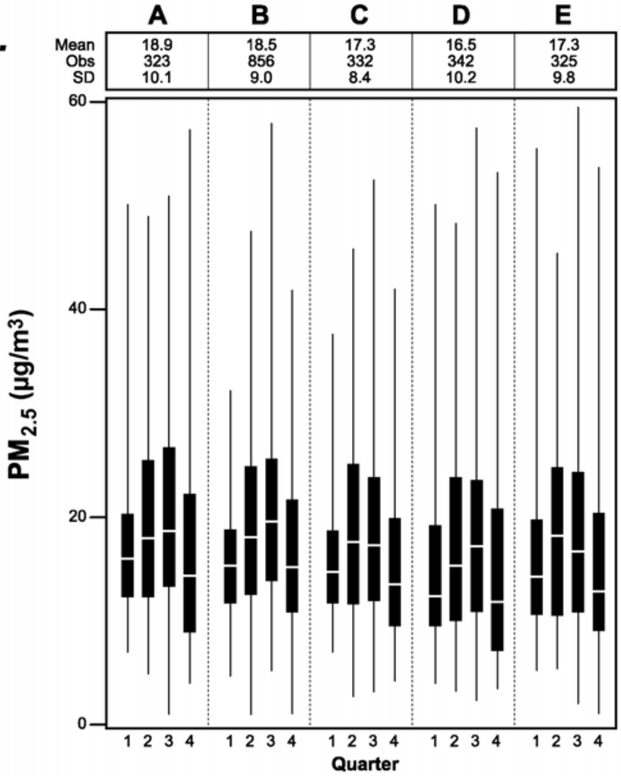
Steubenville, OH MSA

a.



	AIRS Site ID
Site A	39-081-0016
Site B	39-081-1001
Site C	54-009-0005
Site D	54-029-0011
Site E	54-029-1004

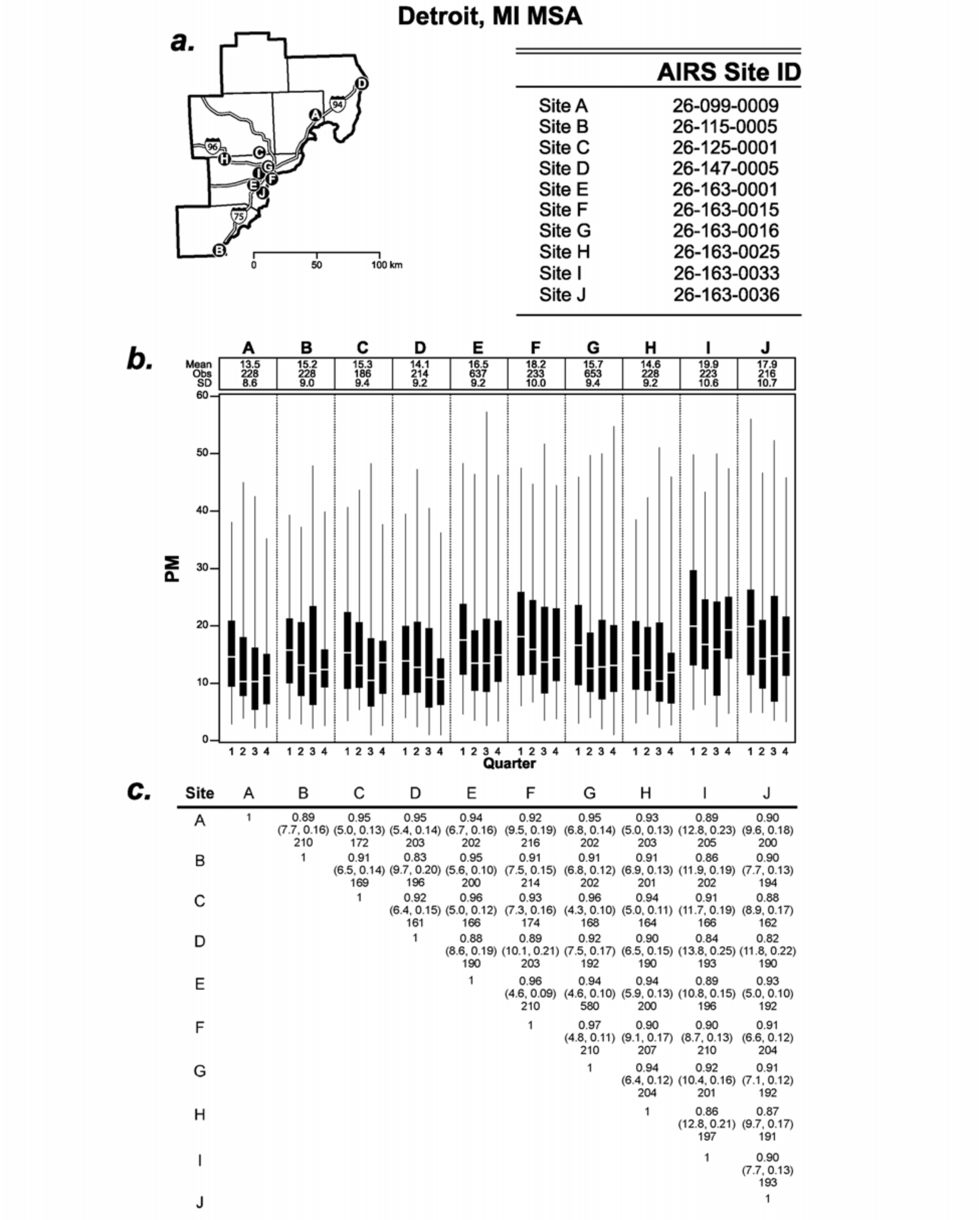
b.



c.

Site	A	B	C	D	E
A	1	0.85 (9.6, 0.16) 269	0.88 (8.0, 0.16) 294	0.86 (7.7, 0.16) 302	0.85 (7.9, 0.18) 290
B		1	0.87 (6.3, 0.16) 267	0.84 (8.6, 0.17) 277	0.79 (10, 0.20) 266
C			1	0.90 (7.4, 0.15) 320	0.89 (7.1, 0.16) 295
D				1	0.93 (6.2, 0.16) 307
E					1

Figure 3A-10. Steubenville, OH-Weirton, WV MSA. *(a)* Locations of sampling sites by AIRS ID#; *(b)* Quarterly distribution of 24-h average $PM_{2.5}$ concentrations for 1999-2001; *(c)* Intersite correlation statistics, for each data pair, the correlation coefficient, (P_{90}, COD) and number of measurements are given.



	AIRS Site ID
Site A	26-099-0009
Site B	26-115-0005
Site C	26-125-0001
Site D	26-147-0005
Site E	26-163-0001
Site F	26-163-0015
Site G	26-163-0016
Site H	26-163-0025
Site I	26-163-0033
Site J	26-163-0036

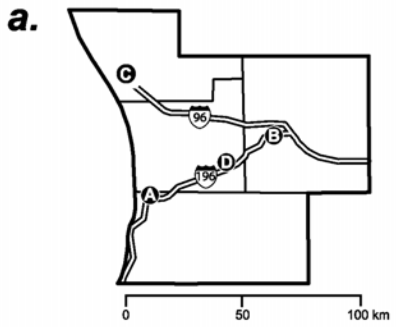
	A	B	C	D	E	F	G	H	I	J
Mean	13.5	15.2	15.3	14.1	16.5	18.2	15.7	14.6	19.9	17.9
Obs	228	228	186	214	637	233	653	228	223	216
SD	8.6	9.0	9.4	9.2	9.2	10.0	9.4	9.2	10.6	10.7

Site	A	B	C	D	E	F	G	H	I	J
A	1	0.89 (7.7, 0.16) 210	0.95 (5.0, 0.13) 172	0.95 (5.4, 0.14) 203	0.94 (6.7, 0.16) 202	0.92 (9.5, 0.19) 216	0.95 (6.8, 0.14) 202	0.93 (5.0, 0.13) 203	0.89 (12.8, 0.23) 205	0.90 (9.6, 0.18) 200
B		1	0.91 (6.5, 0.14) 169	0.83 (9.7, 0.20) 196	0.95 (5.6, 0.10) 200	0.91 (7.5, 0.15) 214	0.91 (6.8, 0.12) 202	0.91 (6.9, 0.13) 201	0.86 (11.9, 0.19) 202	0.90 (7.7, 0.13) 194
C			1	0.92 (6.4, 0.15) 161	0.96 (5.0, 0.12) 166	0.93 (7.3, 0.16) 174	0.96 (4.3, 0.10) 168	0.94 (5.0, 0.11) 164	0.91 (11.7, 0.19) 166	0.88 (8.9, 0.17) 162
D				1	0.88 (8.6, 0.19) 190	0.89 (10.1, 0.21) 203	0.92 (7.5, 0.17) 192	0.90 (6.5, 0.15) 190	0.84 (13.8, 0.25) 193	0.82 (11.8, 0.22) 190
E					1	0.96 (4.6, 0.09) 210	0.94 (4.6, 0.10) 580	0.94 (5.9, 0.13) 200	0.89 (10.8, 0.15) 196	0.93 (5.0, 0.10) 192
F						1	0.97 (4.8, 0.11) 210	0.90 (9.1, 0.17) 207	0.90 (8.7, 0.13) 210	0.91 (6.6, 0.12) 204
G							1	0.94 (6.4, 0.12) 204	0.92 (10.4, 0.16) 201	0.91 (7.1, 0.12) 192
H								1	0.86 (12.8, 0.21) 197	0.87 (9.7, 0.17) 191
I									1	0.90 (7.7, 0.13) 193
J										1

Figure 3A-11. Detroit MI MSA. *(a)* Locations of sampling sites by AIRS ID#; (*b*) Quarterly distribution of 24-h average $PM_{2.5}$ concentrations for 2000-2001; (*c*) Intersite correlation statistics, for each data pair, the correlation coefficient, (P_{90}, COD) and number of measurements are given.

Grand Rapids, MI MSA

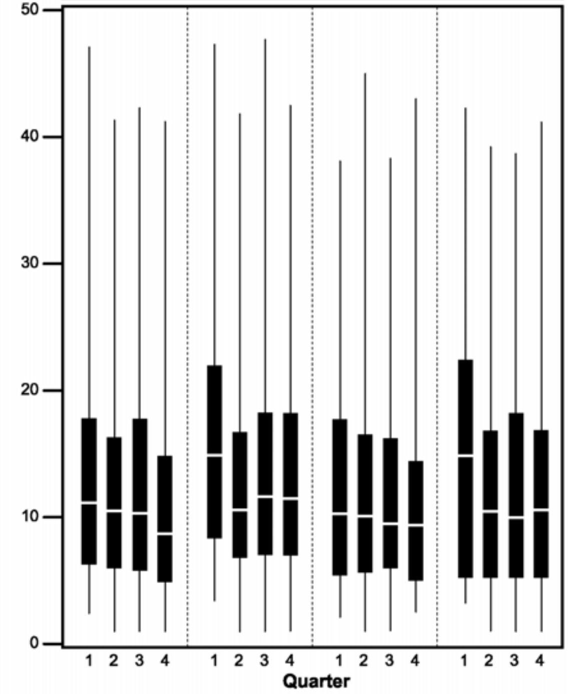
a.



	AIRS Site ID
Site A	26-005-0003
Site B	26-081-0020
Site C	26-121-0040
Site D	26-139-0005

b.

	A	B	C	D
Mean	12.2	14.0	12.1	13.3
Obs	1036	1050	378	351
SD	8.4	8.6	8.3	8.5

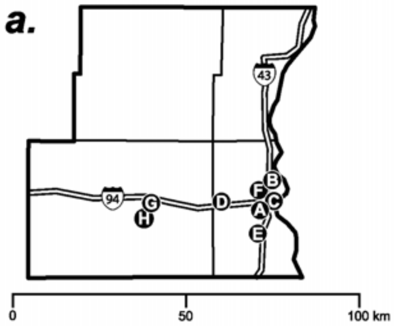


c.

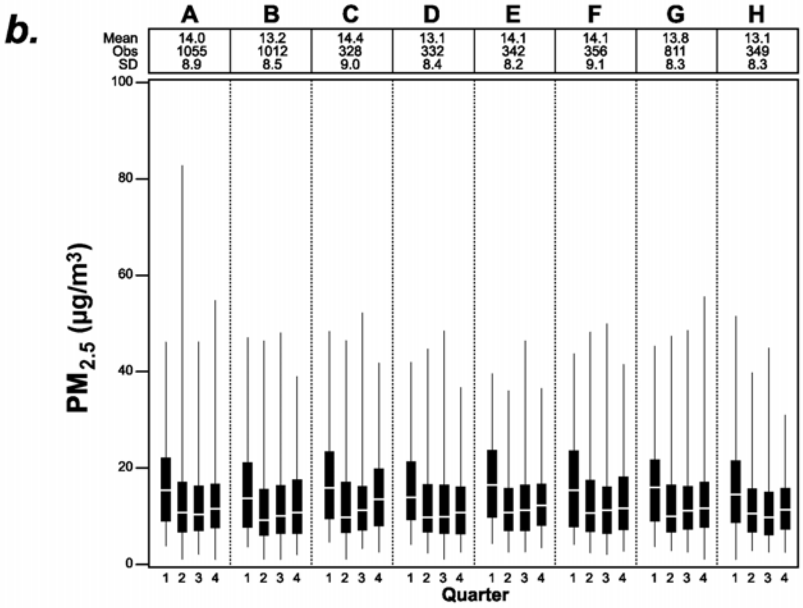
Site	A	B	C	D
A	1	0.94 (5.7, 0.15) 998	0.93 (4.4, 0.13) 357	0.95 (4.4, 0.12) 337
B		1	0.93 (6.1, 0.16) 359	0.98 (3.1, 0.10) 332
C			1	0.94 (5.2, 0.13) 324
D				1

Figure 3A-12. Grand Rapids, MI MSA. *(a)* Locations of sampling sites by AIRS ID#; *(b)* Quarterly distribution of 24-h average $PM_{2.5}$ concentrations for 1999-2001; *(c)* Intersite correlation statistics, for each data pair, the correlation coefficient, (P_{90}, COD) and number of measurements are given.

Milwaukee, WI MSA



	AIRS Site ID
Site A	55-079-0010
Site B	55-079-0026
Site C	55-079-0043
Site D	55-079-0051
Site E	55-079-0059
Site F	55-079-0099
Site G	55-133-0027
Site H	55-133-0034



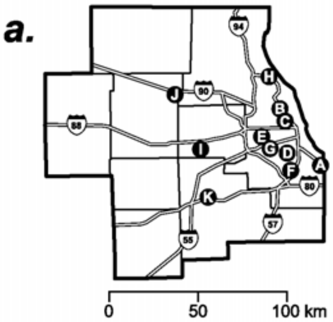
	A	B	C	D	E	F	G	H
Mean	14.0	13.2	14.4	13.1	14.1	14.1	13.8	13.1
Obs	1055	1012	328	332	342	356	811	349
SD	8.9	8.5	9.0	8.4	8.2	9.1	8.3	8.3

c.

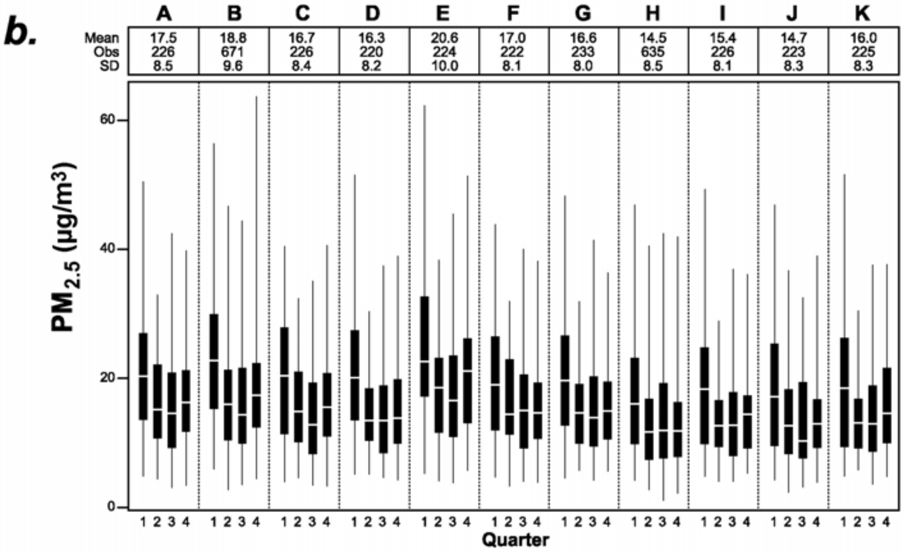
Site	A	B	C	D	E	F	G	H
A	1	0.91 (3.3, 0.11) 974	0.84 (4.0, 0.12) 319	0.86 (3.0, 0.11) 321	0.97 (2.9, 0.10) 332	0.87 (3.4, 0.09) 345	0.91 (3.3, 0.10) 782	0.82 (3.4, 0.11) 338
B		1	0.95 (3.7, 0.12) 311	0.95 (3.9, 0.12) 315	0.96 (3.1, 0.11) 324	0.97 (3.5, 0.10) 337	0.96 (3.6, 0.12) 749	0.91 (3.6, 0.13) 330
C			1	0.94 (4.4, 0.13) 285	0.96 (3.8, 0.09) 284	0.97 (3.4, 0.09) 296	0.94 (4.0, 0.12) 315	0.89 (5.3, 0.14) 293
D				1	0.96 (3.9, 0.12) 306	0.96 (4.5, 0.12) 327	0.97 (3.5, 0.10) 319	0.92 (3.6, 0.11) 318
E					1	0.97 (3.5, 0.09) 319	0.96 (3.4, 0.09) 325	0.93 (3.6, 0.12) 317
F						1	0.97 (3.7, 0.10) 335	0.92 (5.0, 0.12) 335
G							1	0.93 (2.8, 0.10) 330
H								1

Figure 3A-13. Milwaukee, WI MSA. *(a)* Locations of sampling sites by AIRS ID#; (*b*) Quarterly distribution of 24-h average $PM_{2.5}$ concentrations for 1999-2001; *(c)* Intersite correlation statistics, for each data pair, the correlation coefficient, (P_{90}, COD) and number of measurements are given.

Chicago, IL MSA



	AIRS Site ID
Site A	17-031-0022
Site B	17-031-0052
Site C	17-031-0057
Site D	17-031-0076
Site E	17-031-1016
Site F	17-031-2001
Site G	17-031-3301
Site H	17-031-4201
Site I	17-043-4002
Site J	17-089-0003
Site K	17-197-1002

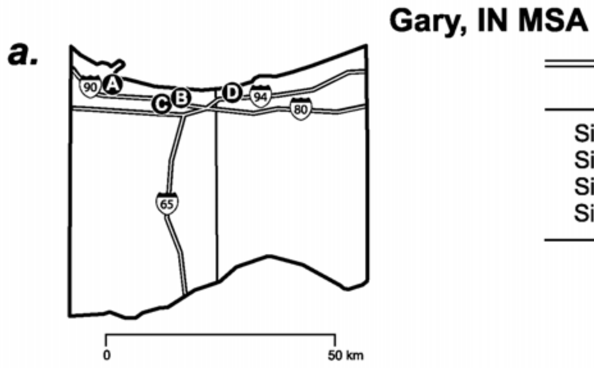


	A	B	C	D	E	F	G	H	I	J	K
Mean	17.5	18.8	16.7	16.3	20.6	17.0	16.6	14.5	15.4	14.7	16.0
Obs	226	671	226	220	224	222	233	635	226	223	225
SD	8.5	9.6	8.4	8.2	10.0	8.1	8.0	8.5	8.1	8.3	8.3

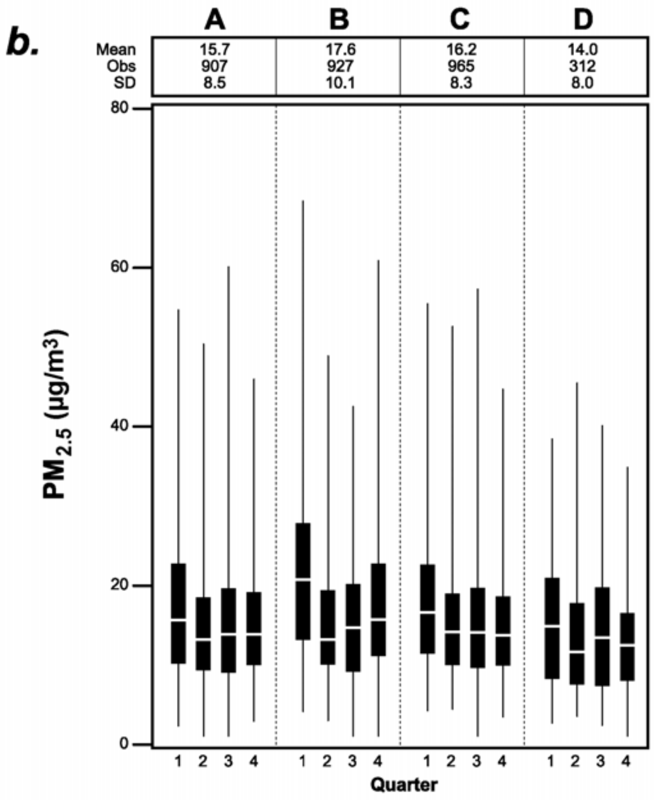
c.

Site	A	B	C	D	E	F	G	H	I	J	K
A	1	0.89 (7.0, 0.14) 210	0.90 (5.3, 0.12) 205	0.94 (4.4, 0.10) 202	0.89 (8.9, 0.15) 211	0.92 (5.0, 0.11) 201	0.90 (5.8, 0.12) 208	0.89 (8.1, 0.18) 196	0.89 (7.0, 0.16) 197	0.89 (7.6, 0.18) 178	0.85 (6.6, 0.16) 173
B		1	0.90 (6.2, 0.12) 210	0.91 (6.6, 0.13) 208	0.90 (7.9, 0.13) 212	0.88 (7.9, 0.13) 209	0.89 (7.6, 0.13) 217	0.90 (9.8, 0.19) 584	0.87 (10.2, 0.17) 212	0.90 (9.3, 0.18) 205	0.81 (10.1, 0.17) 208
C			1	0.93 (3.9, 0.09) 201	0.92 (7.7, 0.14) 204	0.92 (5.1, 0.10) 197	0.90 (5.2, 0.10) 206	0.92 (6.2, 0.14) 199	0.90 (6.3, 0.12) 189	0.91 (6.2, 0.13) 175	0.89 (6.8, 0.12) 173
D				1	0.92 (9.0, 0.14) 201	0.96 (3.5, 0.07) 198	0.95 (3.5, 0.07) 205	0.93 (6.5, 0.14) 191	0.94 (5.0, 0.10) 188	0.94 (5.5, 0.13) 181	0.93 (5.0, 0.10) 172
E					1	0.92 (9.1, 0.14) 199	0.90 (9.6, 0.14) 206	0.91 (10.9, 0.22) 195	0.90 (10.7, 0.18) 192	0.92 (11.3, 0.20) 177	0.87 (10.8, 0.18) 174
F						1	0.93 (4.5, 0.09) 204	0.91 (7.0, 0.16) 190	0.94 (4.9, 0.11) 188	0.92 (6.7, 0.14) 172	0.90 (5.8, 0.12) 167
G							1	0.91 (6.7, 0.15) 200	0.94 (4.8, 0.10) 193	0.92 (6.0, 0.14) 178	0.89 (5.5, 0.12) 173
H								1	0.92 (5.5, 0.13) 198	0.95 (5.0, 0.11) 195	0.85 (6.6, 0.15) 197
I									1	0.95 (4.2, 0.10) 168	0.94 (3.9, 0.09) 164
J										1	0.93 (5.5, 0.11) 153
K											1

Figure 3A-14. Chicago, IL MSA. ***(a)*** **Locations of sampling sites by AIRS ID#;** ***(b)*** **Quarterly distribution of 24-h average PM$_{2.5}$ concentrations for 2000-2001;** ***(c)*** **Intersite correlation statistics, for each data pair, the correlation coefficient, (P$_{90}$, COD) and number of measurements are given.**



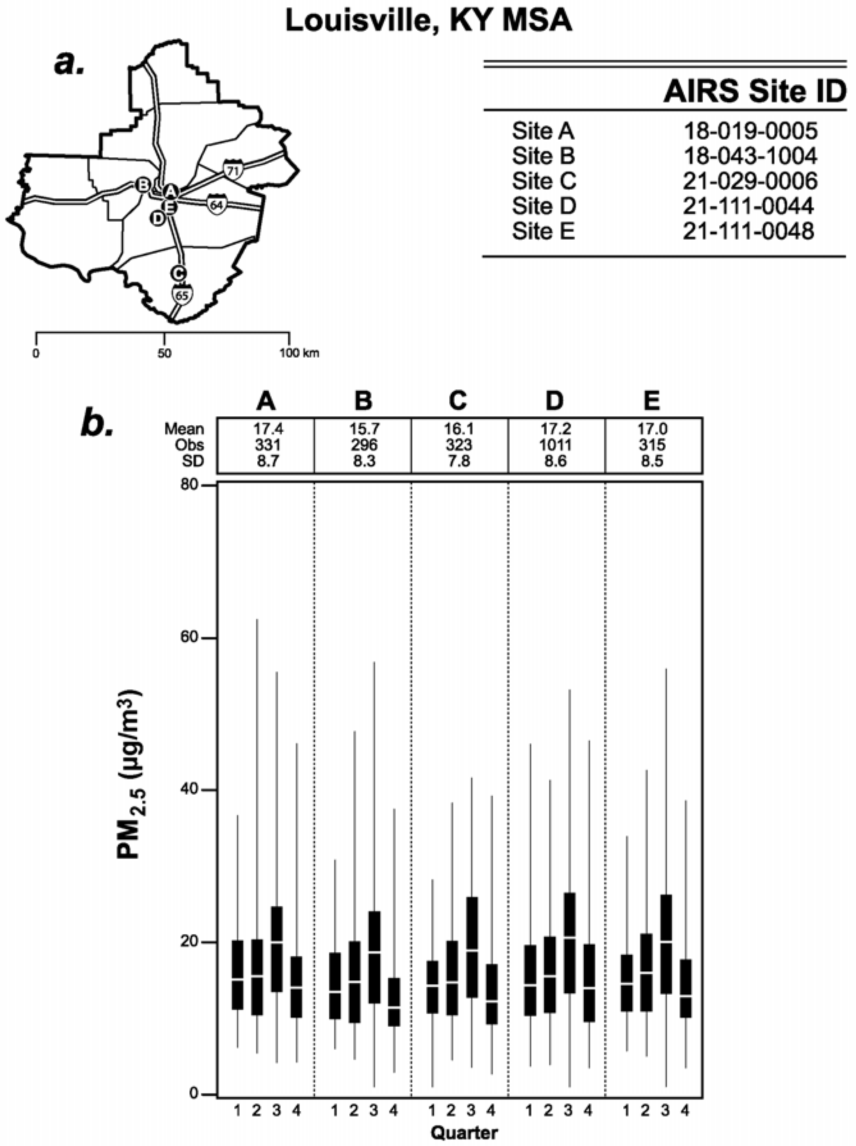
	AIRS Site ID
Site A	18-089-0006
Site B	18-089-0022
Site C	18-089-1016
Site D	18-127-0024



c.

Site	A	B	C	D
A	1	0.65 (9.1, 0.19) 823	0.93 (4.2, 0.13) 822	0.91 (5.0, 0.17) 277
B		1	0.59 (11.3, 0.20) 841	0.56 (10.9, 0.23) 277
C			1	0.92 (6.4, 0.17) 281
D				1

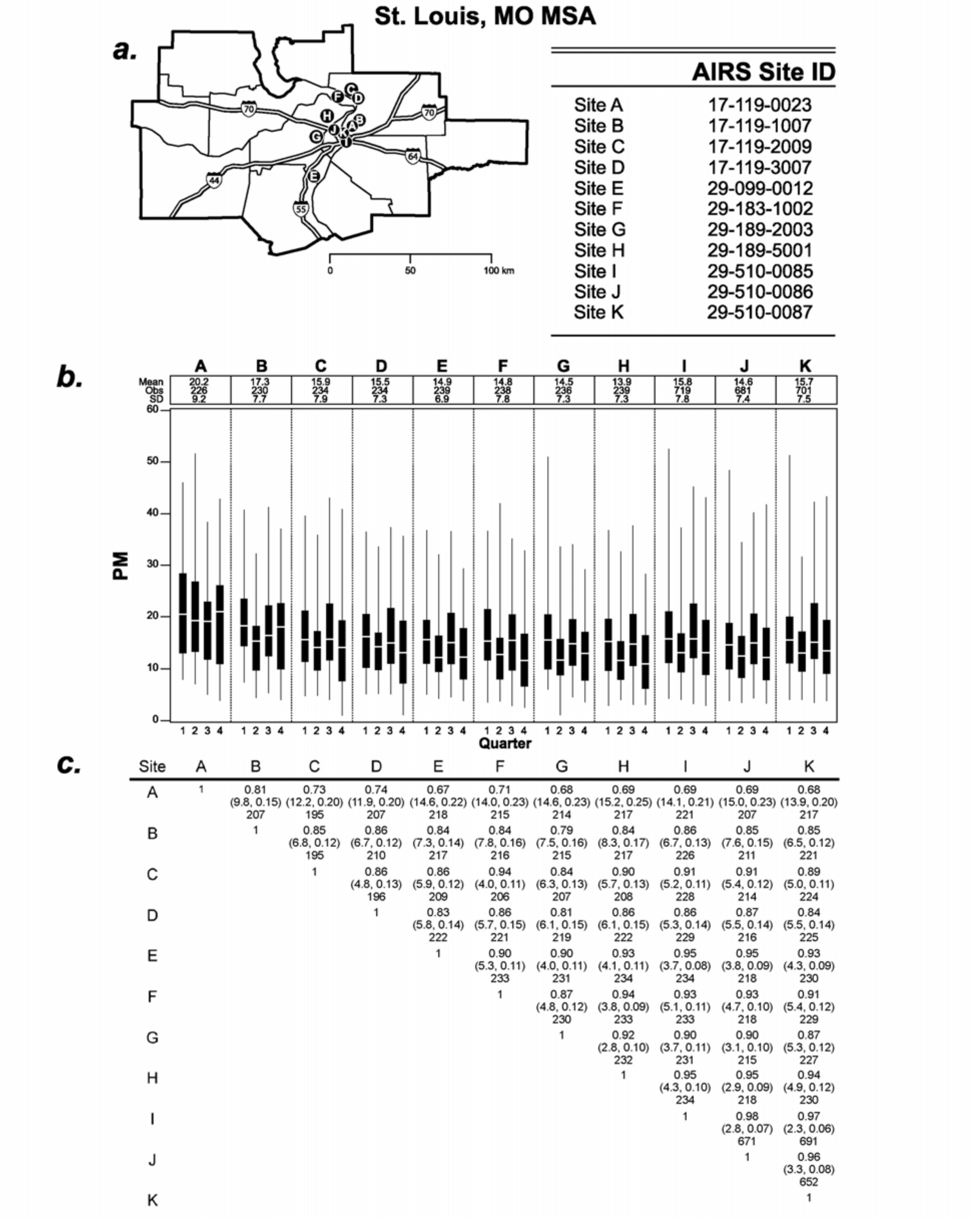
Figure 3A-15. Gary, IN MSA. *(a)* Locations of sampling sites by AIRS ID#; *(b)* Quarterly distribution of 24-h average PM$_{2.5}$ concentrations for 1999-2001; *(c)* Intersite correlation statistics, for each data pair, the correlation coefficient, (P$_{90}$, COD) and number of measurements are given.



c.

Site	A	B	C	D	E
A	1	0.86 (5.8, 0.13) 279	0.90 (6.0, 0.12) 289	0.91 (3.9, 0.10) 315	0.91 (3.8, 0.08) 273
B		1	0.87 (6.0, 0.15) 260	0.89 (5.9, 0.14) 282	0.91 (5.3, 0.13) 250
C			1	0.93 (5.4, 0.12) 307	0.90 (5.6, 0.12) 256
D				1	0.93 (4.2, 0.11) 302
E					1

Figure 3A-16. Louisville, KY MSA. *(a)* Locations of sampling sites by AIRS ID#; (*b*) Quarterly distribution of 24-h average PM$_{2.5}$ concentrations for 2000-2001; (*c*) Intersite correlation statistics, for each data pair, the correlation coefficient, (P$_{90}$, COD) and number of measurements are given.

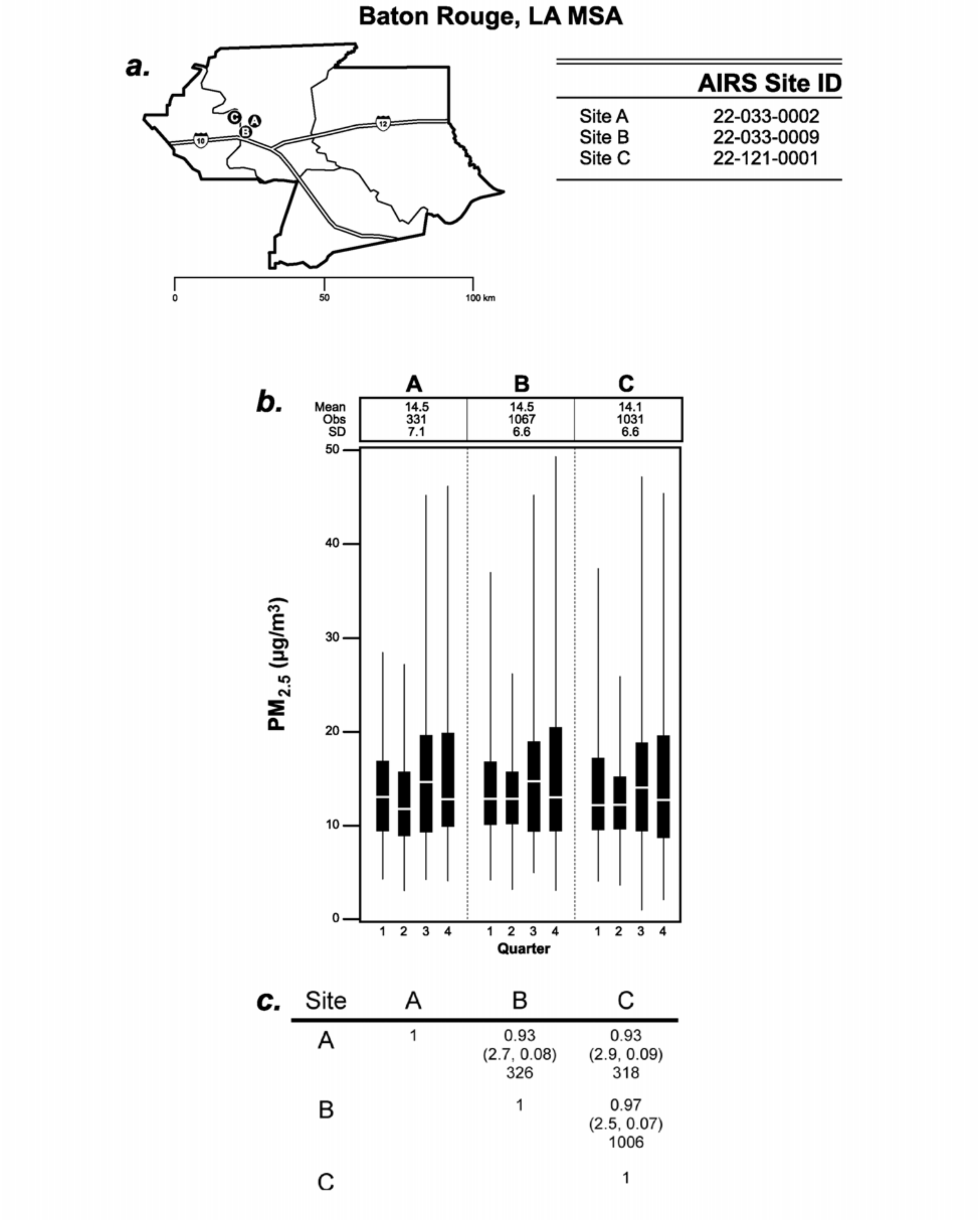


	AIRS Site ID
Site A	17-119-0023
Site B	17-119-1007
Site C	17-119-2009
Site D	17-119-3007
Site E	29-099-0012
Site F	29-183-1002
Site G	29-189-2003
Site H	29-189-5001
Site I	29-510-0085
Site J	29-510-0086
Site K	29-510-0087

	A	B	C	D	E	F	G	H	I	J	K
Mean	20.2	17.3	15.9	15.5	14.9	14.8	14.5	13.9	15.8	14.6	15.7
Obs	226	230	234	234	239	238	236	239	719	681	701
SD	9.2	7.7	7.9	7.3	6.9	7.8	7.3	7.3	7.8	7.4	7.5

Site	A	B	C	D	E	F	G	H	I	J	K
A	1	0.81 (9.8, 0.15) 207	0.73 (12.2, 0.20) 195	0.74 (11.9, 0.20) 207	0.67 (14.6, 0.22) 218	0.71 (14.0, 0.23) 215	0.68 (14.6, 0.23) 214	0.69 (15.2, 0.25) 217	0.69 (14.1, 0.21) 221	0.69 (15.0, 0.23) 207	0.68 (13.9, 0.20) 217
B		1	0.85 (6.8, 0.12) 195	0.86 (6.7, 0.12) 210	0.84 (7.3, 0.14) 217	0.84 (7.8, 0.16) 216	0.79 (7.5, 0.16) 215	0.84 (8.3, 0.17) 217	0.86 (6.7, 0.13) 226	0.85 (7.6, 0.15) 211	0.85 (6.5, 0.12) 221
C			1	0.86 (4.8, 0.13) 196	0.86 (5.9, 0.12) 209	0.94 (4.0, 0.11) 206	0.84 (6.3, 0.13) 207	0.90 (5.7, 0.13) 208	0.91 (5.2, 0.11) 228	0.91 (5.4, 0.12) 214	0.89 (5.0, 0.11) 224
D				1	0.83 (5.8, 0.14) 222	0.86 (5.7, 0.15) 221	0.81 (6.1, 0.15) 219	0.86 (6.1, 0.15) 222	0.86 (5.3, 0.14) 229	0.87 (5.5, 0.14) 216	0.84 (5.5, 0.14) 225
E					1	0.90 (5.3, 0.11) 233	0.90 (4.0, 0.11) 231	0.93 (4.1, 0.11) 234	0.95 (3.7, 0.08) 234	0.95 (3.8, 0.09) 218	0.93 (4.3, 0.09) 230
F						1	0.87 (4.8, 0.12) 230	0.94 (3.8, 0.09) 233	0.93 (5.1, 0.11) 233	0.93 (4.7, 0.10) 218	0.91 (5.4, 0.12) 229
G							1	0.92 (2.8, 0.10) 232	0.90 (3.7, 0.11) 231	0.90 (3.1, 0.10) 215	0.87 (5.3, 0.12) 227
H								1	0.95 (4.3, 0.10) 234	0.95 (2.9, 0.09) 218	0.94 (4.9, 0.12) 230
I									1	0.98 (2.8, 0.07) 671	0.97 (2.3, 0.06) 691
J										1	0.96 (3.3, 0.08) 652
K											1

Figure 3A-17. St. Louis, MO MSA. *(a)* Locations of sampling sites by AIRS ID#; (*b*) Quarterly distribution of 24-h average $PM_{2.5}$ concentrations for 2000-2001; (*c*) Intersite correlation statistics, for each data pair, the correlation coefficient, (P_{90}, COD) and number of measurements are given.

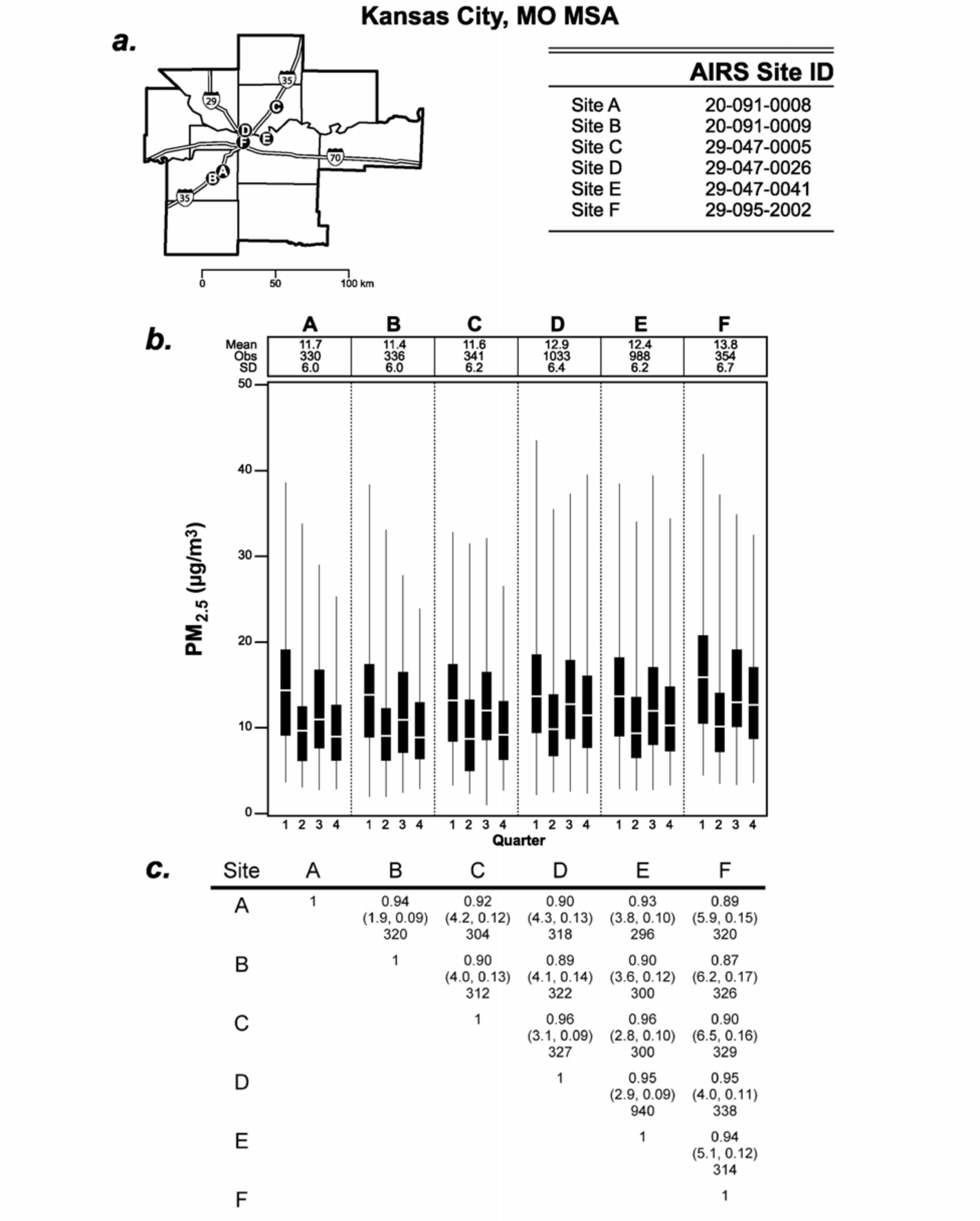


	AIRS Site ID
Site A	22-033-0002
Site B	22-033-0009
Site C	22-121-0001

	A	B	C
Mean	14.5	14.5	14.1
Obs	331	1067	1031
SD	7.1	6.6	6.6

Site	A	B	C
A	1	0.93 (2.7, 0.08) 326	0.93 (2.9, 0.09) 318
B		1	0.97 (2.5, 0.07) 1006
C			1

Figure 3A-18. Baton Rouge, LA MSA. *(a)* Locations of sampling sites by AIRS ID#; *(b)* Quarterly distribution of 24-h average PM$_{2.5}$ concentrations for 1999-2001; *(c)* Intersite correlation statistics, for each data pair, the correlation coefficient, (P$_{90}$, COD) and number of measurements are given.



Kansas City, MO MSA

a.

	AIRS Site ID
Site A	20-091-0008
Site B	20-091-0009
Site C	29-047-0005
Site D	29-047-0026
Site E	29-047-0041
Site F	29-095-2002

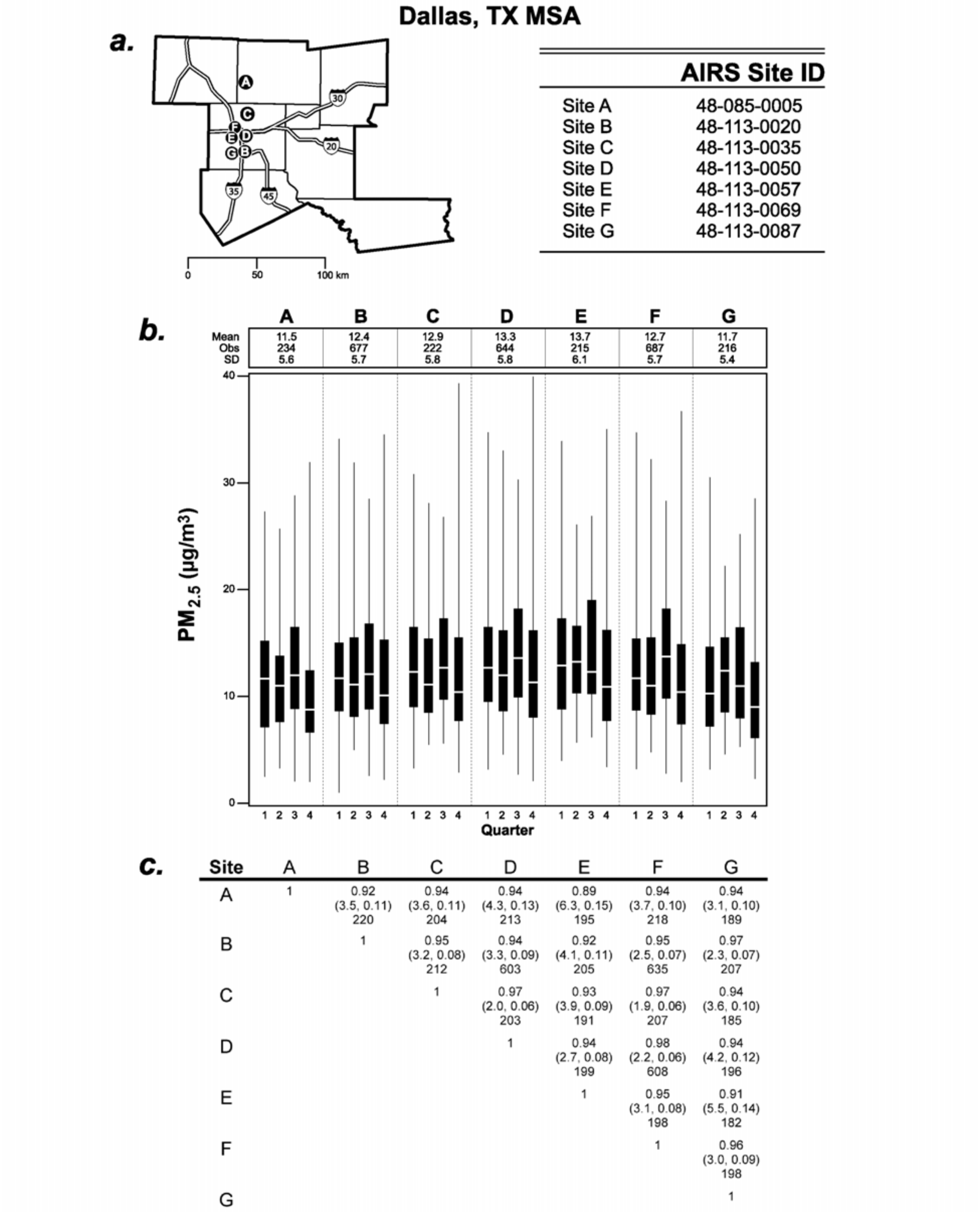
b.

	A	B	C	D	E	F
Mean	11.7	11.4	11.6	12.9	12.4	13.8
Obs	330	336	341	1033	988	354
SD	6.0	6.0	6.2	6.4	6.2	6.7

c.

Site	A	B	C	D	E	F
A	1	0.94 (1.9, 0.09) 320	0.92 (4.2, 0.12) 304	0.90 (4.3, 0.13) 318	0.93 (3.8, 0.10) 296	0.89 (5.9, 0.15) 320
B		1	0.90 (4.0, 0.13) 312	0.89 (4.1, 0.14) 322	0.90 (3.6, 0.12) 300	0.87 (6.2, 0.17) 326
C			1	0.96 (3.1, 0.09) 327	0.96 (2.8, 0.10) 300	0.90 (6.5, 0.16) 329
D				1	0.95 (2.9, 0.09) 940	0.95 (4.0, 0.11) 338
E					1	0.94 (5.1, 0.12) 314
F						1

Figure 3A-19. Kansas City, KS-MO MSA. *(a)* Locations of sampling sites by AIRS ID#; (*b*) Quarterly distribution of 24-h average $PM_{2.5}$ concentrations for 1999-2001; *(c)* Intersite correlation statistics, for each data pair, the correlation coefficient, (P_{90}, COD) and number of measurements are given.

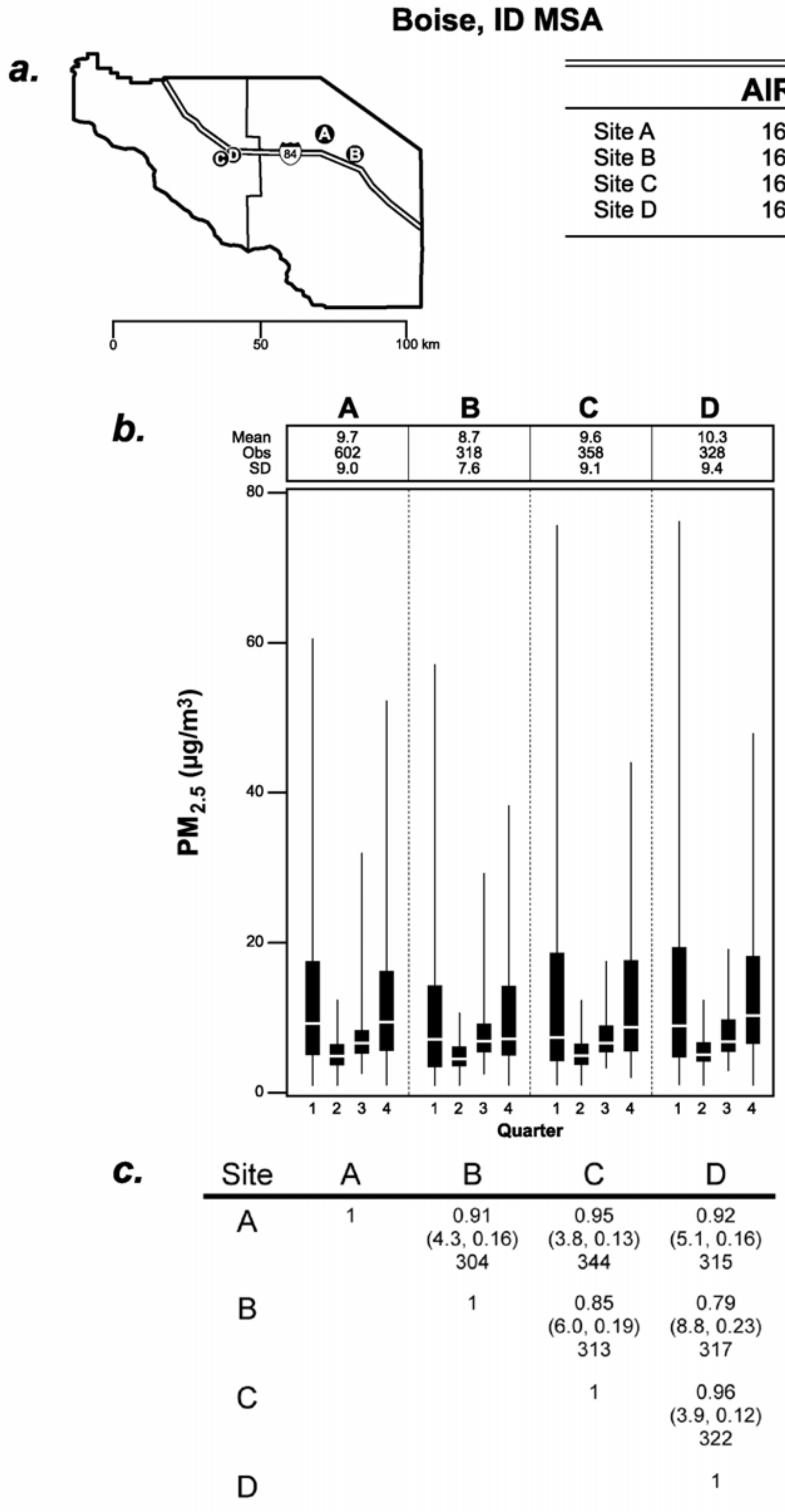


	AIRS Site ID
Site A	48-085-0005
Site B	48-113-0020
Site C	48-113-0035
Site D	48-113-0050
Site E	48-113-0057
Site F	48-113-0069
Site G	48-113-0087

	A	B	C	D	E	F	G
Mean	11.5	12.4	12.9	13.3	13.7	12.7	11.7
Obs	234	677	222	644	215	687	216
SD	5.6	5.7	5.8	5.8	6.1	5.7	5.4

Site	A	B	C	D	E	F	G
A	1	0.92 (3.5, 0.11) 220	0.94 (3.6, 0.11) 204	0.94 (4.3, 0.13) 213	0.89 (6.3, 0.15) 195	0.94 (3.7, 0.10) 218	0.94 (3.1, 0.10) 189
B		1	0.95 (3.2, 0.08) 212	0.94 (3.3, 0.09) 603	0.92 (4.1, 0.11) 205	0.95 (2.5, 0.07) 635	0.97 (2.3, 0.07) 207
C			1	0.97 (2.0, 0.06) 203	0.93 (3.9, 0.09) 191	0.97 (1.9, 0.06) 207	0.94 (3.6, 0.10) 185
D				1	0.94 (2.7, 0.08) 199	0.98 (2.2, 0.06) 608	0.94 (4.2, 0.12) 196
E					1	0.95 (3.1, 0.08) 198	0.91 (5.5, 0.14) 182
F						1	0.96 (3.0, 0.09) 198
G							1

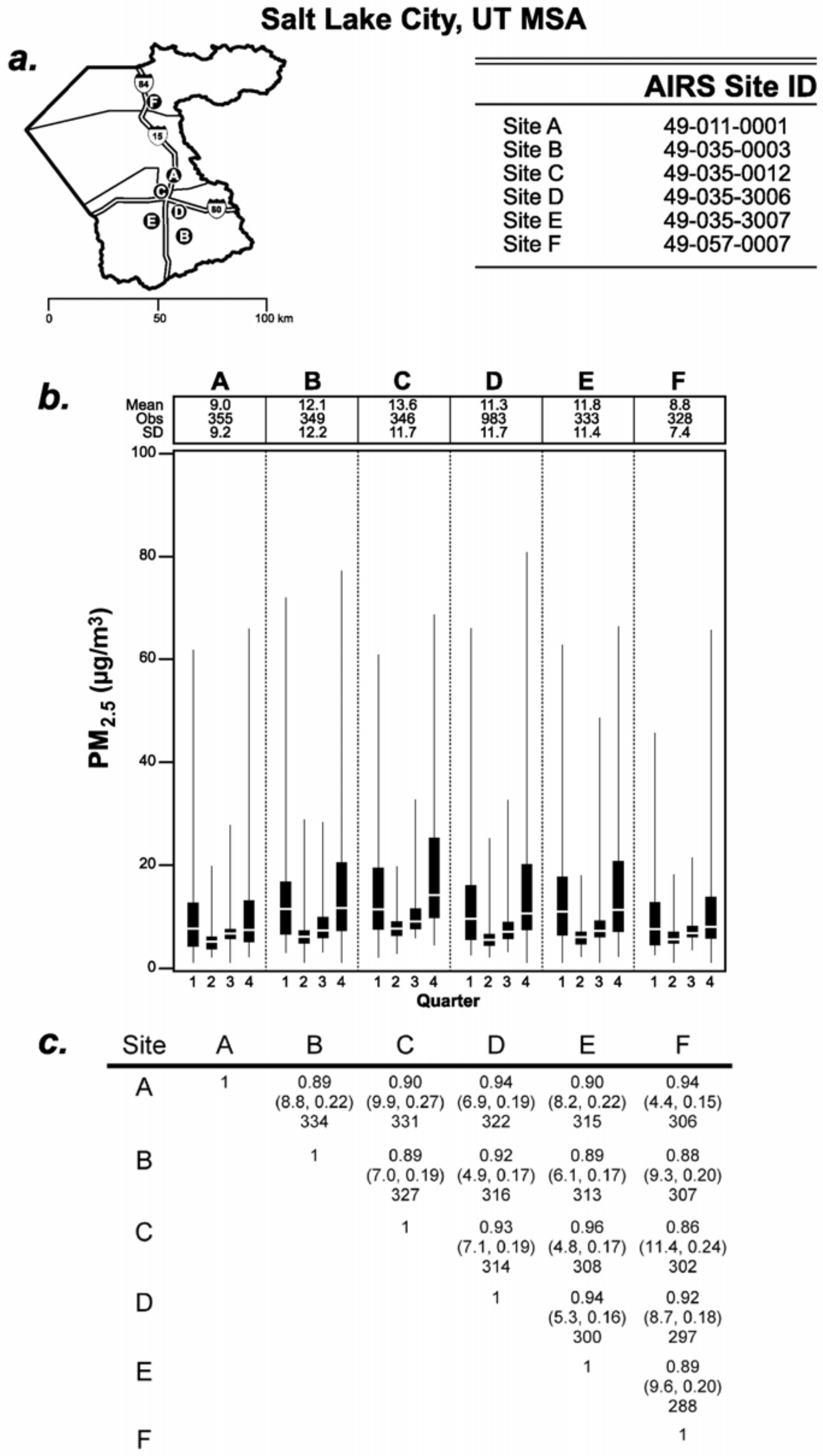
Figure 3A-20. Dallas, TX MSA. *(a)* Locations of sampling sites by AIRS ID#; *(b)* Quarterly distribution of 24-h average PM$_{2.5}$ concentrations for 2000-2001; *(c)* Intersite correlation statistics, for each data pair, the correlation coefficient, (P$_{90}$, COD) and number of measurements are given.



	AIRS Site ID
Site A	16-001-0011
Site B	16-001-0017
Site C	16-027-0004
Site D	16-027-0005

Site	A	B	C	D
A	1	0.91 (4.3, 0.16) 304	0.95 (3.8, 0.13) 344	0.92 (5.1, 0.16) 315
B		1	0.85 (6.0, 0.19) 313	0.79 (8.8, 0.23) 317
C			1	0.96 (3.9, 0.12) 322
D				1

Figure 3A-21. Boise, ID MSA. *(a)* Locations of sampling sites by AIRS ID#; *(b)* Quarterly distribution of 24-h average $PM_{2.5}$ concentrations for 1999-2001; *(c)* Intersite correlation statistics, for each data pair, the correlation coefficient, (P_{90}, COD) and number of measurements are given.

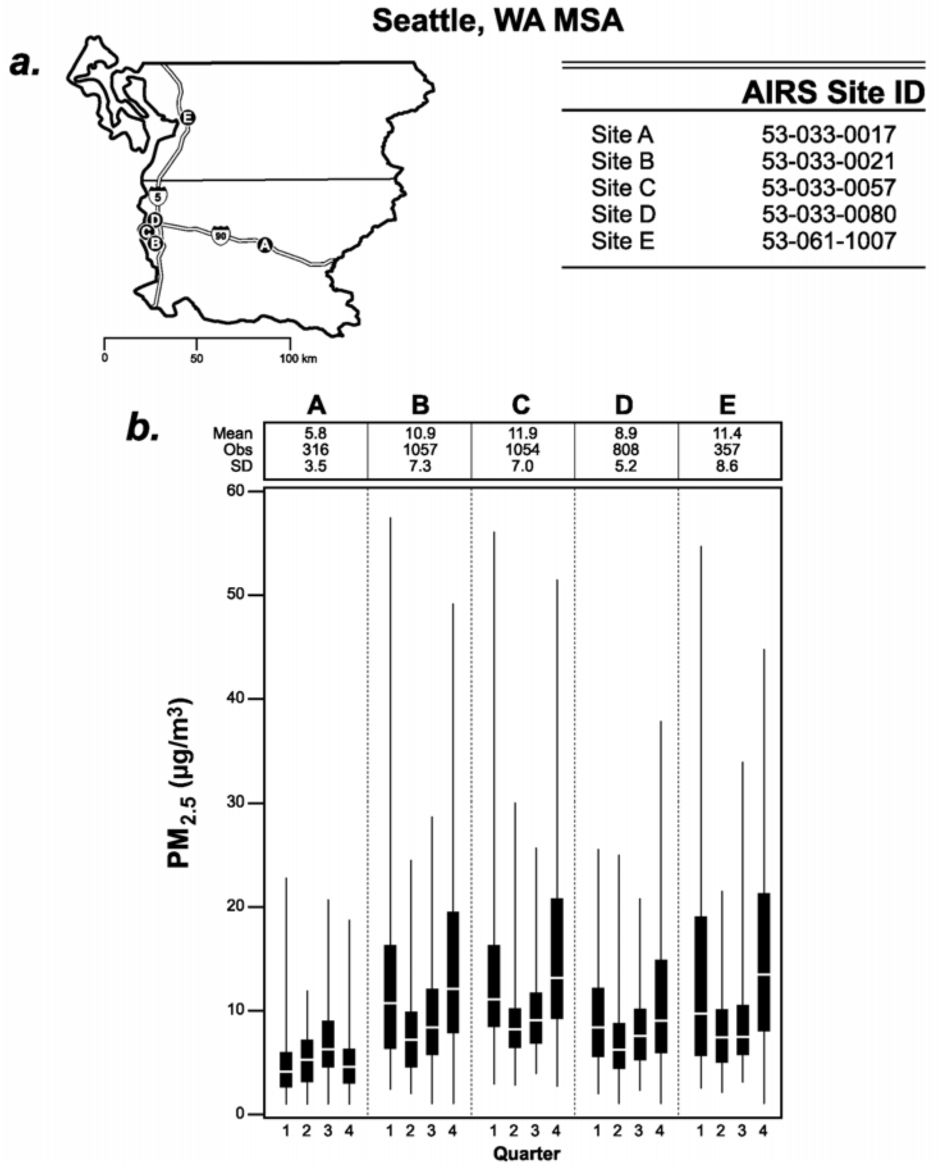


	AIRS Site ID
Site A	49-011-0001
Site B	49-035-0003
Site C	49-035-0012
Site D	49-035-3006
Site E	49-035-3007
Site F	49-057-0007

	A	B	C	D	E	F
Mean	9.0	12.1	13.6	11.3	11.8	8.8
Obs	355	349	346	983	333	328
SD	9.2	12.2	11.7	11.7	11.4	7.4

Site	A	B	C	D	E	F
A	1	0.89 (8.8, 0.22) 334	0.90 (9.9, 0.27) 331	0.94 (6.9, 0.19) 322	0.90 (8.2, 0.22) 315	0.94 (4.4, 0.15) 306
B		1	0.89 (7.0, 0.19) 327	0.92 (4.9, 0.17) 316	0.89 (6.1, 0.17) 313	0.88 (9.3, 0.20) 307
C			1	0.93 (7.1, 0.19) 314	0.96 (4.8, 0.17) 308	0.86 (11.4, 0.24) 302
D				1	0.94 (5.3, 0.16) 300	0.92 (8.7, 0.18) 297
E					1	0.89 (9.6, 0.20) 288
F						1

Figure 3A-22. Salt Lake City, UT MSA. *(a)* Locations of sampling sites by AIRS ID#; *(b)* Quarterly distribution of 24-h average PM$_{2.5}$ concentrations for 1999-2001; *(c)* Intersite correlation statistics, for each data pair, the correlation coefficient, (P$_{90}$, COD) and number of measurements are given.

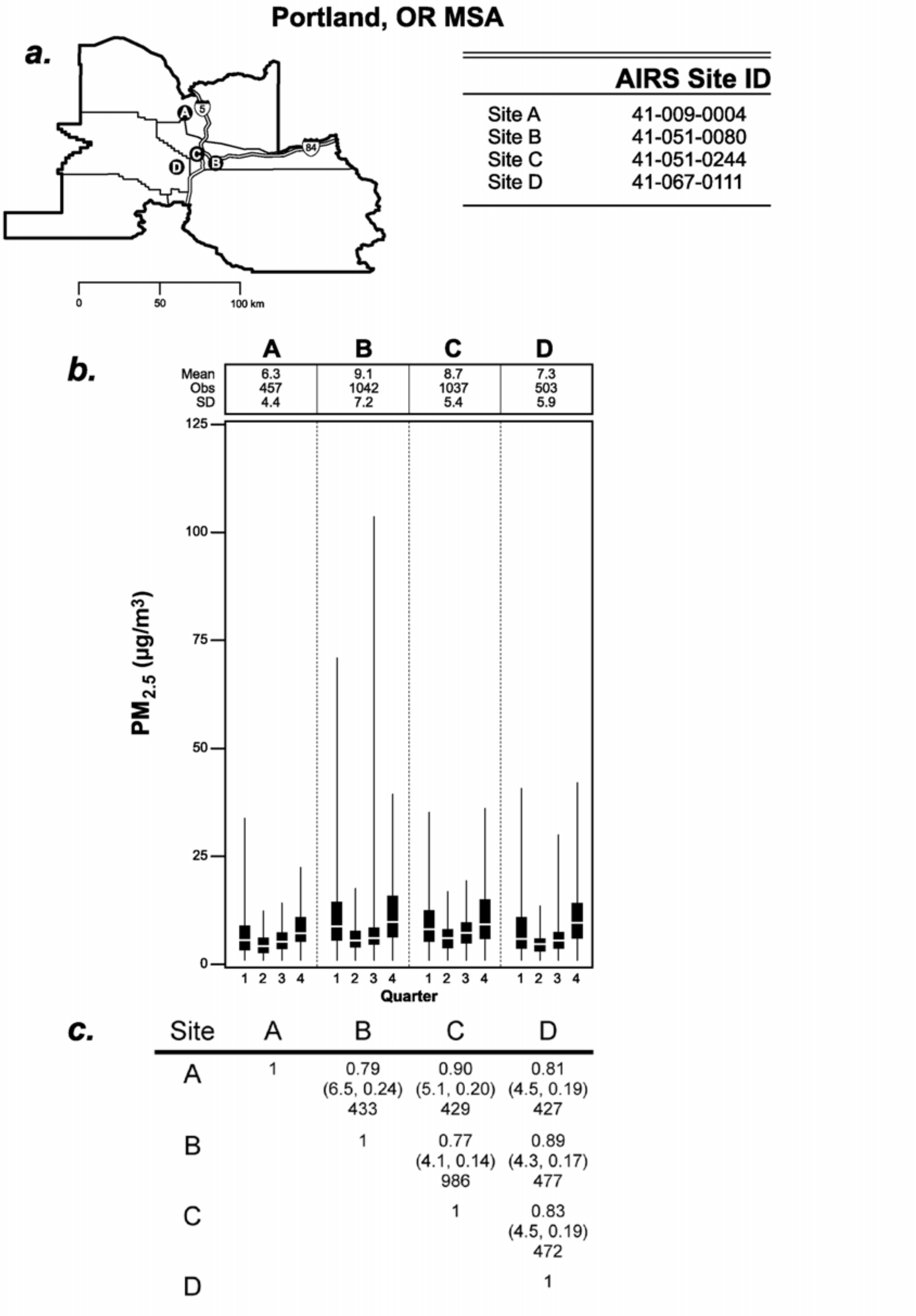


	AIRS Site ID
Site A	53-033-0017
Site B	53-033-0021
Site C	53-033-0057
Site D	53-033-0080
Site E	53-061-1007

c.

Site	A	B	C	D	E
A	1	0.31 (15.0, 0.39) 303	0.28 (15.7, 0.43) 304	0.45 (8.8, 0.32) 291	0.37 (17.9, 0.39) 298
B		1	0.96 (3.6, 0.14) 1021	0.92 (6.8, 0.16) 774	0.81 (6.2, 0.17) 344
C			1	0.91 (7.5, 0.20) 779	0.79 (8.2, 0.20) 344
D				1	0.75 (8.5, 0.20) 327
E					1

Figure 3A-23. Seattle, WA MSA. *(a)* Locations of sampling sites by AIRS ID#; *(b)* Quarterly distribution of 24-h average $PM_{2.5}$ concentrations for 1999-2001; *(c)* Intersite correlation statistics, for each data pair, the correlation coefficient, (P_{90}, COD) and number of measurements are given.

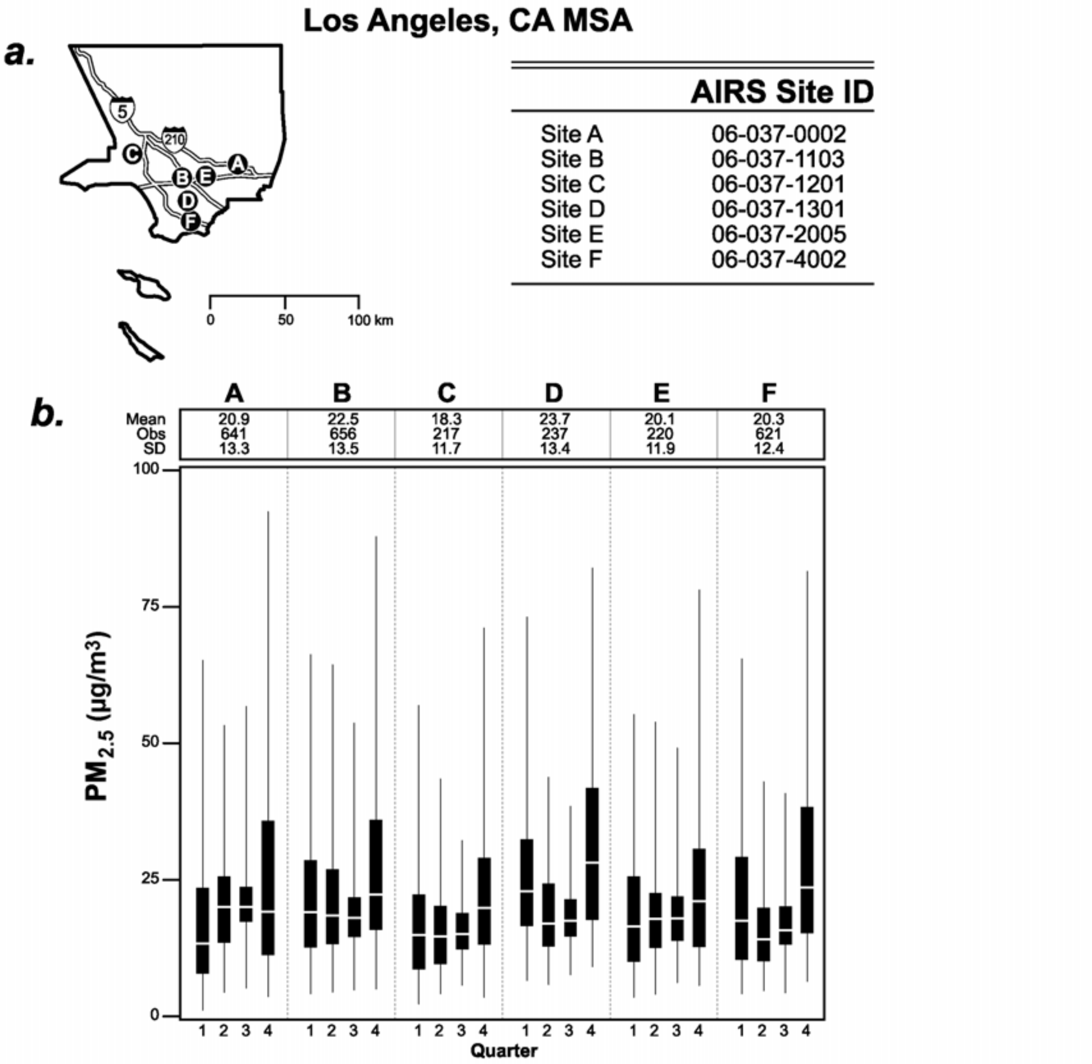


	AIRS Site ID
Site A	41-009-0004
Site B	41-051-0080
Site C	41-051-0244
Site D	41-067-0111

	A	B	C	D
Mean	6.3	9.1	8.7	7.3
Obs	457	1042	1037	503
SD	4.4	7.2	5.4	5.9

Site	A	B	C	D
A	1	0.79 (6.5, 0.24) 433	0.90 (5.1, 0.20) 429	0.81 (4.5, 0.19) 427
B		1	0.77 (4.1, 0.14) 986	0.89 (4.3, 0.17) 477
C			1	0.83 (4.5, 0.19) 472
D				1

Figure 3A-24. Portland, OR MSA. *(a)* Locations of sampling sites by AIRS ID#; (*b*) Quarterly distribution of 24-h average PM$_{2.5}$ concentrations for 1999-2001; *(c)* Intersite correlation statistics, for each data pair, the correlation coefficient, (P$_{90}$, COD) and number of measurements are given.



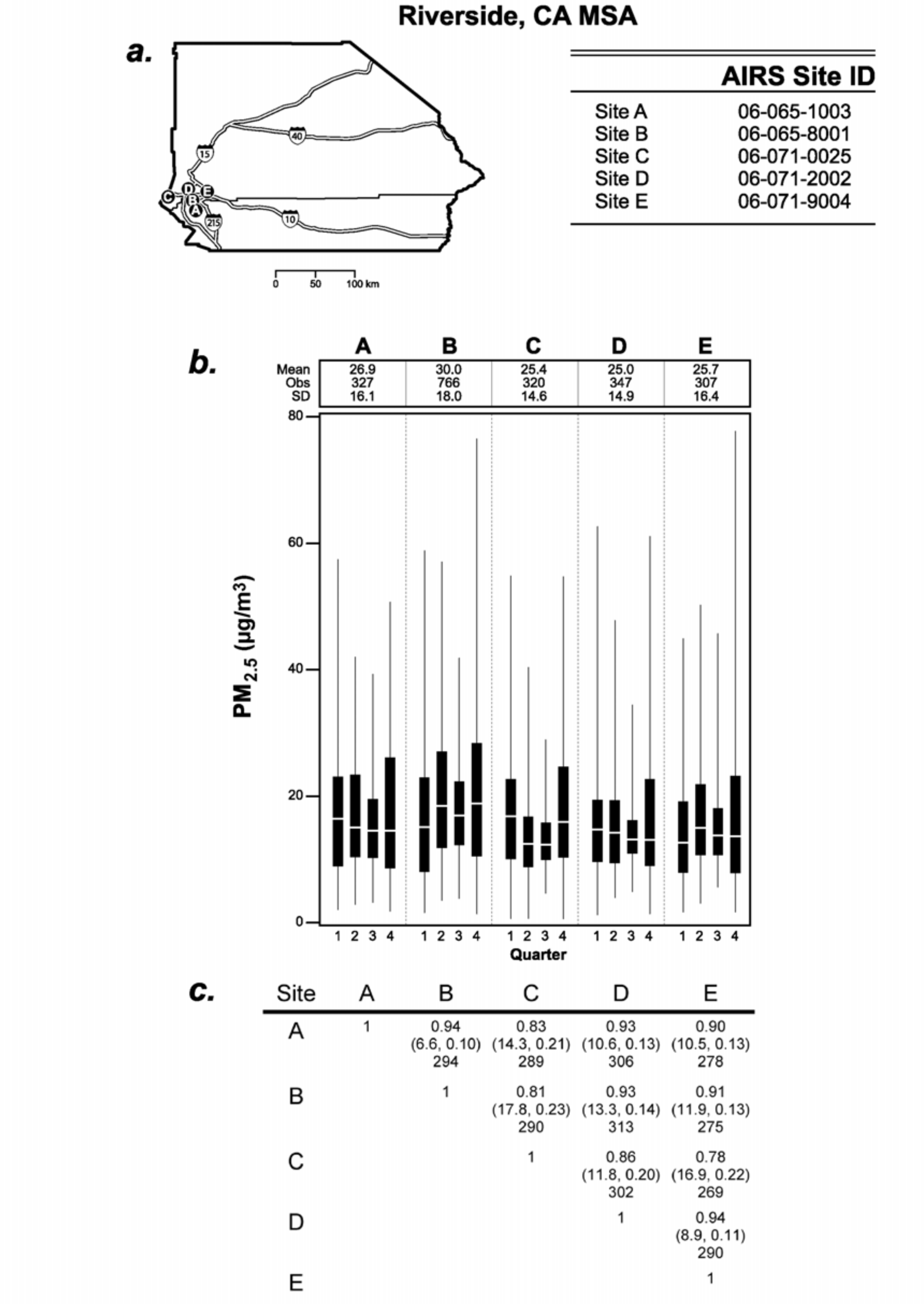
	AIRS Site ID
Site A	06-037-0002
Site B	06-037-1103
Site C	06-037-1201
Site D	06-037-1301
Site E	06-037-2005
Site F	06-037-4002

	A	B	C	D	E	F
Mean	20.9	22.5	18.3	23.7	20.1	20.3
Obs	641	656	217	237	220	621
SD	13.3	13.5	11.7	13.4	11.9	12.4

c.

Site	A	B	C	D	E	F
A	1	0.87 (10.7, 0.18) 581	0.76 (14.6, 0.23) 208	0.68 (17.9, 0.25) 229	0.95 (6.2, 0.14) 212	0.60 (18.1, 0.26) 553
B		1	0.86 (12.8, 0.20) 205	0.89 (10.1, 0.12) 222	0.93 (7.1, 0.11) 207	0.80 (13.6, 0.17) 563
C			1	0.76 (18.1, 0.24) 212	0.85 (12.1, 0.18) 197	0.66 (18.2, 0.24) 197
D				1	0.78 (13.2, 0.18) 214	0.95 (8.1, 0.11) 216
E					1	0.62 (15, 0.20) 204
F						1

Figure 3A-25. Los Angeles-Long Beach, CA MSA. *(a)* Locations of sampling sites by AIRS ID; *(b)* Quarterly distribution of 24-h average PM$_{2.5}$ concentrations for 1999-2001; *(c)* Intersite correlation statistics, for each data pair, the correlation coefficient, (P$_{90}$, COD) and number of measurements are given.



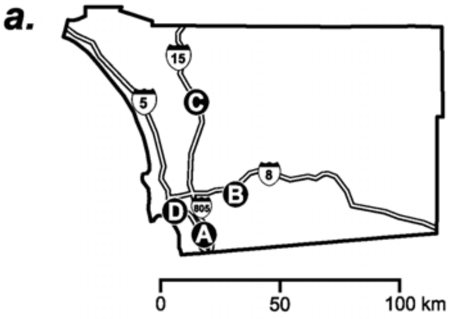
	AIRS Site ID
Site A	06-065-1003
Site B	06-065-8001
Site C	06-071-0025
Site D	06-071-2002
Site E	06-071-9004

	A	B	C	D	E
Mean	26.9	30.0	25.4	25.0	25.7
Obs	327	766	320	347	307
SD	16.1	18.0	14.6	14.9	16.4

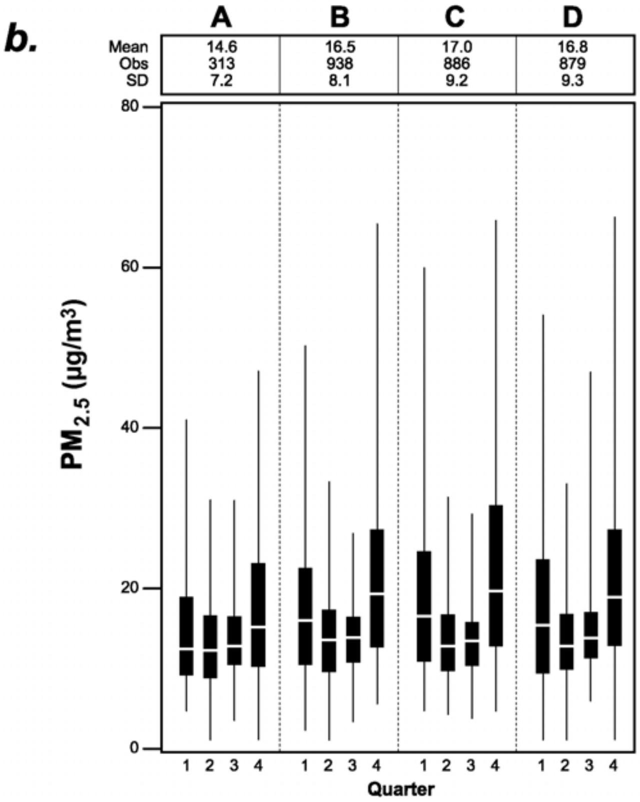
Site	A	B	C	D	E
A	1	0.94 (6.6, 0.10) 294	0.83 (14.3, 0.21) 289	0.93 (10.6, 0.13) 306	0.90 (10.5, 0.13) 278
B		1	0.81 (17.8, 0.23) 290	0.93 (13.3, 0.14) 313	0.91 (11.9, 0.13) 275
C			1	0.86 (11.8, 0.20) 302	0.78 (16.9, 0.22) 269
D				1	0.94 (8.9, 0.11) 290
E					1

Figure 3A-26. Riverside-San Bernadino, CA MSA. *(a)* Locations of sampling sites by AIRS ID#; *(b)* Quarterly distribution of 24-h average PM$_{2.5}$ concentrations for 1999-2001; *(c)* Intersite correlation statistics, for each data pair, the correlation coefficient, (P$_{90}$, COD) and number of measurements are given.

San Diego, CA MSA



	AIRS Site ID
Site A	06-073-0001
Site B	06-073-0003
Site C	06-073-1002
Site D	06-073-1007



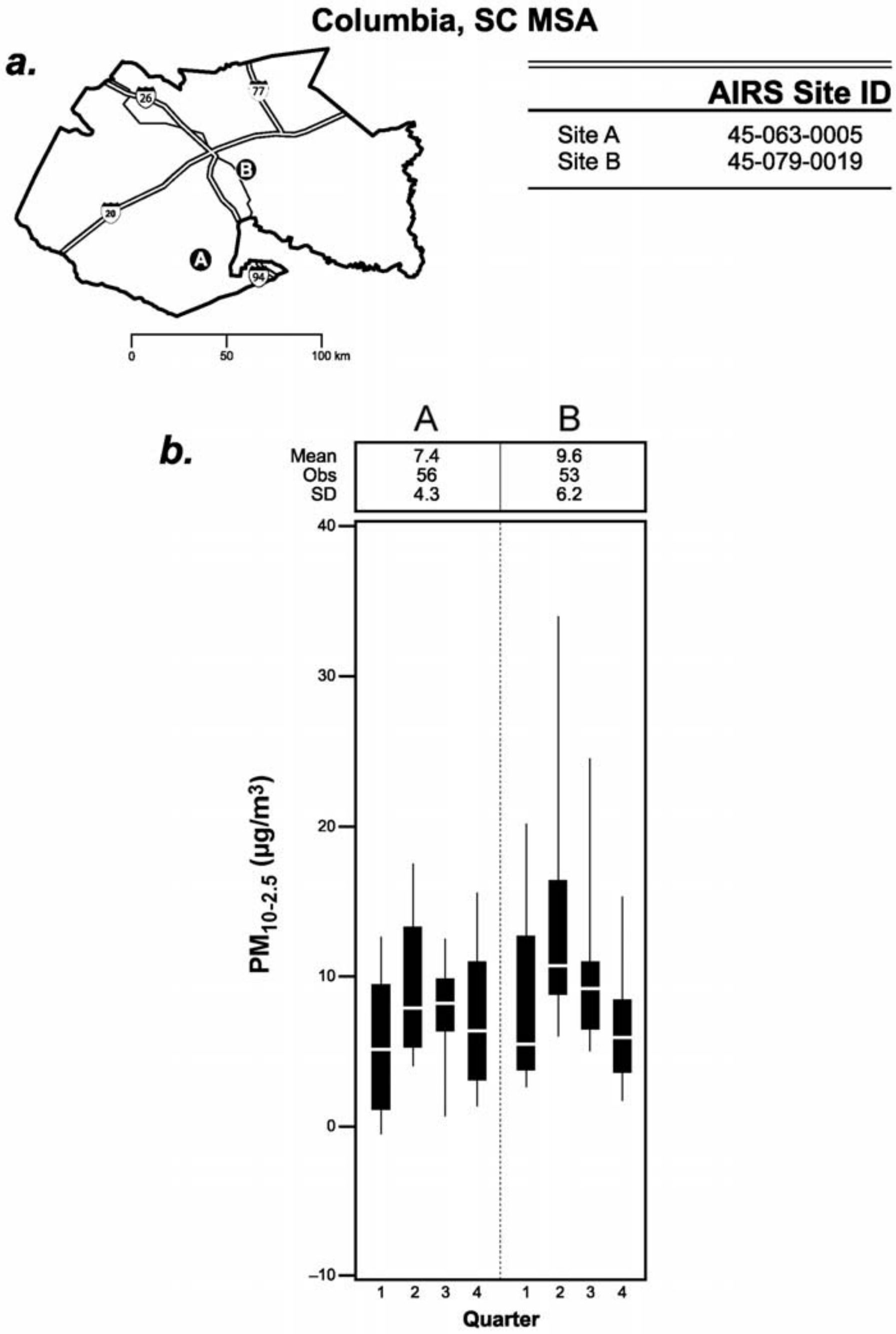
c.

Site	A	B	C	D
A	1	0.76 (10.0, 0.16) 270	0.73 (10.0, 0.19) 253	0.83 (7.6, 0.16) 255
B		1	0.85 (6.3, 0.13) 773	0.78 (9.7, 0.18) 769
C			1	0.73 (11.0, 0.20) 728
D				1

Figure 3A-27. San Diego, CA MSA. *(a)* Locations of sampling sites by AIRS ID#; *(b)* Quarterly distribution of 24-h average $PM_{2.5}$ concentrations for 1999-2001; *(c)* Intersite correlation statistics, for each data pair, the correlation coefficient, (P_{90}, COD) and number of measurements are given.

TABLE 3A-1. PERFORMANCE METRICS FOR $PM_{2.5}$ FROM COLLOCATED SAMPLERS (Mean concentrations, the number of samples, the standard deviation at each site, and the Pearson correlation coefficient and the coefficient of divergence for the site pair are shown; concentrations are given in $\mu g/m^3$).

Columbia, SC	**Sampler 1**		**Sampler 2**
	45-079-0019		45-079-0019
MEAN	15.3		15.5
N	226		211
SD	6.5		6.5
r		0.995	
COD		0.022	
Dallas, TX	**Sampler 1**		**Sampler 2**
	48-113-0069		48-113-0069
MEAN	12.7		13.1
N	687		116
SD	5.7		6.0
r		0.996	
COD		0.032	
Detroit, MI	**Sampler 1**		**Sampler 2**
	26-163-0001		26-163-0001
MEAN	16.5		16.2
N	637		111
SD	9.2		8.8
r		0.986	
COD		0.041	
Grand Rapids, MI	**Sampler 1**		**Sampler 2**
	26-081-0020		26-081-0020
MEAN	14.0		14.3
N	1050		181
SD	8.6		8.3
r		0.992	
COD		0.059	
Louisville, KY	**Sampler 1**		**Sampler 2**
	18-043-1004		18-043-1004
MEAN	15.8		16.0
N	196		104
SD	8.2		7.8
r		0.997	
COD		0.027	
Steubenville, OH	**Sampler 1**		**Sampler 2**
	54-029-0011		54-029-0011
Mean	16.5		16.6
Obs	342		325
SD	10.2		10.3
r		0.985	
COD		0.087	
Washington DC	**Sampler 1**		**Sampler 2**
	11-001-0041		11-001-0041
Mean	16.8		17.5
Obs	600		132
SD	9.7		11.1
r		0.953	
COD		0.150	



	AIRS Site ID
Site A	45-063-0005
Site B	45-079-0019

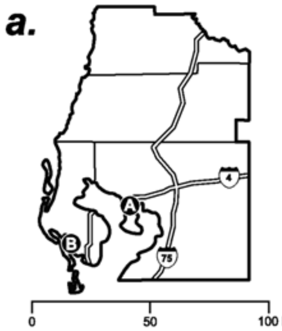
c.

Site	A	B
A	1	0.70 (8.0, 0.37) 49
B		1

Figure 3A-28. Columbia, SC MSA. ***(a)*** **Locations of sampling sites by AIRS ID#;** ***(b)*** **Quarterly distribution of 24-h average $PM_{10\text{-}2.5}$ concentrations (µg/m³) for 2000;** ***(c)*** **Intersite correlation coefficients, number of observations, 90th percentile differences in concentrations, and CODs.**

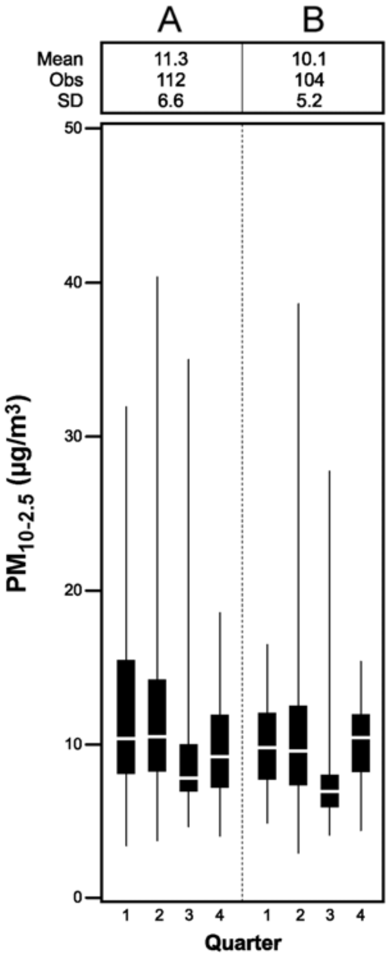
Tampa, FL MSA

a.



	AIRS Site ID
Site A	12-057-0030
Site B	12-103-0018

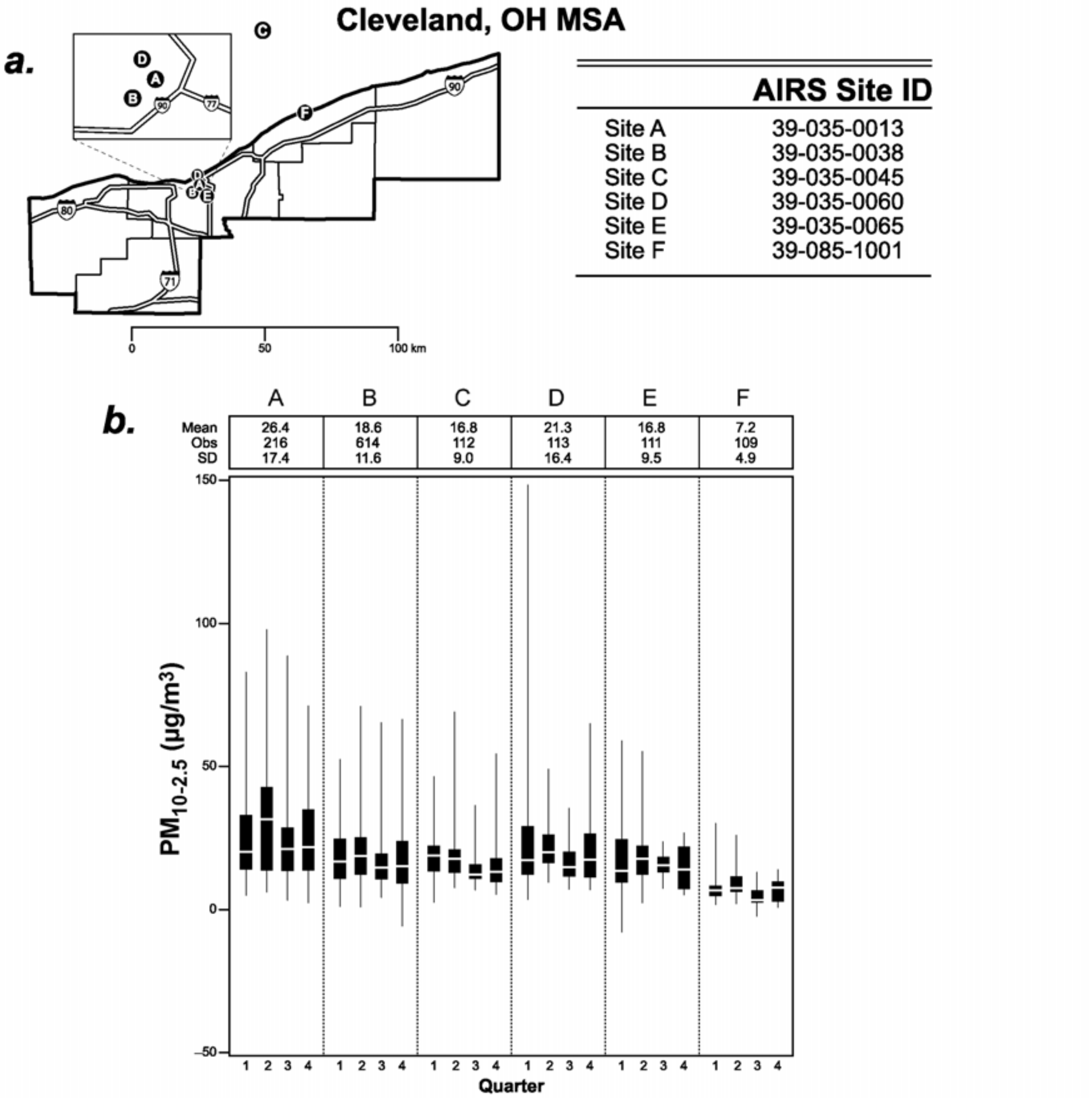
b.



c.

Site	A	B
A	1	0.81 (5.3, 0.17) 95
B		1

Figure 3A-29. Tampa, FL MSA *(a)* Locations of sampling sites by AIRS ID#; *(b)* Quarterly distribution of 24-h average $PM_{10-2.5}$ concentrations (µg/m^3) for 2000-2001; *(c)* Intersite correlation coefficients, number of observations, 90th percentile differences in concentrations, and CODs.



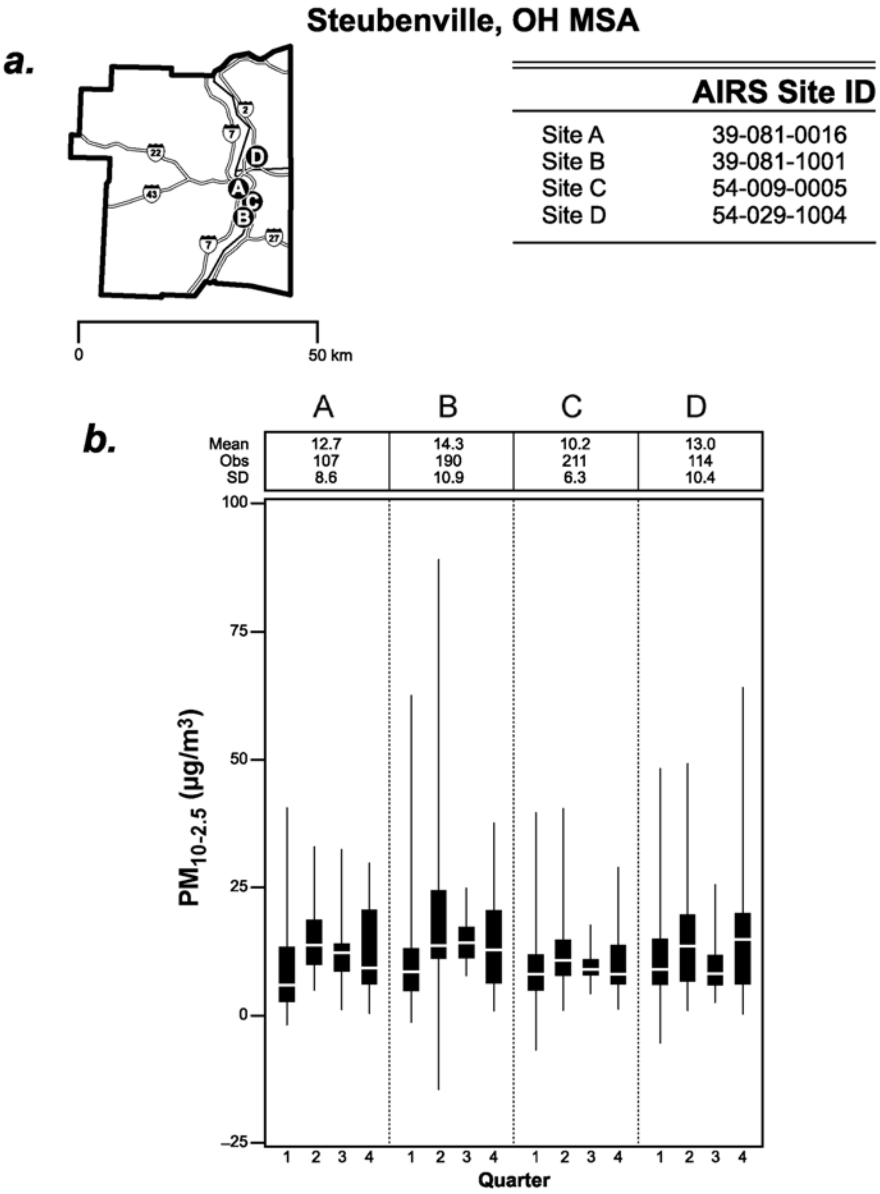
	AIRS Site ID
Site A	39-035-0013
Site B	39-035-0038
Site C	39-035-0045
Site D	39-035-0060
Site E	39-035-0065
Site F	39-085-1001

	A	B	C	D	E	F
Mean	26.4	18.6	16.8	21.3	16.8	7.2
Obs	216	614	112	113	111	109
SD	17.4	11.6	9.0	16.4	9.5	4.9

c.

Site	A	B	C	D	E	F
A	1	0.67 (23.2, 0.26) 182	0.67 (28.5, 0.28) 95	0.73 (17.9, 0.22) 97	0.62 (27.0, 0.31) 98	0.41 (40.0, 0.60) 94
B		1	0.65 (16.1, 0.22) 90	0.73 (11.7, 0.18) 93	0.69 (13.9, 0.62) 90	0.44 (24.9, 0.53) 89
C			1	0.66 (18.1, 0.23) 94	0.71 (10.6, 0.31) 102	0.49 (19.9, 0.50) 99
D				1	0.74 (15.4, 0.38) 93	0.31 (28.0, 0.59) 94
E					1	0.22 (20.4, 0.55) 99
F						1

Figure 3A-30. Cleveland, OH MSA *(a)* Locations of sampling sites by AIRS ID#; *(b)* Quarterly distribution of 24-h average PM$_{10-2.5}$ concentrations (µg/m^3) for 2000-2001; *(c)* Intersite correlation coefficients, number of observations, 90th percentile differences in concentrations, and CODs.

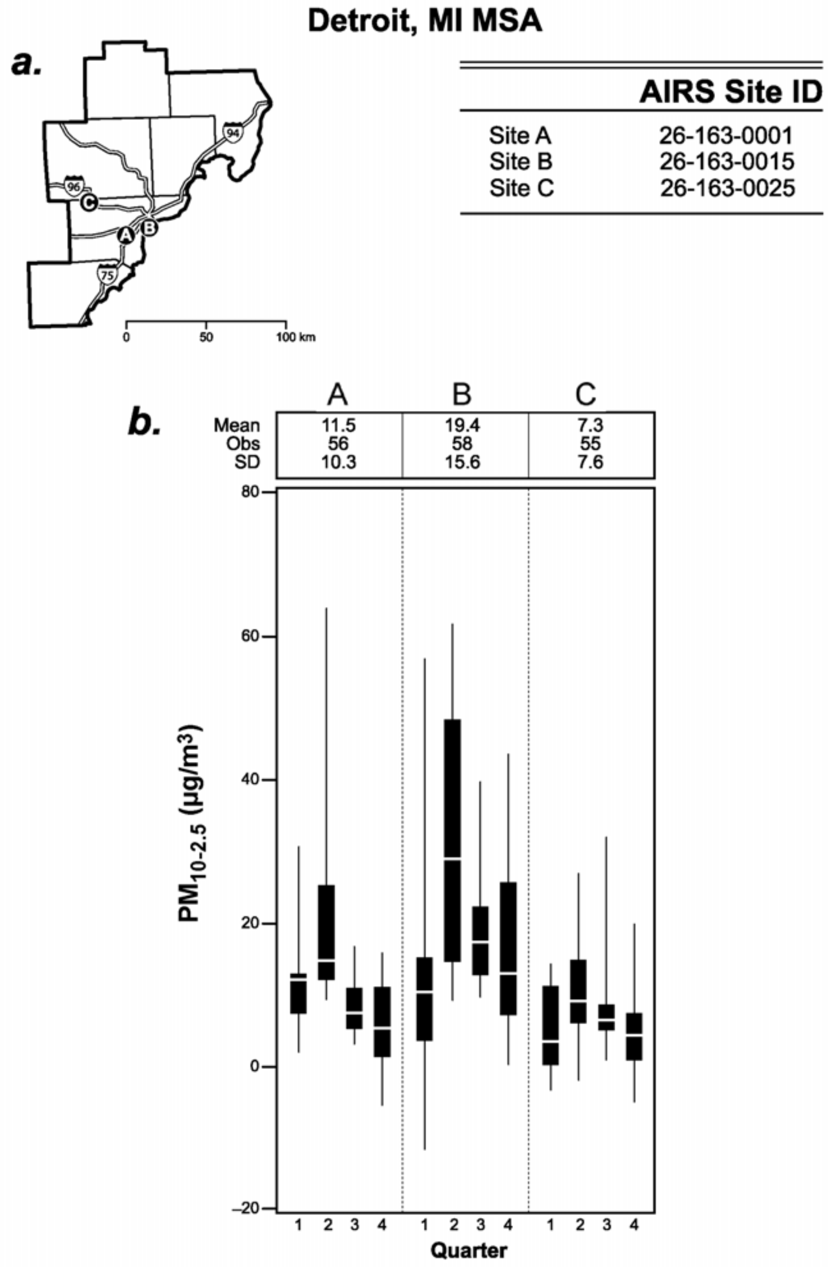


	AIRS Site ID
Site A	39-081-0016
Site B	39-081-1001
Site C	54-009-0005
Site D	54-029-1004

c.

Site	A	B	C	D
A	1	0.64 (10.9, 0.77) 83	0.69 (11.6, --) 91	0.68 (11.3, --) 100
B		1	0.54 (14.7, --) 166	0.48 (18.5, --) 88
C			1	0.69 (12.8, --) 97
D				1

Figure 3A-31. Steubenville, OH MSA *(a)* Locations of sampling sites by AIRS ID#; *(b)* Quarterly distribution of 24-h average $PM_{10-2.5}$ concentrations (µg/m^3) for 2000-2001; *(c)* Intersite correlation coefficients, number of observations, 90th percentile differences in concentrations, and CODs.



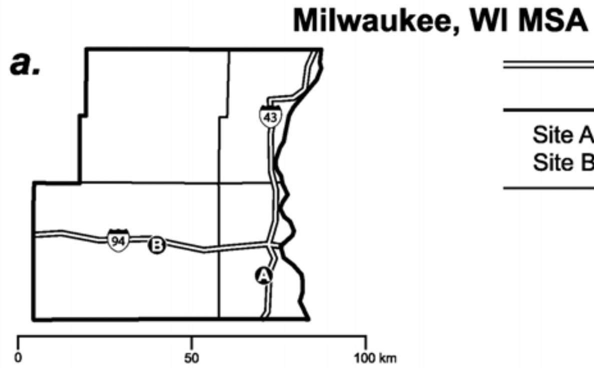
	AIRS Site ID
Site A	26-163-0001
Site B	26-163-0015
Site C	26-163-0025

	A	B	C
Mean	11.5	19.4	7.3
Obs	56	58	55
SD	10.3	15.6	7.6

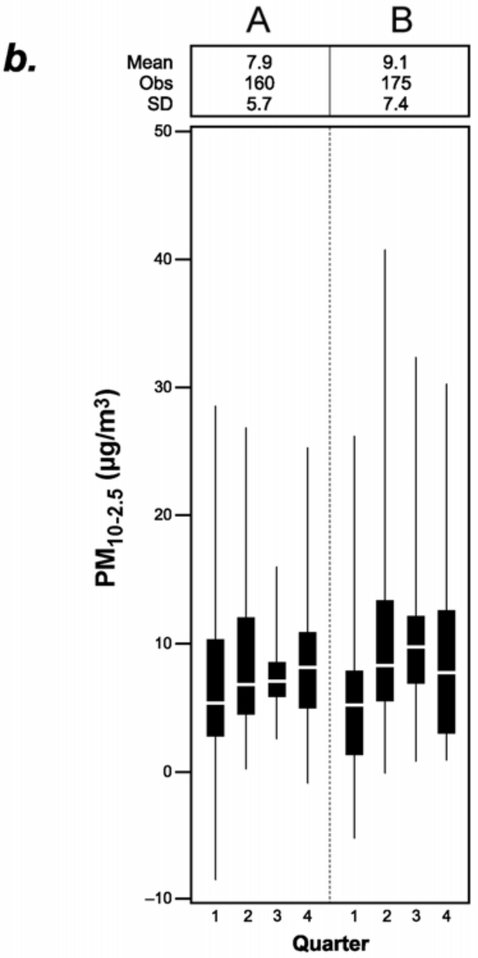
c.

Site	A	B	C
A	1	0.58 (29.4, --) 53	0.54 (15.7, 0.54) 50
B		1	0.39 (34.9, 0.79) 51
C			1

Figure 3A-32. Detroit, MI MSA *(a)* Locations of sampling sites by AIRS ID#; *(b)* Quarterly distribution of 24-h average PM$_{10-2.5}$ concentrations (µg/m^3) for 2000; *(c)* Intersite correlation coefficients, number of observations, 90th percentile differences in concentrations, and CODs.



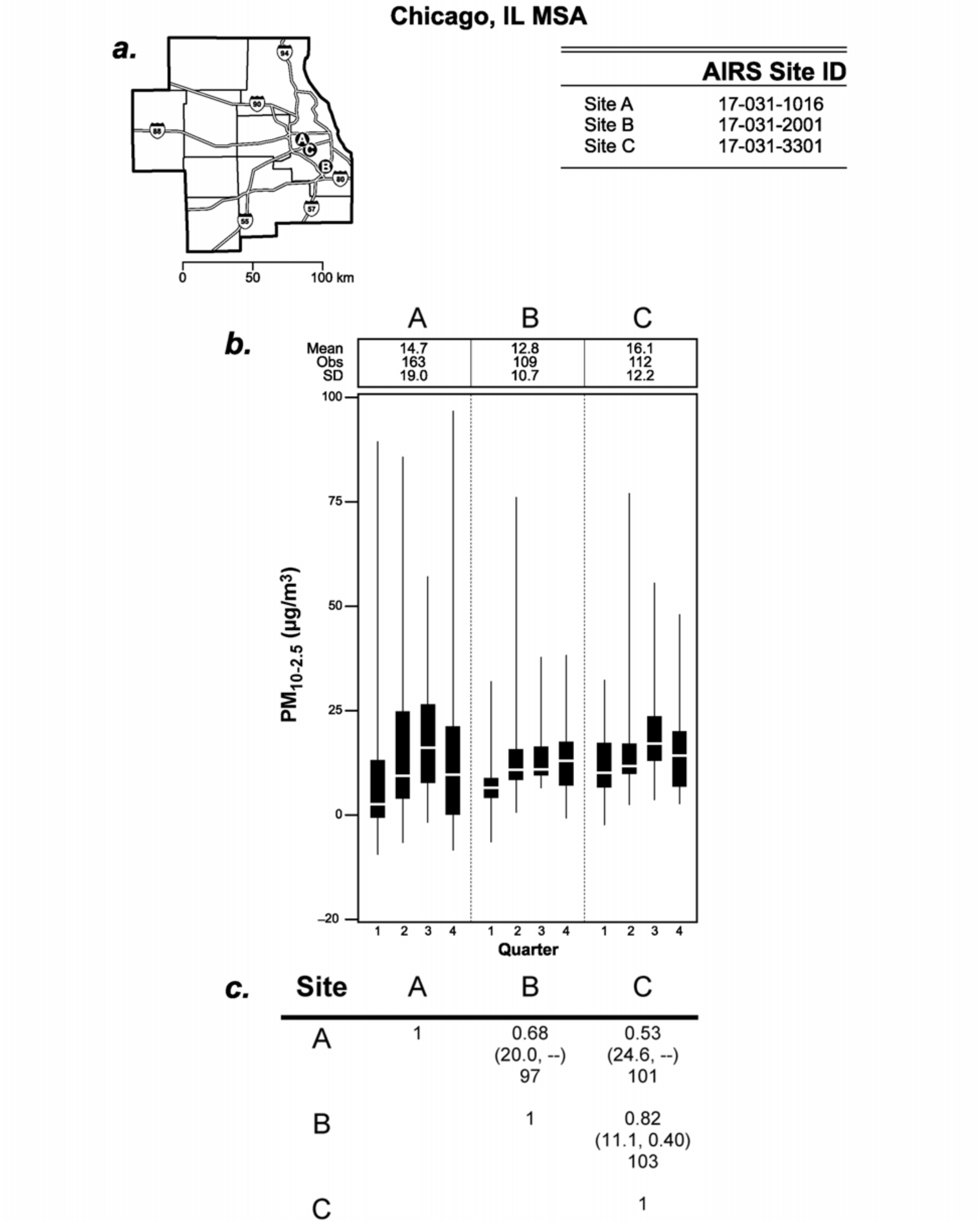
	AIRS Site ID
Site A	55-079-0059
Site B	55-133-0027



c.

Site	A	B
A	1	0.65 (9.2, 0.53) 150
B		1

Figure 3A-33. Milwaukee, WI MSA *(a)* Locations of sampling sites by AIRS ID#; *(b)* Quarterly distribution of 24-h average PM$_{10-2.5}$ concentrations (μg/m^3) for 1999-2001; *(c)* Intersite correlation coefficients, number of observations, 90th percentile differences in concentrations, and CODs.

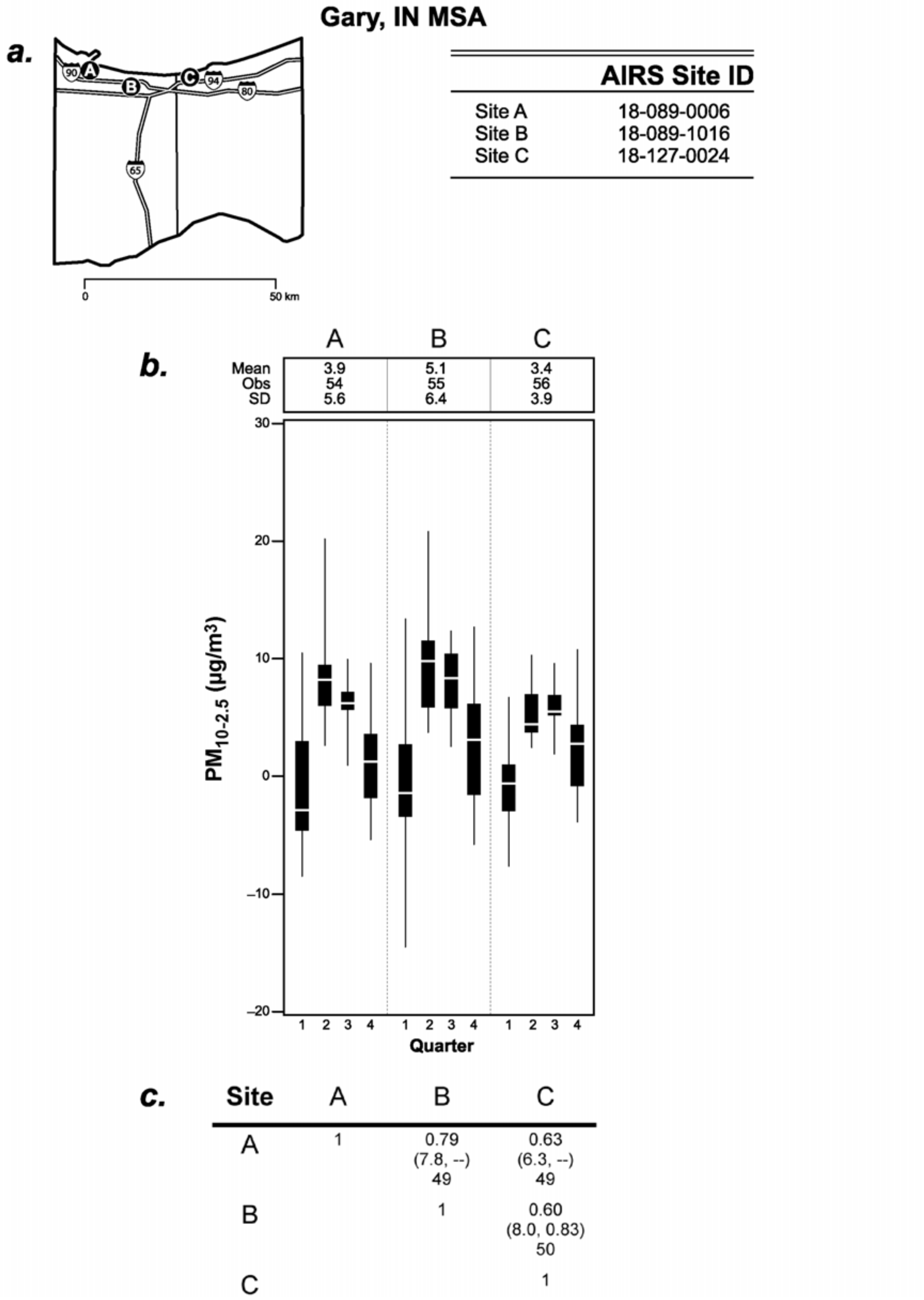


	AIRS Site ID
Site A	17-031-1016
Site B	17-031-2001
Site C	17-031-3301

	A	B	C
Mean	14.7	12.8	16.1
Obs	163	109	112
SD	19.0	10.7	12.2

Site	A	B	C
A	1	0.68 (20.0, --) 97	0.53 (24.6, --) 101
B		1	0.82 (11.1, 0.40) 103
C			1

Figure 3A-34. Chicago, IL MSA *(a)* Locations of sampling sites by AIRS ID#; *(b)* Quarterly distribution of 24-h average PM$_{10-2.5}$ concentrations (µg/m^3) for 1999-2000; *(c)* Intersite correlation coefficients, number of observations, 90th percentile differences in concentrations, and CODs.

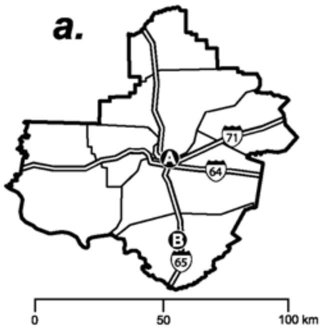


	AIRS Site ID
Site A	18-089-0006
Site B	18-089-1016
Site C	18-127-0024

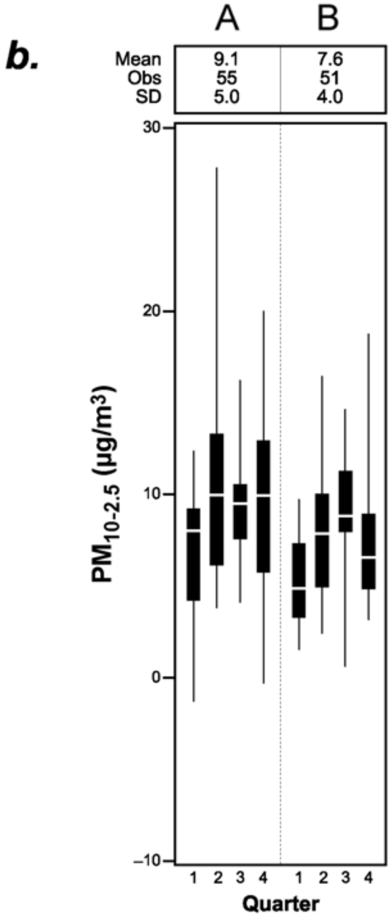
Site	A	B	C
A	1	0.79 (7.8, --) 49	0.63 (6.3, --) 49
B		1	0.60 (8.0, 0.83) 50
C			1

Figure 3A-35. Gary, IN MSA *(a)* Locations of sampling sites by AIRS ID#; *(b)* Quarterly distribution of 24-h average $PM_{10-2.5}$ concentrations (µg/m^3) for 2001; *(c)* Intersite correlation coefficients, number of observations, 90th percentile differences in concentrations, and CODs.

Louisville, KY MSA



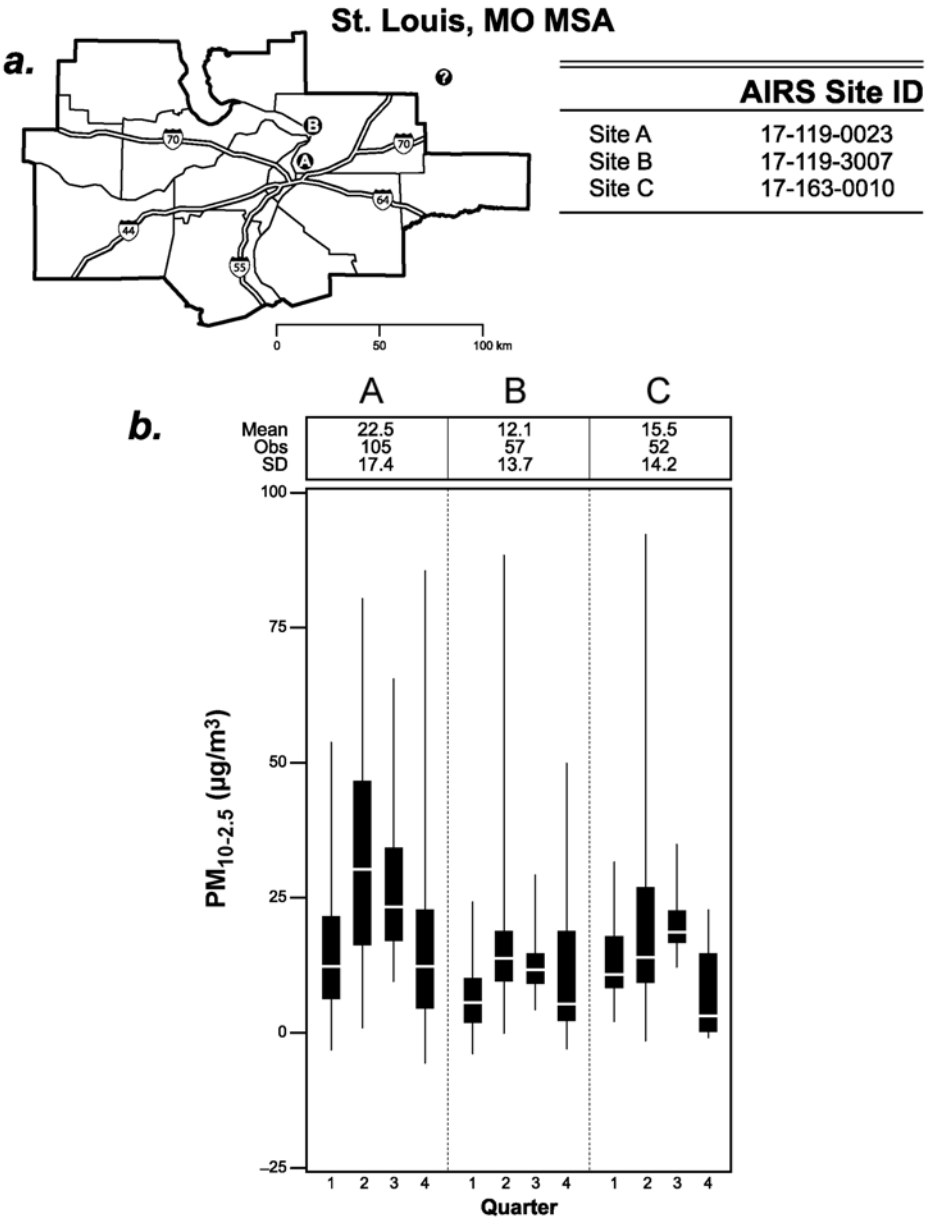
	AIRS Site ID
Site A	18-019-0005
Site B	21-029-0006



c.

Site	A	B
A	1	0.65 (5.5, 0.48) 46
B		1

Figure 3A-36. Louisville, KY MSA *(a)* Locations of sampling sites by AIRS ID#; *(b)* Quarterly distribution of 24-h average $PM_{10-2.5}$ concentrations (µg/m^3) for 2001; *(c)* Intersite correlation coefficients, number of observations, 90th percentile differences in concentrations, and CODs.

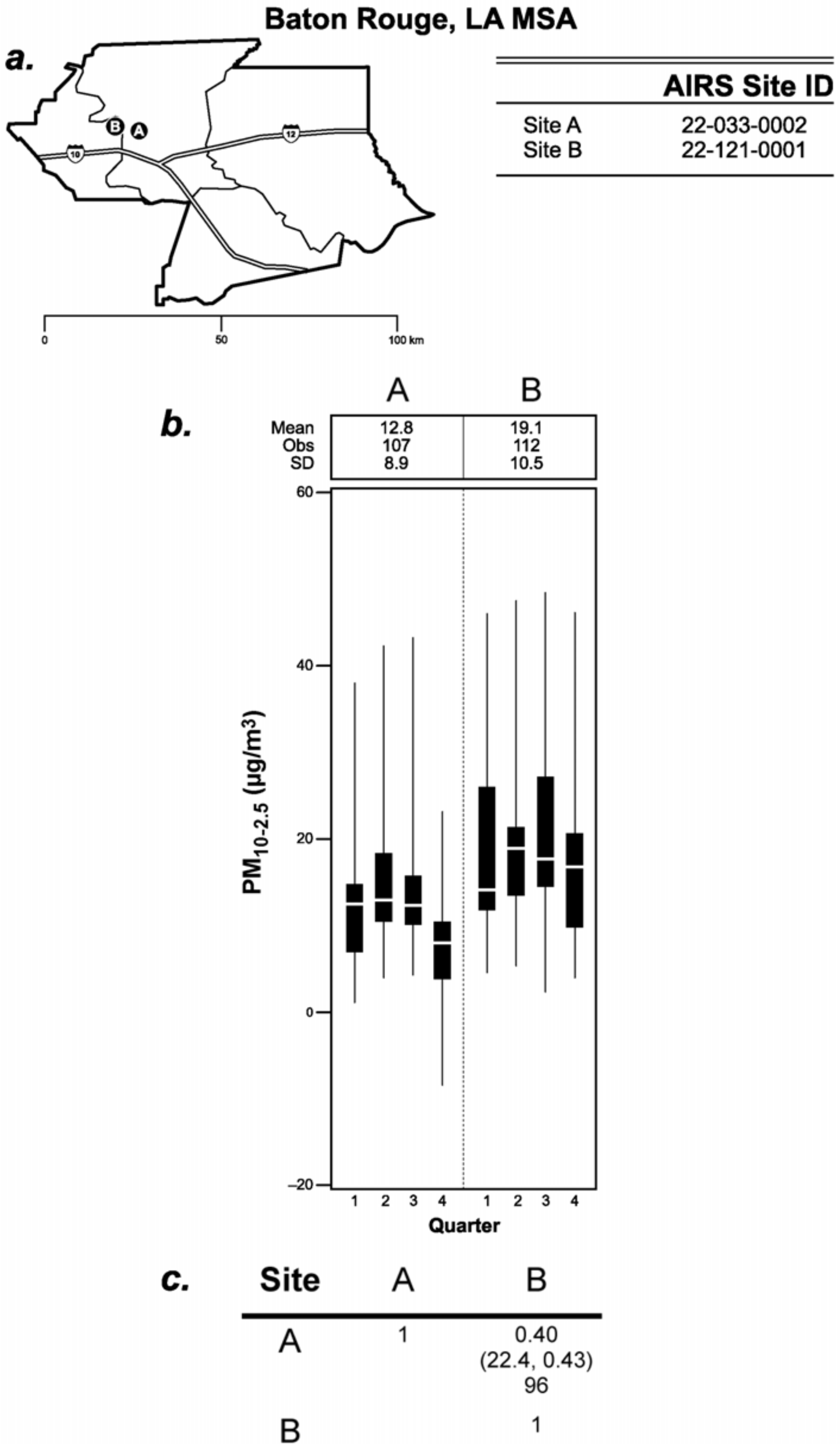


	AIRS Site ID
Site A	17-119-0023
Site B	17-119-3007
Site C	17-163-0010

c.

Site	A	B	C
A	1	0.70 (27.2, --) 51	0.73 (26.2, 0.76) 47
B		1	0.82 (13.0, 0.91) 50
C			1

Figure 3A-37. St. Louis, MI MSA *(a)* Locations of sampling sites by AIRS ID#; *(b)* Quarterly distribution of 24-h average $PM_{10-2.5}$ concentrations (µg/m^3) for 2000; *(c)* Intersite correlation coefficients, number of observations, 90th percentile differences in concentrations, and CODs.

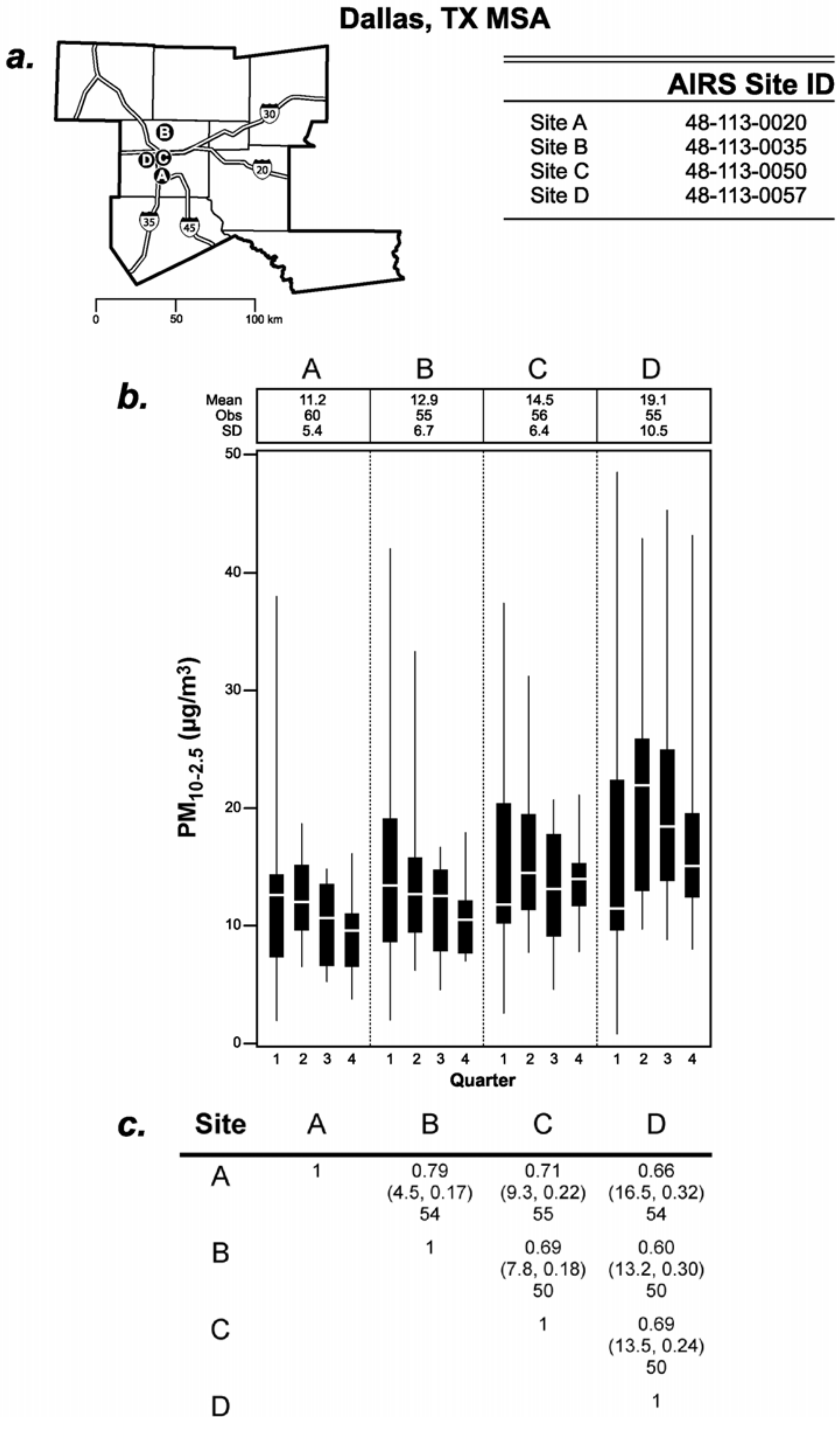


	AIRS Site ID
Site A	22-033-0002
Site B	22-121-0001

	A	B
Mean	12.8	19.1
Obs	107	112
SD	8.9	10.5

Site	A	B
A	1	0.40 (22.4, 0.43) 96
B		1

Figure 3A-38. **Baton Rouge, LA MSA *(a)* Locations of sampling sites by AIRS ID#; *(b)* Quarterly distribution of 24-h average PM$_{10-2.5}$ concentrations (µg/m^3) for 2000-2001; *(c)* Intersite correlation coefficients, number of observations, 90th percentile differences in concentrations, and CODs.**

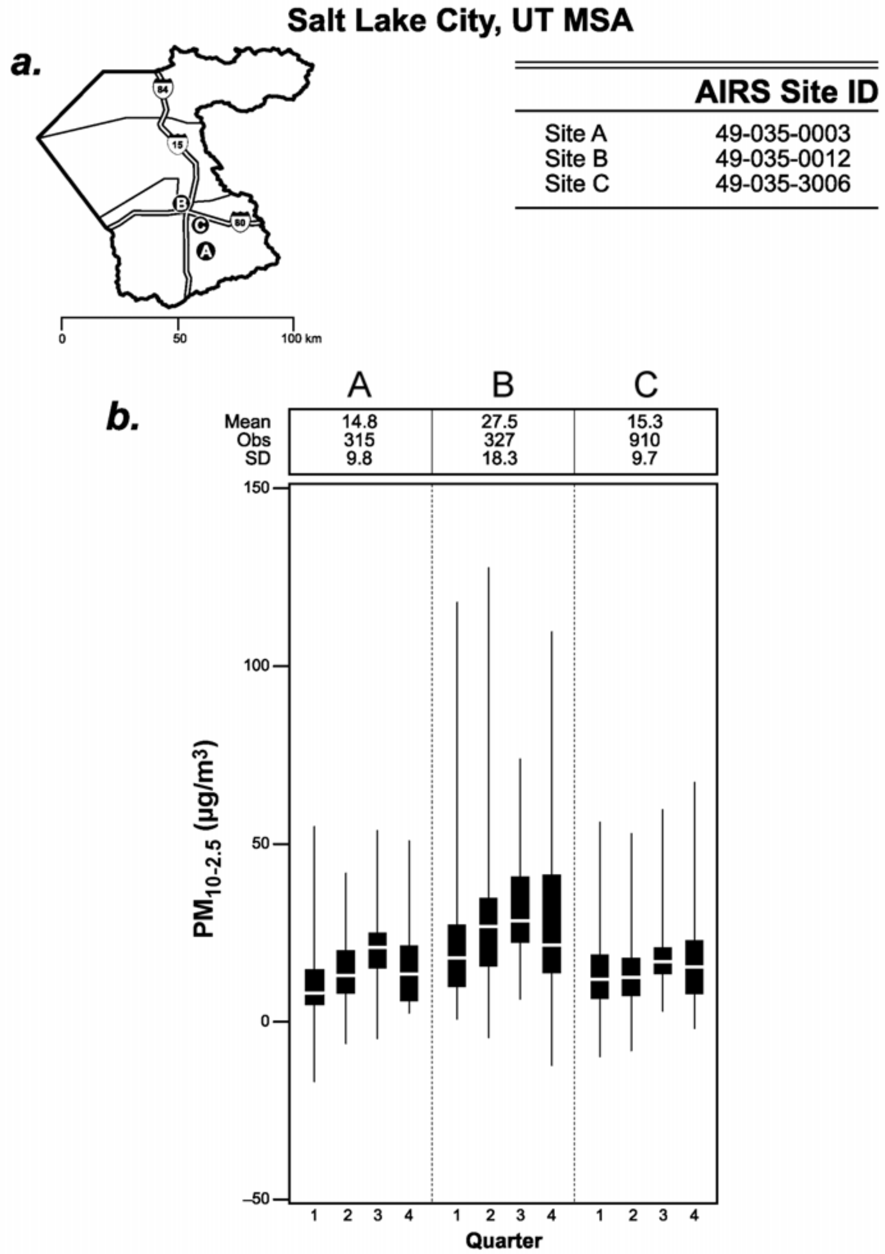


	AIRS Site ID
Site A	48-113-0020
Site B	48-113-0035
Site C	48-113-0050
Site D	48-113-0057

	A	B	C	D
Mean	11.2	12.9	14.5	19.1
Obs	60	55	56	55
SD	5.4	6.7	6.4	10.5

Site	A	B	C	D
A	1	0.79 (4.5, 0.17) 54	0.71 (9.3, 0.22) 55	0.66 (16.5, 0.32) 54
B		1	0.69 (7.8, 0.18) 50	0.60 (13.2, 0.30) 50
C			1	0.69 (13.5, 0.24) 50
D				1

Figure 3A-39. Dallas, TX MSA *(a)* Locations of sampling sites by AIRS ID#; *(b)* Quarterly distribution of 24-h average PM$_{10-2.5}$ concentrations (µg/m^3) for 2001; *(c)* Intersite correlation coefficients, number of observations, 90th percentile differences in concentrations, and CODs.

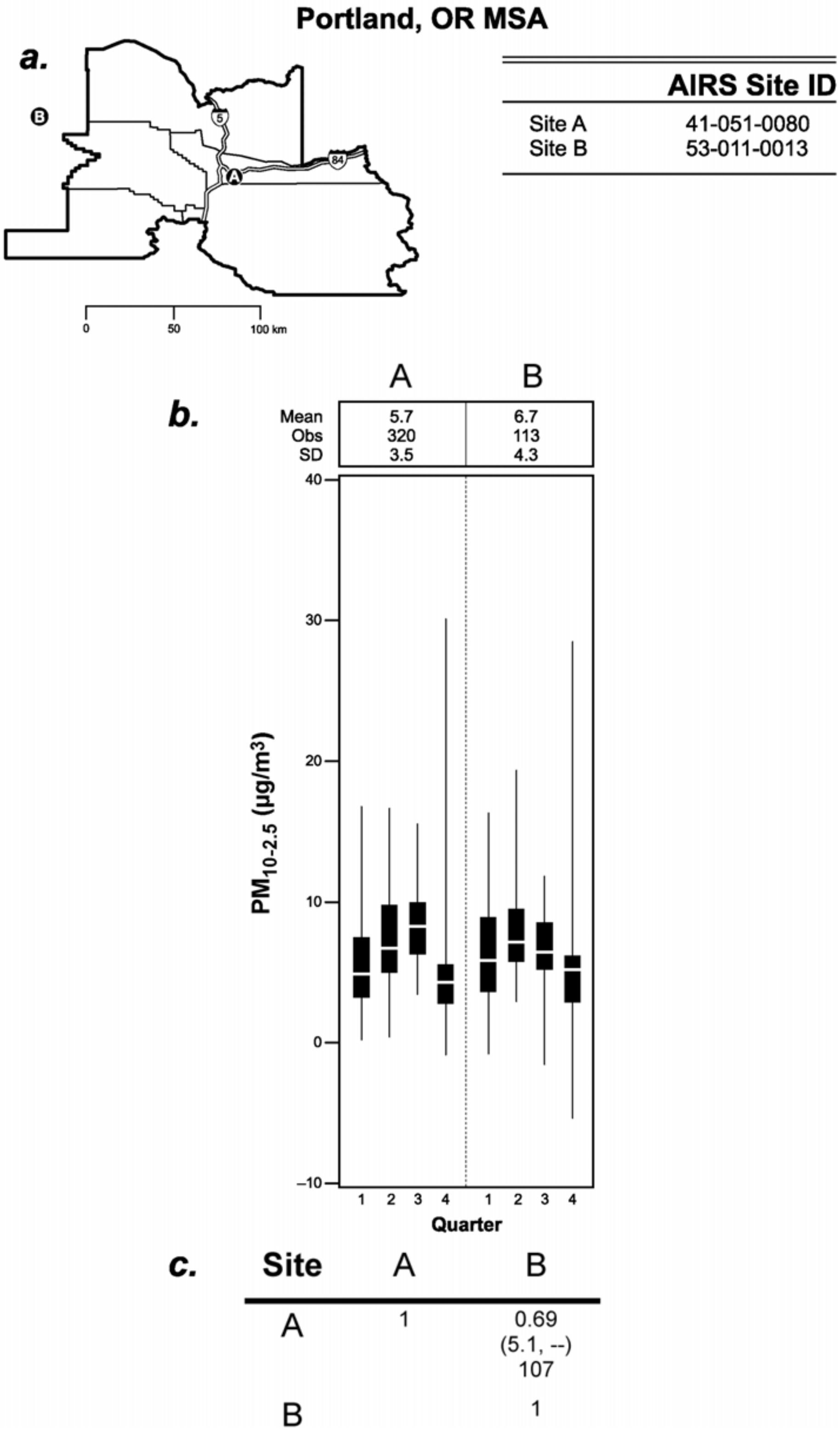


	AIRS Site ID
Site A	49-035-0003
Site B	49-035-0012
Site C	49-035-3006

c.

Site	A	B	C
A	1	0.72 (28.7, --) 283	0.74 (9.8, --) 264
B		1	0.70 (27.6, 0.47) 274
C			1

Figure 3A-40. Salt Lake City, UT MSA *(a)* Locations of sampling sites by AIRS ID#; *(b)* Quarterly distribution of 24-h average $PM_{10-2.5}$ concentrations (µg/m^3) for 1999-2001; *(c)* Intersite correlation coefficients, number of observations, 90th percentile differences in concentrations, and CODs.

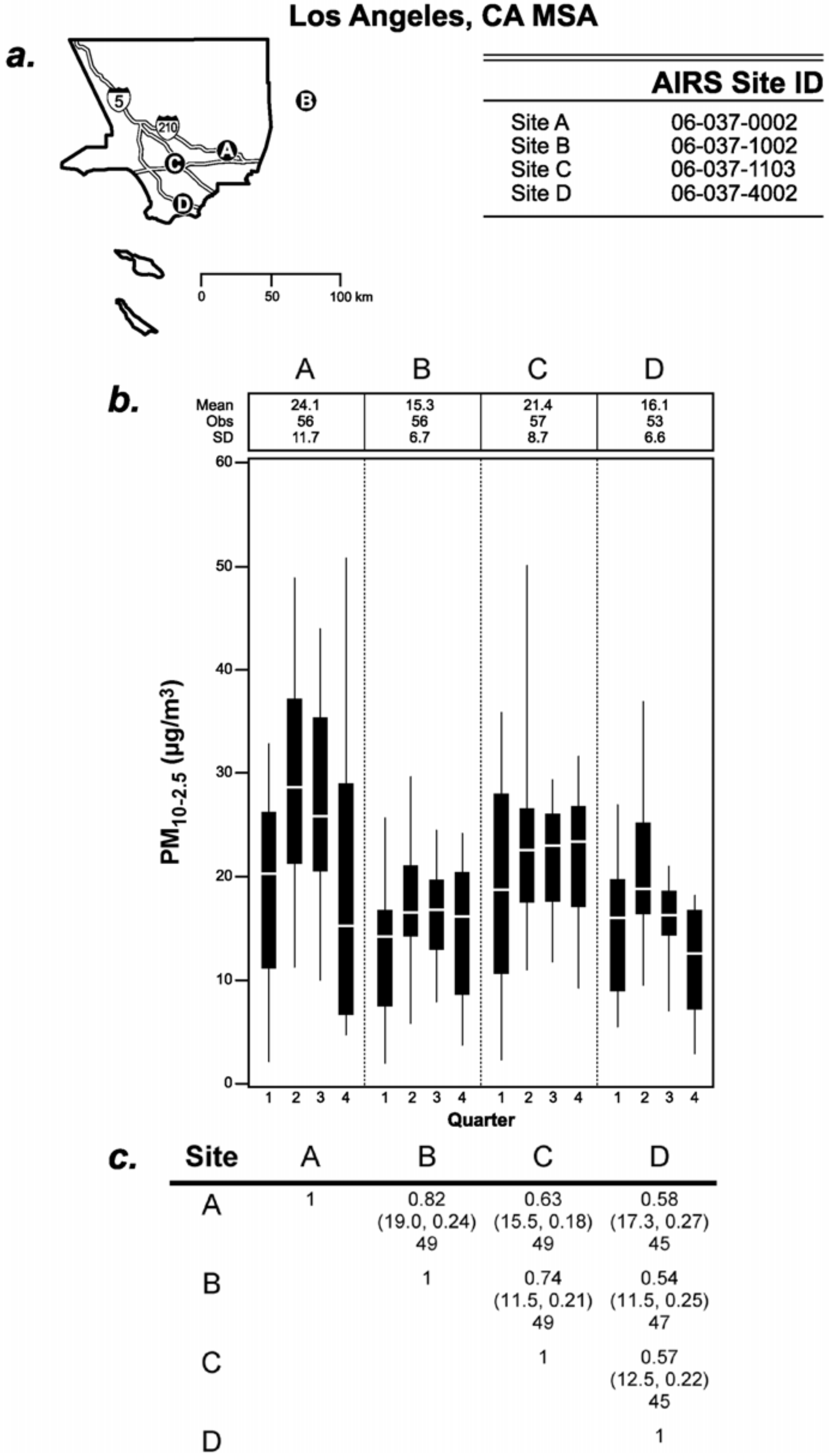


	AIRS Site ID
Site A	41-051-0080
Site B	53-011-0013

	A	B
Mean	5.7	6.7
Obs	320	113
SD	3.5	4.3

Site	A	B
A	1	0.69 (5.1, --) 107
B		1

Figure 3A-41. Portland, OR MSA *(a)* Locations of sampling sites by AIRS ID#; *(b)* Quarterly distribution of 24-h average PM$_{10-2.5}$ concentrations (µg/m^3) for 2000-2001; *(c)* Intersite correlation coefficients, number of observations, 90th percentile differences in concentrations, and CODs.

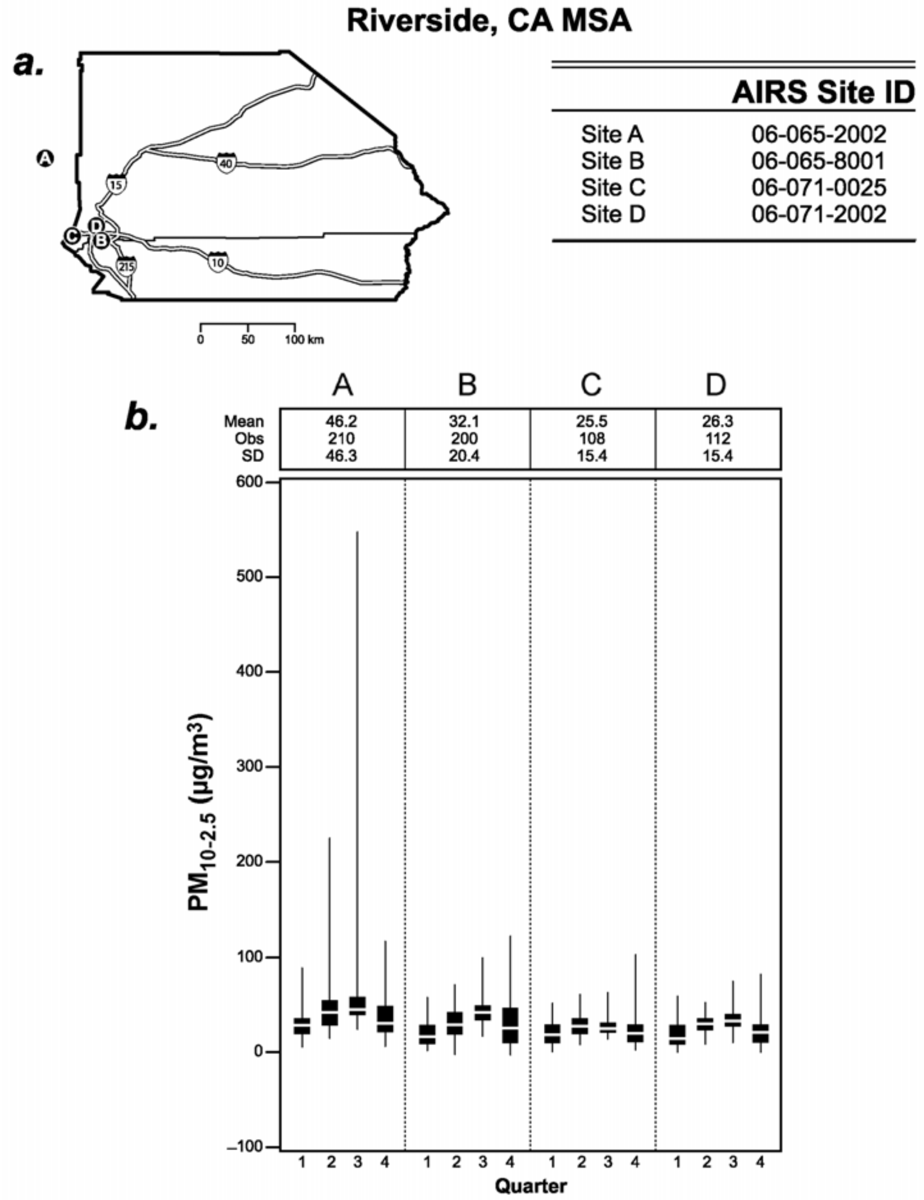


	AIRS Site ID
Site A	06-037-0002
Site B	06-037-1002
Site C	06-037-1103
Site D	06-037-4002

	A	B	C	D
Mean	24.1	15.3	21.4	16.1
Obs	56	56	57	53
SD	11.7	6.7	8.7	6.6

Site	A	B	C	D
A	1	0.82 (19.0, 0.24) 49	0.63 (15.5, 0.18) 49	0.58 (17.3, 0.27) 45
B		1	0.74 (11.5, 0.21) 49	0.54 (11.5, 0.25) 47
C			1	0.57 (12.5, 0.22) 45
D				1

Figure 3A-42. Los Angeles, CA MSA *(a)* Locations of sampling sites by AIRS ID#; *(b)* Quarterly distribution of 24-h average PM$_{10-2.5}$ concentrations (µg/m^3) for 2001; *(c)* Intersite correlation coefficients, number of observations, 90th percentile differences in concentrations, and CODs.



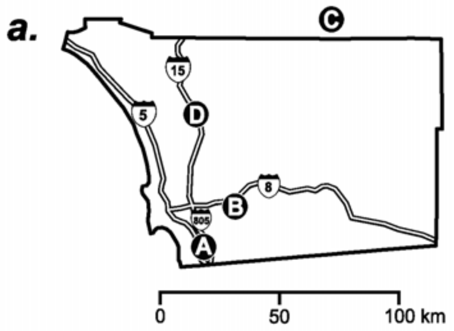
	AIRS Site ID
Site A	06-065-2002
Site B	06-065-8001
Site C	06-071-0025
Site D	06-071-2002

c.

Site	A	B	C	D
A	1	0.36 (42.6, 0.38) 184	0.32 (36.6, 0.39) 102	0.45 (39.0, 0.38) 107
B		1	0.62 (25.9, 0.32) 104	0.79 (18.2, 0.33) 108
C			1	0.80 (13.3, 0.28) 98
D				1

Figure 3A-43. Riverside, CA MSA *(a)* Locations of sampling sites by AIRS ID#; *(b)* Quarterly distribution of 24-h average $PM_{10\text{-}2.5}$ concentrations (µg/m^3) for 2000-2001; *(c)* Intersite correlation coefficients, number of observations, 90th percentile differences in concentrations, and CODs.

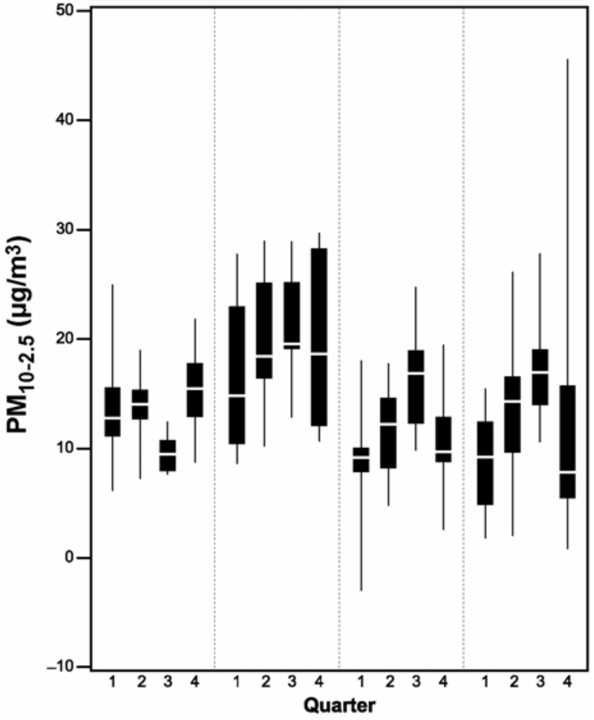
San Diego, CA MSA



	AIRS Site ID
Site A	06-073-0001
Site B	06-073-0003
Site C	06-073-1006
Site D	06-073-1002

b.

	A	B	C	D
Mean	13.3	19.4	11.6	12.9
Obs	55	51	57	56
SD	4.0	6.2	5.1	7.7



c.

Site	A	B	C	D
A	1	0.38 (14.4, 0.25) 46	0.01 (9.5, 0.34) 51	0.09 (11.7, 0.32) 50
B		1	0.65 (12.6, 0.28) 46	0.63 (14.7, 0.34) 46
C			1	0.70 (8.3, 0.45) 51
D				1

Figure 3A-44. San Diego, CA MSA *(a)* Locations of sampling sites by AIRS ID#; *(b)* Quarterly distribution of 24-h average $PM_{10-2.5}$ concentrations (µg/m^3) for 2001; *(c)* Intersite correlation coefficients, number of observations, 90th percentile differences in concentrations, and CODs.

APPENDIX 3B

Aerosol Composition Data from the Speciation Network

The United States Environmental Protection Agency (EPA), working with state and local air quality agencies, began implementing an ambient air monitoring network in 1999/2000 to provide a consistent data set for the characterization and evaluation of trends in PM components (chemical species). The network was designed to include about 52 core trends sites across the United States and to provide a stable ongoing national perspective. In 1999, an initial thirteen sites were installed and operated to be used as a model for the deployment of the more comprehensive network consisting of the 52 core trends sites and roughly two hundred additional locally relevant sites.

Data from the initial thirteen sites were presented in the Air Quality Criteria for Particulate Matter (3rd External Review Draft) by the EPA in 2001 for public comment and CASAC review. These sites were designed and operated to evaluate the suitability of various aerosol sampling devices for obtaining $PM_{2.5}$ composition data. These data were summarized in Appendix 3B of the 2001 3rd External Review Draft. Three types of collocated aerosol sampling devices were used in this study, which lasted from February 2000 through July 2000; data were obtained from the three sampling devices shown for each site. A complete description of the data, techniques used to analyze the filters, and the results of the evaluation of the performance of the sampling devices (including a number of caveats regarding the data) can be found in Coutant and Stetzer (2001) and the analyses of data in Coutant et al. (2001).

More recent measurements of ambient levels of $PM_{2.5}$ constituents are provided in the tables below. Table 3B-1 presents the locations and sample type for a different set of 13 monitoring sites representing a cross section of the country. Many of these sites were chosen because they are located in MSAs (or close to MSAs) in which risk assessments are to be performed. Sacramento, CA, and Riverside, CA, are located near San Francisco and Los Angeles, respectively. The data reported here are from the period October 2001 to September 2002. For this time period, a total of 51 sites (this includes both “Trends” and “non-Trends” sites) across the country have complete data (as defined by 50% of observations available for every quarter for each of the major chemical species: sulfate, ammonium, nitrate, elemental carbon, organic carbon, and the five trace elements that go into the calculation of the crustal contribution to $PM_{2.5}$ (Al, Fe, Ca, Ti, and Si).

Summary statistics for concentrations of $PM_{2.5}$ and chemical species are given for each of the 13 sites in Table 3B-2. The number of samples (n) and the AIRS site code are given above each table. Entries in the tables give for each component the mean, minimum and maximum component concentrations, and minimum detection limits. Minimum detection levels (MDL) differ among the various sampling methods; these limits were estimated by Research Triangle Institute in July of 2001 and are subject to review, revision, and reinterpretation. Anions and cations (ammonium, nitrate, sodium, potassium, and sulfate) were determined by ion chromatography; carbonaceous species were determined by the thermal optical transmittance method (NIOSH method); and trace elements (aluminum through zirconium) were determined by X-ray fluorescence spectrometry. The sulfate (calculated) entry is based on the XRF determination of S. In general, relatively good agreement is found between the reconstructed mass and the $PM_{2.5}$ concentration measured by the collocated FRM monitor at each site. However, there are exceptions at several locations as can be seen from inspection of Table 3B-2. Somewhat different sampling trains are used in the different sampling systems. These differences can result in differences in performance metrics and in differences in the entities that are measured. All samplers use a denuder in front of the filter for species to be analyzed by ion chromatography. In the RAAS and SASS samplers the denuder is followed by a nylon filter; whereas in the MASS samplers (Chicago, Houston, Seattle) a teflon filter is followed by a nylon filter. Particulate nitrate is collected on the teflon filter and is referred to as nonvolatile nitrate. However, there may be volatilization of nitrate containing compound from the teflon filter which is then adsorbed on the nylon filter. Nitrate extracted from the nylon filter is referred to as volatile nitrate.

Organic carbon (OC) concentrations are multiplied by a factor of 1.4 when calculating mass to account for the presence of H, N, and O in organic compounds on all samplers. Carbonate carbon has never been detected in any of the samples. Field blank corrections that could be applied to elemental carbon (EC) and OC concentrations are shown in Table 3B-3 for different samplers. Blank corrections for OC and EC shown in Table 3B-3 were applied to concentrations shown in Table 3B-2. However, subtracting blank corrections from OC concentrations results in negative values in several cases. A possible cause for results such as these could have been that not enough blank samples were obtained to fully characterize the blank levels. Although the concentrations of 47 elements could be obtained by X-ray fluorescence spectrometry, the concentrations of many of these elements are beneath MDLs and are not shown. The same elements shown in Appendix 6A of the 1996 PM AQCD are shown here. The usual practice of denoting table entry values below MDL by (—) is followed here. Missing data for $PM_{2.5}$ are also indicated by (—).

REFERENCES

Coutant, B.; Stetzer, S. (2001) Evaluation of $PM_{2.5}$ speciation sampler performance and related sample collection and stability issues: final report. Research Triangle Park, NC: U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards; report no. EPA-454/R-01-008. Available: http://www.epa.gov/ttn/amtic/pmspec.html [5 April, 2002].

Coutant, B.; Zhang, X.; Pivetz, T. (2001) Summary statistics and data displays for the speciation minitrends study: final report. Research Triangle Park, NC: U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards; contract no. 68-D-98-030.

TABLE 3B-1. $PM_{2.5}$ SPECIATION SAMPLERS BY LOCATION: SITES SELECTED FOR PM CD SUMMARY

Sampler Type	Location_Name	State	Began Operation	AIRS_Code	POC	Schedule	Reason for Inclusion
SASS	Burlington	VT	12/14/2000	000500070012	5	1-in-3	3
SASS	Philadelphia (AMS Laboratory)	PA	9/10/2001	000421010004	7	1-in-3	3
RAAS	Atlanta (South DeKalb)	GA	3/2/2001	000130890002	5	1-in-3	2
SASS	Detroit (Allen Park)	MI	12/14/2000	000261630001	5	1-in-3	1
MASS	Chicago (Com ED)	IL	5/22/2001	000170310076	5	Alt 1-in-3	3
RAAS	St. Louis (Blair Street)	MO	2/9/2000	000295100085	6	1-in-3	1
MASS	Houston (Deer Park)	TX	2/9/2000	000482011039	6/7	1-in-3	3
SASS	Minneapolis (Philips)	MN	12/14/2000	000270530963	5	Alt 1-in-3	2
SASS	Boulder (Commerce City)	CO	2/18/2001	000080010006	5	Alt 1-in-3	3
SASS	Phoenix (Supersite)	AZ	2/21/2000	000040139997	7	1-in-3	1
MASS	Seattle (Beacon Hill)	WA	2/9/2000	000530330080	6	1-in-3	3
SASS	Sacramento (Del Paso Manor)	CA	2/9/2000	000060670006	5	1-in-3	2
SASS	Riverside-Rubidoux	CA	5/13/2001	000060658001	5/6	1-in-3	1

1 = Completeness of geographic coverage
2 = PM_{10} risk assessment city
3 = $PM_{2.5}$ and PM_{10} risk assessment city

TABLE 3B-2a. BURLINGTON, VT SUMMARY DATA
(October 2001 to September 2002).
All concentrations are given in μg/m^3; n = 201; AIRS Site Code: 500070012

Parameter	Mean	Max	Min	MDL
$PM_{2.5}$ (FRM Mass)	10.0	61.0	1.0	—
$PM_{2.5}$ (Reconstructed Mass)	10.9	63.0	1.6	—
Sulfate (Calculated)	2.6	17.7	0.001	—
Sulfate (by I.C.)	2.8	18.8	0.17	0.012
Ammonium (by I.C.)	1.1	6.8	—	0.017
Sodium Ion (by I.C.)	0.22	2.1	—	0.030
Potassium (by I.C.)	0.035	0.38	—	0.014
Nitrate	1.3	8.8	—	0.008
Volatile Nitrate	—	—	—	—
Nonvolatile Nitrate	—	—	—	—
Elemental Carbon	0.26	0.84	—	0.15
Carbonate Carbon	—	—	—	0.15
Organic Carbon	2.5	31.4	-0.43	0.15
Aluminum	0.020	0.28	—	0.011
Arsenic	—	0.005	—	0.002
Barium	—	0.12	—	0.059
Bromine	0.002	0.007	—	0.002
Cadmium	—	0.014	—	0.011
Calcium	0.035	0.19	—	0.003
Chlorine	—	0.12	—	0.006
Chromium	0.002	0.060	—	0.002
Copper	0.002	0.014	0.001	0.001
Iron	0.041	0.390	0.007	0.002
Lead	—	0.016	—	0.006
Magnesium	0.014	0.19	—	0.018
Manganese	0.002	0.007	—	0.002
Molybdenum	0.003	0.012	—	0.005
Nickel	0.002	0.022	0.001	0.001
Phosphorous	0.005	0.092	—	0.006
Potassium	0.041	0.41	—	0.003
Rubidium	0.001	0.003	—	0.002
Selenium	0.001	0.005	—	0.002
Silicon	0.069	0.54	—	0.008
Sodium	0.10	0.40	—	0.051
Strontium	0.001	0.004	—	0.003
Sulfur	0.88	5.9	—	0.007
Tin	0.013	0.033	—	0.018
Titanium	0.004	0.023	—	0.002
Vanadium	0.001	0.006	—	0.002
Zinc	0.008	0.057	0.007	0.002

TABLE 3B-2b. PHILADELPHIA, PA SUMMARY DATA (October 2001 to September 2002). All concentrations are given in µg/m^3; n = 262; AIRS Site Code: 421010004

Parameter	Mean	Max	Min	MDL
$PM_{2.5}$ (FRM Mass)	14.2	86.8	2.1	—
$PM_{2.5}$ (Reconstructed Mass)	16.0	239.0	0.0	—
Sulfate (Calculated)	4.3	29.0	0.004	—
Sulfate (by I.C.)	4.4	30.5	0.020	0.012
Ammonium (by I.C.)	2.0	11.4	—	0.017
Sodium Ion (by I.C.)	0.21	1.6	—	0.030
Potassium (by I.C.)	0.042	0.83	—	0.014
Nitrate	2.1	8.7	0.050	0.008
Volatile Nitrate	0.84	4.0	0.030	—
Nonvolatile Nitrate	0.61	5.6	0.020	—
Elemental Carbon	0.66	2.3	—	0.15
Carbonate Carbon	—	—	—	0.15
Organic Carbon	3.1	50.5	-1.13	0.15
Aluminum	0.019	0.54	—	0.011
Arsenic	—	0.006	—	0.002
Barium	—	0.12	—	0.059
Bromine	0.004	0.013	—	0.002
Cadmium	—	0.017	—	0.011
Calcium	0.037	0.18	—	0.003
Chlorine	0.011	0.68	—	0.006
Chromium	0.002	0.018	—	0.002
Copper	0.004	0.025	0.003	0.001
Iron	0.084	0.53	—	0.002
Lead	0.005	0.025	—	0.005
Magnesium	0.014	0.30	—	0.018
Manganese	0.002	0.009	—	0.002
Molybdenum	—	0.012	—	0.005
Nickel	0.006	0.13	0.001	0.001
Phosphorous	—	0.039	—	0.006
Potassium	0.053	1.1	—	0.003
Rubidium	—	0.003	—	0.002
Selenium	0.002	0.005	—	0.002
Silicon	0.086	1.1	—	0.008
Sodium	0.087	0.63	—	0.051
Strontium	—	0.016	—	0.003
Sulfur	1.45	9.6	—	0.007
Tin	—	0.035	—	0.018
Titanium	0.006	0.049	—	0.002
Vanadium	0.004	0.035	—	0.002
Zinc	0.015	0.095	0.007	0.001

TABLE 3B-2c. ATLANTA, GA SUMMARY DATA (October 2001 to September 2002).
All concentrations are given in µg/m^3; n = 183; AIRS Site Code: 130890002

Parameter	Mean	Max	Min	MDL
$PM_{2.5}$ (FRM Mass)	—	—	—	—
$PM_{2.5}$ (Reconstructed Mass)	16.3	40.0	4.7	—
Sulfate (Calculated)	4.8	14.5	0.27	—
Sulfate (by I.C.)	4.8	15.2	0.88	0.011
Ammonium (by I.C.)	1.3	4.2	—	0.015
Sodium Ion (by I.C.)	0.27	1.7	—	0.028
Potassium (by I.C.)	0.044	0.31	—	0.013
Nitrate	0.70	3.5	0.16	0.008
Volatile Nitrate	—	—	—	—
Nonvolatile Nitrate	—	—	—	—
Elemental Carbon	0.90	3.5	—	0.13
Carbonate Carbon	—	—	—	0.13
Organic Carbon	4.3	11.2	0.8	0.13
Aluminum	0.028	0.65	—	0.004
Arsenic	0.001	0.014	—	0.001
Barium	0.018	0.054	0.012	0.024
Bromine	0.003	0.009	—	0.001
Cadmium	0.002	0.006	—	0.004
Calcium	0.037	0.28	0.006	0.001
Chlorine	0.003	0.049	—	0.002
Chromium	—	0.003	—	0.001
Copper	0.002	0.011	—	0.001
Gold	—	0.004	—	0.002
Iron	0.084	0.47	0.013	0.001
Lead	0.003	0.008	—	0.002
Magnesium	0.008	0.16	—	0.007
Manganese	0.002	0.011	—	0.001
Molybdenum	—	0.003	—	0.002
Nickel	—	0.002	—	0.001
Phosphorous	—	0.017	—	0.003
Potassium	0.060	0.36	0.015	0.001
Rubidium	0.005	0.002	—	0.001
Selenium	0.001	0.004	0.000	0.001
Silicon	0.11	1.4	0.010	0.003
Sodium	0.056	0.31	—	0.021
Strontium	0.001	0.005	0.001	0.001
Sulfur	1.6	4.8	0.089	0.003
Tin	—	0.019	—	0.007
Titanium	0.006	0.043	—	0.001
Vanadium	0.001	0.003	—	0.001
Zinc	0.008	0.034	0.001	0.001

TABLE 3B-2d. DETROIT, MI SUMMARY DATA (October 2001 to September 2002). All concentrations are given in µg/m^3; n = 189; AIRS Site Code: 261630001

Parameter	Mean	Max	Min	MDL
$PM_{2.5}$ (FRM Mass)	16.6	53.1	2.6	
$PM_{2.5}$ (Reconstructed Mass)	18.0	52.9	3.2	—
Sulfate (Calculated)	4.4	22.0	0.010	
Sulfate (by I.C.)	4.6	24.4	0.040	0.012
Ammonium (by I.C.)	2.2	9.3	0.009	0.017
Sodium Ion (by I.C.)	0.27	1.7	0.015	0.030
Potassium (by I.C.)	0.061	1.2	0.007	0.014
Nitrate	3.1	15.2	0.004	0.008
Volatile Nitrate	—	—	—	—
Nonvolatile Nitrate	—	—	—	—
Elemental Carbon	0.68	3.7	—	0.15
Carbonate Carbon	—	—	—	0.15
Organic Carbon	3.2	11.2	-0.46	0.15
Aluminum	0.025	0.53	—	0.011
Arsenic	0.002	0.010	—	0.002
Barium	0.043	0.11	—	0.059
Bromine	0.003	0.011	—	0.002
Cadmium	—	0.014	—	0.011
Calcium	0.069	0.33	—	0.003
Chlorine	0.017	0.65	—	0.006
Chromium	0.002	0.033	—	0.002
Copper	0.006	0.043	0.001	0.001
Iron	0.12	0.60	0.003	0.002
Lead	0.006	0.034	—	0.005
Magnesium	0.020	0.30	—	0.018
Manganese	0.004	0.025	—	0.002
Molybdenum	—	0.013	—	0.005
Nickel	0.002	0.022	0.001	0.001
Phosphorous	—	0.028	—	0.006
Potassium	0.078	1.3	—	0.003
Rubidium	—	0.003	—	0.002
Selenium	0.002	0.011	—	0.002
Silicon	0.11	0.84	—	0.008
Sodium	0.098	0.53	—	0.051
Strontium	—	0.021	—	0.003
Sulfur	1.5	7.3	—	0.007
Tin	—	0.032	—	0.018
Titanium	0.007	0.079	—	0.002
Vanadium	0.002	0.012	—	0.002
Zinc	0.025	0.19	0.001	0.001

TABLE 3B-2e. CHICAGO, IL SUMMARY DATA (October 2001 to September 2002). All concentrations are given in $\mu g/m^3$; n = 139; AIRS Site Code: 170310076

Parameter	Mean	Max	Min	MDL
$PM_{2.5}$ (FRM Mass)	15.7	42.7	3.6	—
$PM_{2.5}$ (Reconstructed Mass)	15.0	44.5	3.4	—
Sulfate (Calculated)	4.3	22.8	0.64	—
Sulfate (by I.C.)	4.2	21.2	0.56	0.005
Ammonium (by I.C.)	1.9	8.8	0.17	0.007
Sodium Ion (by I.C.)	0.052	0.26	—	0.012
Potassium (by I.C.)	0.068	3.1	—	0.006
Nitrate	2.0	10.2	0.12	0.003
Volatile Nitrate	0.71	3.6	0.04	0.003
Nonvolatile Nitrate	1.3	9.9	0.03	0.003
Elemental Carbon	0.61	1.6	—	0.059
Carbonate Carbon	—	—	—	0.059
Organic Carbon	2.8	7.4	0.31	0.059
Aluminum	0.03	1.1	—	0.004
Arsenic	0.001	0.006	0.001	0.001
Barium	0.018	0.22	0.012	0.024
Bromine	0.003	0.011	—	0.001
Cadmium	—	0.007	—	0.004
Calcium	0.058	0.55	0.10	0.001
Chlorine	0.017	0.67	—	0.002
Chromium	0.001	0.005	—	0.001
Copper	0.004	0.056	—	0.001
Iron	0.091	0.53	0.014	0.001
Lead	0.006	0.040	—	0.002
Magnesium	0.017	0.69	—	0.007
Manganese	0.003	0.014	—	0.001
Molybdenum	—	0.006	—	0.002
Nickel	0.001	0.007	—	0.001
Phosphorous	0.002	0.015	—	0.003
Potassium	0.085	3.1	0.005	0.001
Rubidium	—	0.001	—	0.001
Selenium	0.001	0.004	0.001	0.001
Silicon	0.11	2.2	0.010	0.003
Sodium	0.048	0.58	0.010	0.021
Strontium	0.001	0.061	0.001	0.001
Sulfur	1.4	7.6	0.21	0.003
Tin	—	0.023	—	0.007
Titanium	0.004	0.070	—	0.001
Vanadium	0.001	0.002	—	0.001
Zinc	0.023	0.093	0.001	0.001

TABLE 3B-2f. ST. LOUIS, MO SUMMARY DATA (October 2001 to September 2002). All concentrations are given in μg/m^3; n = 324; AIRS Site Code: 295100085

Parameter	Mean	Max	Min	MDL
$PM_{2.5}$ (FRM Mass)	15.6	52.1	3.8	—
$PM_{2.5}$ (Reconstructed Mass)	16.4	53.2	2.8	—
Sulfate (Calculated)	4.3	22.5	0.61	—
Sulfate (by I.C.)	4.3	20.6	0.64	0.011
Ammonium (by I.C.)	1.9	7.2	0.14	0.015
Sodium Ion (by I.C.)	0.19	1.6	0.014	0.028
Potassium (by I.C.)	0.069	5.9	0.007	0.013
Nitrate	2.3	14.0	0.20	0.008
Volatile Nitrate	—	—	—	—
Nonvolatile Nitrate	—	—	—	—
Elemental Carbon	0.72	2.7	—	0.13
Carbonate Carbon	—	—	—	0.13
Organic Carbon	3.5	11.5	—	0.13
Aluminum	0.044	2.5	—	0.004
Arsenic	0.002	0.011	0.001	0.001
Barium	0.024	0.38	—	0.024
Bromine	0.004	0.16	—	0.001
Cadmium	—	0.010	—	0.004
Calcium	0.13	1.1	0.010	0.001
Chlorine	0.027	0.57	—	0.002
Chromium	0.002	0.034	—	0.001
Copper	0.018	0.72	—	0.001
Iron	0.24	1.3	0.012	0.001
Lead	0.014	0.09	—	0.002
Magnesium	0.011	0.79	0.004	0.007
Manganese	0.014	0.13	—	0.001
Molybdenum	—	0.007	—	0.002
Nickel	0.002	0.04	—	0.001
Phosphorous	0.004	0.095	—	0.003
Potassium	0.099	5.6	0.016	0.001
Rubidium	—	0.002	—	0.001
Selenium	0.001	0.006	—	0.001
Silicon	0.17	4.0	0.011	0.003
Sodium	0.045	0.43	0.010	0.021
Strontium	0.001	0.12	0.001	0.001
Sulfur	1.4	7.5	0.20	0.003
Tin	0.008	0.028	—	0.007
Titanium	0.008	0.14	—	0.001
Vanadium	0.001	0.011	—	0.001
Zinc	0.033	0.48	0.002	0.001

TABLE 3B-2g. HOUSTON, TX SUMMARY DATA (October 2001 to September 2002).
All concentrations are given in $\mu g/m^3$; n = 229; AIRS Site Code: 482011039

Parameter	Mean	Max	Min	MDL
$PM_{2.5}$ (FRM Mass)	12.4	21.9	5.9	—
$PM_{2.5}$ (Reconstructed Mass)	11.0	48.0	0.0	—
Sulfate (Calculated)	3.4	24.5	0.004	—
Sulfate (by I.C.)	3.5	26.0	0.030	0.005
Ammonium (by I.C.)	1.2	8.8	—	0.007
Sodium Ion (by I.C.)	0.22	1.1	—	0.012
Potassium (by I.C.)	0.051	0.38	—	0.006
Nitrate	0.68	5.8	0.040	0.003
Volatile Nitrate	0.37	3.5	0.010	0.003
Nonvolatile Nitrate	0.32	4.2	0.020	0.003
Elemental Carbon	0.30	1.1	—	0.059
Carbonate Carbon	—	—	—	0.059
Organic Carbon	2.2	12.1	—	0.059
Aluminum	0.092	1.6	—	0.004
Arsenic	0.001	0.006	0.001	0.001
Barium	—	0.059	—	0.024
Bromine	0.003	0.022	—	0.001
Cadmium	0.002	0.008	—	0.004
Calcium	0.055	0.44	0.001	0.001
Chlorine	0.050	0.70	—	0.002
Chromium	0.001	0.009	—	0.001
Copper	0.003	0.024	—	0.001
Iron	0.073	0.83	—	0.001
Lead	0.002	0.007	—	0.002
Magnesium	0.020	0.38	—	0.007
Manganese	0.002	0.013	—	0.001
Molybdenum	0.002	0.022	—	0.002
Nickel	0.002	0.047	—	0.001
Phosphorous	0.002	0.021	—	0.003
Potassium	0.072	0.64	0.001	0.001
Rubidium	—	0.002	—	0.001
Selenium	0.001	0.001	0.001	0.001
Silicon	0.23	2.8	—	0.003
Sodium	0.17	1.1	—	0.021
Strontium	0.001	0.009	0.001	0.001
Sulfur	1.1	8.2	—	0.003
Tin	0.006	0.019	—	0.007
Titanium	0.007	0.091	—	0.001
Vanadium	0.003	0.011	—	0.001
Zinc	0.006	0.030	—	0.001

TABLE 3B-2h. MINNEAPOLIS, MN SUMMARY DATA (October 2001 to September 2002). All concentrations are given in μg/m^3; n = 163; AIRS Site Code: 270530963

Parameter	Mean	Max	Min	MDL
$PM_{2.5}$ (FRM Mass)	10.3	33.4	1.8	—
$PM_{2.5}$ (Reconstructed Mass)	12.4	37.7	2.2	—
Sulfate (Calculated)	2.3	8.6	0.12	—
Sulfate (by I.C.)	2.4	8.9	0.24	0.012
Ammonium (by I.C.)	1.2	6.0	—	0.017
Sodium Ion (by I.C.)	0.27	3.7	—	0.030
Potassium (by I.C.)	0.059	1.7	—	0.014
Nitrate	2.3	16.4	0.098	0.008
Volatile Nitrate	—	—	—	—
Nonvolatile Nitrate	—	—	—	—
Elemental Carbon	0.39	1.8	—	0.15
Carbonate Carbon	—	—	—	0.15
Organic Carbon	2.6	9.9	−0.63	0.15
Aluminum	0.028	0.67	—	0.011
Arsenic	0.002	0.012	—	0.002
Barium	—	0.15	—	0.059
Bromine	0.002	0.008	—	0.002
Cadmium	—	0.028	—	0.011
Calcium	0.071	0.46	—	0.003
Chlorine	0.008	0.17	—	0.006
Chromium	0.002	0.016	—	0.002
Copper	0.003	0.045	0.001	0.001
Iron	0.065	0.37	0.016	0.002
Lead	0.005	0.066	0.003	0.005
Magnesium	0.018	0.52	0.009	0.018
Manganese	0.002	0.009	—	0.002
Molybdenum	—	0.011	—	0.005
Nickel	0.002	0.014	0.001	0.001
Phosphorous	0.005	0.11	—	0.006
Potassium	0.068	1.8	0.005	0.003
Rubidium	—	0.002	—	0.002
Selenium	—	0.004	—	0.002
Silicon	0.12	1.3	—	0.008
Sodium	0.093	0.69	—	0.051
Strontium	—	0.026	—	0.003
Sulfur	0.78	2.9	0.040	0.007
Tin	—	0.034	—	0.018
Titanium	0.006	0.043	—	0.002
Vanadium	0.002	0.021	—	0.002
Zinc	0.008	0.039	0.001	0.001

TABLE 3B-2i. BOULDER, CO SUMMARY DATA (October 2001 to September 2002). All concentrations are given in μg/m^3; n = 161; AIRS Site Code: 080010006

Parameter	Mean	Max	Min	MDL
$PM_{2.5}$ (FRM Mass)	9.5	26.9	2.1	—
$PM_{2.5}$ (Reconstructed Mass)	11.3	28.2	3.7	—
Sulfate (Calculated)	1.5	5.3	0.31	—
Sulfate (by I.C.)	1.6	5.9	0.29	0.012
Ammonium (by I.C.)	0.79	4.3	0.009	0.017
Sodium Ion (by I.C.)	0.24	1.7	0.015	0.030
Potassium (by I.C.)	0.032	0.29	0.007	0.014
Nitrate	1.5	7.9	0.14	0.008
Volatile Nitrate	—	—	—	—
Nonvolatile Nitrate	—	—	—	—
Elemental Carbon	1.0	4.4	0.15	0.15
Carbonate Carbon	—	—	—	0.15
Organic Carbon	3.2	13.8	0.28	0.15
Aluminum	0.092	0.41	0.005	0.011
Arsenic	—	0.005	—	0.002
Barium	—	0.12	—	0.059
Bromine	0.002	0.011	—	0.002
Cadmium	—	0.016	—	0.011
Calcium	0.12	0.55	0.008	0.003
Chlorine	0.019	0.66	—	0.006
Chromium	0.002	0.009	—	0.002
Copper	0.004	0.013	0.001	0.001
Iron	0.13	0.47	0.016	0.002
Lead	0.005	0.036	—	0.005
Magnesium	0.020	0.15	—	0.018
Manganese	0.003	0.015	—	0.002
Molybdenum	—	0.010	—	0.005
Nickel	0.001	0.010	0.001	0.001
Phosphorous	0.006	0.096	—	0.006
Potassium	0.063	0.33	—	0.003
Rubidium	—	0.003	—	0.002
Selenium	—	0.004	—	0.002
Silicon	0.28	0.97	0.027	0.008
Sodium	0.075	0.28	—	0.051
Strontium	—	0.005	—	0.003
Sulfur	0.49	1.8	0.10	0.007
Tin	—	0.033	—	0.018
Titanium	0.010	0.031	—	0.002
Vanadium	—	0.004	—	0.002
Zinc	0.023	0.53	0.001	0.001

TABLE 3B-2j. PHOENIX, AZ SUMMARY DATA (October 2001 to September 2002). All concentrations are given in μg/m^3; n = 275; AIRS Site Code: 040139997

Parameter	Mean	Max	Min	MDL
$PM_{2.5}$ (FRM Mass)	9.9	32.1	3.3	—
$PM_{2.5}$ (Reconstructed Mass)	12.0	158.0	0.8	—
Sulfate (Calculated)	1.2	2.9	0.001	—
Sulfate (by I.C.)	1.3	3.8	0.006	0.012
Ammonium (by I.C.)	0.5	2.6	0.009	0.017
Sodium Ion (by I.C.)	0.28	1.9	0.015	0.030
Potassium (by I.C.)	0.062	0.64	0.007	0.014
Nitrate	1.1	6.9	0.004	0.008
Volatile Nitrate	—	—	—	—
Nonvolatile Nitrate	—	—	—	—
Elemental Carbon	0.75	5.0	—	0.15
Carbonate Carbon	—	—	—	0.15
Organic Carbon	4.0	21.0	-0.66	0.15
Aluminum	0.12	0.87	0.005	0.011
Arsenic	0.002	0.009	—	0.002
Barium	—	0.13	—	0.059
Bromine	0.003	0.009	—	0.002
Cadmium	—	0.024	—	0.011
Calcium	0.15	0.82	0.005	0.003
Chlorine	0.047	0.40	—	0.006
Chromium	0.002	0.021	—	0.002
Copper	0.006	0.038	0.001	0.001
Iron	0.17	0.95	0.003	0.002
Lead	—	0.020	—	0.005
Magnesium	0.025	0.38	—	0.018
Manganese	0.004	0.027	—	0.002
Molybdenum	—	0.011	—	0.005
Nickel	0.003	0.13	—	0.001
Phosphorous	0.006	0.13	—	0.006
Potassium	0.11	0.69	—	0.003
Rubidium	—	0.003	—	0.002
Selenium	—	0.005	—	0.002
Silicon	0.36	2.2	—	0.008
Sodium	0.10	0.52	—	0.051
Strontium	0.003	0.10	—	0.003
Sulfur	0.39	0.98	—	0.007
Tin	0.014	0.038	—	0.018
Titanium	0.013	0.058	—	0.002
Vanadium	—	0.005	—	0.002
Zinc	0.009	0.080	0.001	0.001

TABLE 3B-2k. SEATTLE, WA SUMMARY DATA (October 2001 to September 2002). All concentrations are given in µg/m^3; n = 314; AIRS Site Code: 530330080

Parameter	Mean	Max	Min	MDL
$PM_{2.5}$ (FRM Mass)	8.2	29.1	1.9	—
$PM_{2.5}$ (Reconstructed Mass)	8.0	28.5	1.5	—
Sulfate (Calculated)	1.4	4.9	0.057	—
Sulfate (by I.C.)	1.3	4.6	0.14	0.005
Ammonium (by I.C.)	0.47	2.0	—	0.007
Sodium Ion (by I.C.)	0.16	0.76	0.012	0.012
Potassium (by I.C.)	0.045	2.3	—	0.006
Nitrate	0.67	2.9	0.12	0.003
Volatile Nitrate	0.25	1.6	0.010	0.003
Nonvolatile Nitrate	0.41	2.5	0.020	0.003
Elemental Carbon	0.60	2.7	—	0.059
Carbonate Carbon	—	—	—	0.059
Organic Carbon	2.6	11.0	—	0.059
Aluminum	0.015	0.24	—	0.004
Arsenic	0.001	0.007	0.001	0.001
Barium	—	0.15	—	0.024
Bromine	0.002	0.014	—	0.001
Cadmium	—	0.007	—	0.004
Calcium	0.029	0.20	0.001	0.001
Chlorine	0.055	0.84	—	0.002
Chromium	0.002	0.016	—	0.001
Copper	0.003	0.045	—	0.001
Iron	0.053	0.29	0.001	0.001
Lead	0.004	0.078	—	0.002
Magnesium	0.014	0.19	—	0.007
Manganese	0.003	0.024	—	0.001
Molybdenum	0.002	0.011	—	0.002
Nickel	0.002	0.020	—	0.001
Phosphorous	—	0.028	—	0.003
Potassium	0.055	2.3	0.007	0.001
Rubidium	—	0.002	—	0.001
Selenium	0.001	0.008	0.001	0.001
Silicon	0.049	0.52	—	0.003
Sodium	0.15	0.84	—	0.021
Strontium	0.001	0.044	0.001	0.001
Sulfur	0.45	1.6	0.019	0.003
Tin	0.007	0.030	—	0.007
Titanium	0.003	0.026	—	0.001
Vanadium	0.003	0.029	—	0.001
Zinc	0.009	0.048	—	0.001

TABLE 3B-2l. SACRAMENTO, CA SUMMARY DATA (October 2001 to September 2002). All concentrations are given in µg/m^3; n = 265; AIRS Site Code: 060670006

Parameter	Mean	Max	Min	MDL
$PM_{2.5}$ (FRM Mass)	9.4	78.0	3.0	—
$PM_{2.5}$ (Reconstructed Mass)	15.0	120.0	3.0	—
Sulfate (Calculated)	1.2	5.5	0.14	—
Sulfate (by I.C.)	1.3	4.1	0.06	0.012
Ammonium (by I.C.)	0.74	7.4	0.009	0.017
Sodium Ion (by I.C.)	0.38	3.5	0.015	0.030
Potassium (by I.C.)	0.077	3.6	0.007	0.014
Nitrate	2.3	23.4	0.004	0.008
Volatile Nitrate	—	—	—	—
Nonvolatile Nitrate	—	—	—	—
Elemental Carbon	0.66	8.4	—	0.15
Carbonate Carbon	—	—	—	0.15
Organic Carbon	5.2	54.1	0.18	0.15
Aluminum	0.040	0.52	—	0.011
Arsenic	0.002	0.006	—	0.002
Barium	—	0.26	—	0.059
Bromine	0.002	0.013	—	0.002
Cadmium	—	0.018	—	0.011
Calcium	0.043	0.56	0.005	0.003
Chlorine	0.052	1.8	—	0.006
Chromium	0.002	0.043	—	0.002
Copper	0.006	0.16	0.001	0.001
Iron	0.079	0.64	0.005	0.002
Lead	—	0.044	—	0.005
Magnesium	0.021	0.88	—	0.018
Manganese	0.002	0.013	—	0.002
Molybdenum	—	0.015	—	0.005
Nickel	0.010	0.61	0.001	0.001
Phosphorous	0.006	0.11	—	0.006
Potassium	0.10	3.3	—	0.003
Rubidium	—	0.003	—	0.002
Selenium	—	0.004	—	0.002
Silicon	0.12	1.1	0.011	0.008
Silver	—	0.015	—	0.010
Sodium	0.19	1.7	—	0.010
Strontium	—	0.077	—	0.051
Sulfur	0.41	1.8	0.045	0.003
Tin	—	0.035	0.009	0.007
Titanium	—	0.052	—	0.018
Vanadium	—	0.006	—	0.002
Zinc	0.005	0.11	—	0.002

TABLE 3B-2m. RIVERSIDE-RUBIDOUX, CA SUMMARY DATA (October 2001 to September 2002). All concentrations are given in µg/m^3; n = 161; AIRS Site Code: 060658001

Parameter	Mean	Max	Min	MDL
$PM_{2.5}$ (FRM Mass)	28.6	78.2	2.6	—
$PM_{2.5}$ (Reconstructed Mass)	30.5	79.2	3.1	—
Sulfate (Calculated)	3.6	9.6	0.23	—
Sulfate (by I.C.)	3.7	10.0	0.28	0.012
Ammonium (by I.C.)	4.8	16.8	—	0.017
Sodium Ion (by I.C.)	0.49	1.8	—	0.030
Potassium (by I.C.)	0.075	1.3	—	0.014
Nitrate	12.3	40.3	0.18	0.008
Volatile Nitrate	—	—	—	—
Nonvolatile Nitrate	—	—	—	—
Elemental Carbon	1.2	4.3	0.12	0.15
Carbonate Carbon	—	—	—	0.15
Organic Carbon	6.0	13.0	0.38	0.15
Aluminum	0.057	0.32	—	0.011
Arsenic	0.002	0.006	—	0.002
Barium	—	0.17	—	0.059
Bromine	0.006	0.016	—	0.002
Cadmium	—	0.017	—	0.011
Calcium	0.17	1.0	0.012	0.003
Chlorine	0.072	0.71	—	0.006
Chromium	0.003	0.024	—	0.002
Copper	0.006	0.037	0.001	0.001
Iron	0.17	0.58	0.019	0.002
Lead	0.006	0.026	—	0.005
Magnesium	0.032	0.31	—	0.018
Manganese	0.004	0.015	—	0.002
Molybdenum	—	0.024	—	0.005
Nickel	0.002	0.014	0.006	0.001
Phosphorous	0.007	0.067	—	0.006
Potassium	0.11	1.31	0.017	0.003
Rubidium	—	0.003	—	0.002
Selenium	—	—	—	0.006
Silicon	0.20	0.88	0.023	0.008
Silver	—	0.015	—	0.010
Sodium	0.20	0.94	—	0.051
Strontium	0.002	0.026	—	0.003
Sulfur	1.2	3.2	0.078	0.007
Tin	0.014	0.081	—	0.018
Titanium	0.012	0.041	—	0.002
Vanadium	0.006	0.017	—	0.002
Zinc	0.023	0.21	0.001	0.001

TABLE 3B-3. BLANK CORRECTIONS FOR ELEMENTAL CARBON (EC), ORGANIC CARBON (OC), AND TOTAL CARBON (TC) IN THE SPECIATION NETWORK

	Elemental Carbon		Organic Carbon		Total Carbon	
Sampler Type	**EC Mass (µgC/filter)**	**EC Conc (µgC/m^3)**	**OC Mass (µgC/filter)**	**OC Conc (µgC/m^3)**	**TC Mass (µgC/filter)**	**TC Conc (µgC/m^3)**
URG MASS	0.63	0.03	7.08	0.29	7.71	0.32
R & P 2300	3.21	0.22	12.93	0.90	16.13	1.12
Anderson RAAS	0.97	0.09	12.54	1.19	13.51	1.29
R & P 2025	1.67	0.07	18.42	0.77	19.91	0.83
MetOne SASS	1.03	0.11	13.75	1.42	14.78	1.53

APPENDIX 3C

Organic Composition of Particulate Matter

Although organic compounds typically constitute approximately 10 to 70% of the total dry fine particle mass in the atmosphere, organic PM concentrations, composition, and formation mechanisms are poorly understood. This is because particulate organic matter is an aggregate of hundreds of individual compounds spanning a wide range of chemical and thermodynamic properties (Saxena and Hildemann, 1996). The presence of multiphase or “semivolatile” compounds complicates collection of organic particulate matter. Furthermore, no single analytical technique currently is capable of analyzing the entire range of compounds present. Rigorous analytical methods frequently identify only 10 to 20% of the organic mass on the molecular level (Rogge et al., 1993). The data shown in Appendix 3C are meant to complement the data given for the inorganic components of particles in Appendix 6A of the 1996 PM AQCD (U. S. Environmental Protection Agency, 1996). Table 3C-1 lists a number of recent urban and some rural measurements of particulate organic and elemental carbon in µg of carbon/m^3 (µg C/m^3). Emphasis is placed on measurements published after 1995. The analysis method and artifact correction procedure, if any, are indicated. Table 3C-2 presents information on recent (post-1990) studies concerning concentrations (in ng C/m^3) of particulate organic compounds found at selected U.S. sites.

TABLE 3C-1. PARTICULATE ORGANIC AND ELEMENTAL CARBON CONCENTRATIONS (in µg C/m^3) BASED ON STUDIES PUBLISHED AFTER 1995

Reference	Location	Dates	OC Mean (Max)	EC Mean (Max)	TC Mean (Max)	Avg. Time	Notes
URBAN PM$_{2.5}$							
Offenberg and Baker (2000)	Chicago, IL	July 1994; Jan 1995			2.2 (3.8)	12 h	PM$_{12}$; Imp; TOT
					1.7		PM$_{1.4}$; Imp; TOT
Allen et al. (1999)	Uniontown, PA	July-Aug 1990	(0.8-8.4)[a]	(0.4-3.5)[a]		3 h	PM$_{2.5}$; DQQ; TOR[b]
				1.3 (3.1)		10 min	Aeth
Pedersen et al. (1999)	Boston, MA	Jan-Dec 1995	5.8	1.7		24 h	PM$_{2.0}$; Q; TOT
	Reading, MA (suburban)		4.0	0.7			
	Quabbin, MA (rural)		2.8	0.5			
	Rochester, NY (urban)		3.3	0.7			
	Brockport, NY (rural)		2.7	0.5			
IMPROVE (2000)	Washington, DC	1994-1998	3.4	1.1		24 h	PM$_{2.5}$; QQ; TOR
	Seattle, WA		1.8	0.3			
Lewtas et al. (2001)	Seattle, WA	Apr-May 1999	8.0	1.4		23 h	PM$_{2.5}$; DQA; EGA[c]
Khwaja (1995)	Schenectady, NY	Oct 24-26, 1991			23.2 (49.9)	6 h	PM$_{1.0}$; Q; Th
Christoforou et al. (2000)	Azusa, CA	Jan-Dec 1993	9.4	1.3		24 h	PM$_{2.1}$; Q; TOR
	Long Beach, CA		8.9	1.8			
	Central, LA		12.3	2.7			
	Rubidoux, LA		9.7	1.5			
	San Nicolas, LA		1.6	1.5			
Turpin and Huntzicker (1995)	Claremont, CA	Jun-Sept	na (29.4)	na (9.0)		2 h	PM$_{2.5}$; Q+TQ; TOT[d]
	Long Beach, CA	Nov-Dec 1987	na (62.6)	na (24.6)		2-6 h	

TABLE 3C-1 (cont'd). PARTICULATE ORGANIC AND ELEMENTAL CARBON CONCENTRATIONS (in μg C/m^3) BASED ON STUDIES PUBLISHED AFTER 1995

Reference	Location	Dates	OC Mean (Max)	EC Mean (Max)	TC Mean (Max)	Avg. Time	Notes
RURAL PM$_{2.5}$							
Klinedinst and Currie (1999)	Welby, CO	Dec 1996-Jan 1997	5.6 (13.4)	3.3 (8.1)		6 h	PM$_{2.5}$; Q; TOR
	Brighton, CO		3.6 (6.4)	1.9 (3.6)			
Andrews et al. (2000)	Look Rock, Smoky Mountains, TN	July-Aug 1995	2.2	0.4		12 h (day)	PM$_{2.1}$; QQ; TOR[e]
			2.7	0.1			PM$_{2.1}$; Q+TQ; TOR[d]
			1.2	0.2			PM$_{1.8}$; Imp; TMO
Malm and Gebhart (1996)	Tahoma Wood, WA	June-Aug 1990	2.6 (7.4)	0.7 (2.2)		12 h	PM$_{2.5}$; QQ; TOR[f]
IMPROVE (2000)	Three Sisters Wilderness, OR	1994-1998	0.9	0.2		24 h	PM$_{2.5}$; QQ; TOR
	Rocky Mountains, CO		1.0	0.2			
	Brigantine, NJ		2.0	0.5			
	Acadia, MA		1.2	0.2			
	Jefferson: James River Face Wilderness, VA		3.8	0.7			
	Glacier, MT		2.4	0.4			
Hegg et al. (1997)	150 km East of Mid-Atlantic Coast (0.02-4 km altitude)	July 1996			2.9 (5.4)		PM$_{1.0}$; QQ ; EGA[e]
Cui et al. (1997)	Meadview, AZ	Aug 6-15, 1992			3.0	12 h	PM$_{2.5}$; VDQA; EGA[c]
Chow et al. (1996)	Point Reyes, CA	July-Aug 1990	1.5 (2.7)	0.4 (0.6)	5-7 hPM$_{2.5}$; Q+TQ; TOR[g]		
	Altamont Pass, CA		4.8 (7.2)	2.6 (3.9)			
	Pacheco Pass, CA		3.2 (6.1)	1.0 (1.3)			
	Crows Landing, CA		7.4 (12.7)	1.8 (2.5)			
	Academy, CA		5.9 (8.7)	1.4 (2.4)			
	Button-Willow, CA		6.4 (10.6)	1.9 (2.7)			
	Edison, CA		10.0 (12.8)	2.9 (4.1)			
	Caliente, CA		7.4 (10.7)	3.3 (4.4)			
	Sequoia, CA		5.3 (7.0)	1.6 (3.0)			
	Yosemite, CA		12.1 (25.8)	1.9 (3.5)			

TABLE 3C-1 (cont'd). PARTICULATE ORGANIC AND ELEMENTAL CARBON CONCENTRATIONS (in µg C/m^3) BASED ON STUDIES PUBLISHED AFTER 1995

Reference	Location	Dates	OC Mean (Max)	EC Mean (Max)	TC Mean (Max)	Avg. Time	Notes
RURAL PM$_{2.5}$							
Malm and Day (2000)	Grand Canyon, AZ	July-Aug 1998	1.1 (1.6)	0.10 (0.3)		24 h	PM$_{2.5}$; QQ; TOR[f]
PM$_{10}$							
Omar et al. (1999)	Bondville, IL	Jan-Dec 1994	2.6	0.2		24-48 h	PM$_{10}$; Q; TOR
Gertler et al. (1995)	Bullhead City, AZ	Sept 1988-Oct 1989	6.0 (16.0)	1.9 (4.0)		24 h	PM$_{10}$; Q; TOR
Chow et al. (1996)	Santa Barbara, CA (urban)	Jan-Dec 1989			8.8	24 h	PM$_{10}$; Q; TOR
	Santa Maria, CA (urban)				4.6		
	Santa Ynez, CA (airport)				3.5		
	Gaviota, CA (rural SB)				3.4		
	Watt Road, CA (rural SB)				2.1		
	Anacapa Island, CA				3.1		
Lioy and Daisey (1987)		1982:					PM$_{15}$; Q
	Newark, NJ	Summer	4.1	3.0			
		Winter	5.9	3.3			
	Elizabeth, NJ	Summer	2.1	1.7			
		Winter	7.1	2.3			
	Camden, NJ	Summer	2.2	1.3			
		Winter	5.2	2.0			

A limited amount of rural data is presented. In some cases, total carbon (TC = OC + EC) is reported. OC concentrations must be multiplied by the average molecular weight per carbon weight to convert to mass of particulate organic compounds. The location and dates over which sampling occurred are provided. Averaging time refers to the sampling duration. Sampling method: Q – quartz fiber filter; QQ – two quartz fiber filters in series; Q+TQ – a quartz fiber filter in one port and a Teflon followed by a quartz filter in a parallel port; Imp – cascade impactor; DQQ – denuder followed by two quartz fiber filters; DQA – denuder followed by quartz fiber filter and adsorbent; VDQA – virtual impactor inlet followed by denuder, quartz filter, and adsorbent. Analysis method is reported as follows: TOR – thermal optical reflectance; TOT – thermal optical transmittance; TMO – thermal MnO$_2$ oxidation; EGA – evolved gas analysis; Th – Thermal analysis; Aeth – Aethalometer. na – data not available.

[a] Range is provided. It should be noted that samples were collected only during elevated pollution episodes and are not representative of average concentrations.
[b] Particulate OC was considered to be the sum of front and back quartz fiber filters.
[c] Sum of adsorbent and filter after correction for inlet losses and denuder efficiency.
[d] Corrected for adsorption by subtracting the Teflon-quartz back-up filter.
[e] Reported concentrations are corrected for adsorption by subtracting the quartz (TQ or QQ) back-up filter.
[f] Sampler contained two quartz fiber filters in series, but publication did not indicate whether the quartz back-up filter was subtracted to correct for adsorption.
[g] Corrected for adsorption using Micro-Orifice Uniform Deposit Impactor (MOUDI) data from a collocated sampler.

TABLE 3C-2. PARTICULATE ORGANIC COMPOUND CONCENTRATIONS (in ng C/m^3) BASED ON STUDIES PUBLISHED AFTER 1990 AT SELECTED SITES

	Rogge et al. (1993)[a] Jan-Dec 1982 (annual average) $PM_{2.1}$		**Schauer and Cass (2000)** Dec 26-28, 1995 (pollution episode) $PM_{2.5}$		**Veltkamp et al. (1996)** July 24-Aug 4, 1989 no precut	**Khwaja (1995)** October 1991 (semiurban) no precut	**Allen et al. (1997)** Summer 1994 (urban) $PM_{1.9}$	**Fraser et al. (1998)** Sept 8-9, 1993 (urban)
	Los Angeles, CA	**Pasadena, CA**	**Fresno, CA**	**Bakersfield, CA**	**Niwot Ridge, CO**	**Schenectady, NY**	**Kenmore Square, Boston, MA**	**Los Angeles Basin, CA**
n-Alkanes								
n-tricosane	6.7	5.4			19.23 (57.7)			
n-tetracosane	6.4	4.7	42.3	12.7	6.04 (21.1)			
n-pentacosane	11.2	9.5	41.2	14.2	7.77 (21.3)			
n-hexacosane	8.2	4.3	29.9	10.7	2.08 (12.7)			
n-heptacosane	6.7	5.6	25.0	10.8	5.62 (15.1)			
n-octacosane	3.1	2.5	12.3	5.24	1.26 (9.0)			
n-nonacosane	7.1	4.7	33.8	23.6	7.70 (20.6)			
n-triacontane	2.7	2.5	7.39	4.27	0.76 (4.6)			
n-hentriacontane	12.6	9.6	16.1	9.66	5.24 (17.9)			
n-dotriacontane	1.5	1.5	2.61	3.50	0.41 (2.1)			
n-tritriacontane	2.1	2.3	5.02	3.31	1.49 (5.5)			
n-tetratriacontane	0.58	0.68						
Total n-alkanes	**68.9**	**53.3**	**215.6**	**98.0**	**57.9**			
n-Alkanoic Acids								
n-nonanoic acid	6.6	5.3						
n-decanoic acid	2.0	2.4	0.711	0.164				
n-undecanoic acid	2.8	6.0						
n-dodecanoic acid	5.3	7.0	0.905	0.803				
n-tridecanoic acid	4.3	4.9	6.17	1.78				
n-tetradecanoic acid	19.7	22.2	9.42	4.01				
n-pentadecanoic acid	5.3	6.1	33.7	5.63				
n-hexadecanoic acid (palmitic acid)	140.5	127.4	166	54.4				
n-heptadecanoic acid	4.7	5.2	13.6	3.77				
n-octadecanoic acid (stearic acid)	59.2	50.0	60.0	24.1				
n-nonadecanoic acid	1.1	1.1	10.7	2.58				
n-eicosanoic acid	5.1	6.1	41.2	10.4				
n-heneicosanoic acid	2.1	2.3	20.8	6.46				

TABLE 3C-2 (cont'd). PARTICULATE ORGANIC COMPOUND CONCENTRATIONS (in ng C/m^3) BASED ON STUDIES PUBLISHED AFTER 1990 AT SELECTED SITES

	Rogge et al. (1993)[a] Jan-Dec 1982 (annual average) $PM_{2.1}$		Schauer and Cass (2000) Dec 26-28, 1995 (pollution episode) $PM_{2.5}$		Veltkamp et al. (1996) July 24-Aug 4, 1989 no precut	Khwaja (1995) October 1991 (semiurban) no precut	Allen et al. (1997) Summer 1994 (urban) $PM_{1.9}$	Fraser et al. (1998) Sept 8-9, 1993 (urban)
	Los Angeles, CA	**Pasadena, CA**	**Fresno, CA**	**Bakersfield, CA**	**Niwot Ridge, CO**	**Schenectady, NY**	**Kenmore Square, Boston, MA**	**Los Angeles Basin, CA**
n-Alkanoic Acids (cont'd)								
n-docosanoic acid	8.7	9.9	160	43.1				
n-tricosanoic acid	2.0	2.5	32.1	9.71				
n-tetracosanoic acid	11.8	16.5	205	78.0				
n-pentacosanoic acid	1.3	1.6	15.4	6.59				
n-hexacosanoic acid	5.6	9.3	174	81.3				
n-heptacosanoic acid	0.49	0.81	2.56	2.38				
n-octacosanoic acid	2.7	4.9	21.3	9.65				
n-nonacosanoic acid	0.33	0.57	1.46	2.11				
n-triacontanoic acid	1.0	2.2	4.32	5.79				
Total n-alcanoic acids	**292.6**	**294.3**	**979.3**	**352.7**				
n-Alkenoic Acids								
n-9-hexadecenoic acid			18.8	3.96				
n-9-octadecenoic acid	24.8	26.0	27.1	3.96				
n-9,12-octadecane-dienoic acid			13.6	1.83				
Total n-alkenoic acids	**24.8**	**26.0**	**59.5**	**9.75**				
n-Alkanals								
1-octanal					3.26 (14.4)			
n-nonanal	5.7	9.5	19.4	3.01	29.01 (62.8)			
n-decanal					23.58 (71.2)			
n-dodecanal					6.01 (16.4)			
n-tridecanal					6.50 (25.8)			
n-tetradecanal					9.62 (30.7)			
n-pentadecanal					12.47 (113.6)			
n-hexadecanal					17.45 (49.3)			
n-heptadecanal					24.09 (88.9)			
n-octadecanal					1.84 (11.7)			
Total n-alkanals	**5.7**	**9.5**	**19.4**	**3.01**	**133.8**			

TABLE 3C-2 (cont'd). PARTICULATE ORGANIC COMPOUND CONCENTRATIONS (in ng C/m^3) BASED ON STUDIES PUBLISHED AFTER 1990 AT SELECTED SITES

	Rogge et al. (1993)[a] Jan-Dec 1982 (annual average) $PM_{2.1}$		**Schauer and Cass (2000)** Dec 26-28, 1995 (pollution episode) $PM_{2.5}$		**Veltkamp et al. (1996)** July 24-Aug 4, 1989 no precut	**Khwaja (1995)** October 1991 (semiurban) no precut	**Allen et al. (1997)** Summer 1994 (urban) $PM_{1.9}$	**Fraser et al. (1998)** Sept 8-9, 1993 (urban)
	Los Angeles, CA	**Pasadena, CA**	**Fresno, CA**	**Bakersfield, CA**	**Niwot Ridge, CO**	**Schenectady, NY**	**Kenmore Square, Boston, MA**	**Los Angeles Basin, CA**
n-Alkanols								
1-decanol					8.66 (64.1)			
1-dodecanol					21.29 (61.7)			
1-tetradecanol					13.59 (41.4)			
1-pentadecanol					4.50 (30.1)			
1-hexadecanol					27.42 (141.1)			
Total n-alkanols					**75.5**			
Aliphatic Dicarboxylic Acids								
oxalic acid (C_2)						198 (360)		
malonic acid (propanedioic)	32.7	44.4				84 (107)		
methylmalonic acid (methylpropanedioic)			2.13	nd				
malonic acid (2-butenedioic)	0.66	1.3						
succinic acid (butanedioic)	66.5	51.2				102 (167)		
methylsuccinic acid (methylbutanedioic)	18.0	15.0	24.0	8.80				
glutaric acid (pentanedioic)	32.3	28.3	21.3	10.5				
methylglutaric acid (methylpentanedioic)	19.3	16.6						
hydroxybutanedioic acid	14.3	16.0						
adipic acid (hexanedioic)	14.1	14.1	3.39	3.07				
pimelic acid (heptanedioic)			2.22	1.03				
suberic acid (octanedioic)	3.4	4.1	4.41	13.4				
axelaic acid (nonanedioic)	29.0	22.8	19.9	8.22				
Total aliphaitc dicarboxylic acids	**230.3**	**213.8**	**77.4**	**45.0**		**384**		

TABLE 3C-2 (cont'd). PARTICULATE ORGANIC COMPOUND CONCENTRATIONS (in ng C/m^3) BASED ON STUDIES PUBLISHED AFTER 1990 AT SELECTED SITES

	Rogge et al. (1993)[a] Jan-Dec 1982 (annual average) $PM_{2.1}$		**Schauer and Cass (2000)** Dec 26-28, 1995 (pollution episode) $PM_{2.5}$		**Veltkamp et al. (1996)** July 24-Aug 4, 1989 no precut	**Khwaja (1995)** October 1991 (semiurban) no precut	**Allen et al. (1997)** Summer 1994 (urban) $PM_{1.9}$	**Fraser et al. (1998)** Sept 8-9, 1993 (urban)
	Los Angeles, CA	**Pasadena, CA**	**Fresno, CA**	**Bakersfield, CA**	**Niwot Ridge, CO**	**Schenectady, NY**	**Kenmore Square, Boston, MA**	**Los Angeles Basin, CA**
Ketocarboxylic Acids								
pyruvic acid (C_3)						59 (103)		
glyoxylic acid (C_2)						44 (68)		
Total ketocarboxylic acids						**103**		
Diterpenoid/Resin Acids								
dehydroabietic acid	23.6	22.6	98.5	8.01				
abietic acid			30.4	0.784				
13-isopropyl-5α-podocarpa-6,8,11,13-tetraen-16-oic acid	0.63	1.2						
8,15-pimaradien-18-oic acid	0.44	0.57	0.48	0.03				
pimaric acid	2.3	4.8	9.97	0.735				
isopimaric acid	1.3	2.3	127	7.95				
7-oxodehydroabietic acid	3.4	4.1	6.68	1.43				
abieta-6,8,11,13,15-pentaen-18-oic acid			11.8	2.43				
abieta-8,11,13,15-tetraen-18-oic acid			2.62	0.251				
sandaracopimaric acid	1.6	2.2	8.91	0.525				
Total diterpenoid acids	**33.3**	**37.6**	**296.4**	**22.15**				
Aromatic Polycarboxylic Acids								
1,2-benzene-dicarboxylic acid (phthalic acid)	60.0	55.7	9.16	6.78				
1,3-benzene-dicarboxylic acid	3.4	2.9	3.41	1.98				

TABLE 3C-2 (cont'd). PARTICULATE ORGANIC COMPOUND CONCENTRATIONS (in ng C/m^3) BASED ON STUDIES PUBLISHED AFTER 1990 AT SELECTED SITES

	Rogge et al. (1993)[a] Jan-Dec 1982 (annual average) $PM_{2.1}$		**Schauer and Cass (2000)** Dec 26-28, 1995 (pollution episode) $PM_{2.5}$		**Veltkamp et al. (1996)** July 24-Aug 4, 1989 no precut	**Khwaja (1995)** October 1991 (semiurban) no precut	**Allen et al. (1997)** Summer 1994 (urban) $PM_{1.9}$	**Fraser et al. (1998)** Sept 8-9, 1993 (urban)
	Los Angeles, CA	**Pasadena, CA**	**Fresno, CA**	**Bakersfield, CA**	**Niwot Ridge, CO**	**Schenectady, NY**	**Kenmore Square, Boston, MA**	**Los Angeles Basin, CA**
Aromatic Polycarboxylic Acids (cont'd)								
1,4-benzene-dicarboxylic acid	2.8	1.5	5.16	4.48				
benzene tricarboxylic acids			14.4	8.77				
4-methyl-1,2-benzenedicarboxylic acid	27.8	28.8						
1,2,4-benzene-tricarboxylic acid (trimellitic acid)	0.52	0.84						
1,3,5-benzene-tricarboxylic acid (trimesic acid)	20.6	17.2						
1,2,4,5-benzene-tetracarboxylic acid (pyromellitic acid)	0.74	0.80						
Total aromatic polycarboxylic acids	**115.9**	**107.7**	**32.1**	**22.0**				
Polycyclic Aromatic Hydrocarbons								
retene	0.07	0.06	6.02	0.563				
fluoranthene	0.15	0.13	2.52	0.553				0.07 (0.26)
acephenanthrylene			0.834	0.302				0.02 (0.05)
pyrene	0.26	0.17	3.28	0.564				0.07 (0.26)
C_1-202 MW PAH			11.7	3.80				0.07 (0.36)
C_2-202 MW PAH								0.03 (0.32)
benz[*a*]anthracene	0.29	0.25	13.8	2.49				0.15 (1.09)
cyclopenta[*cd*]pyrene	0.23	0.41	1.90	0.496				0.14 (1.02)
benzo[*ghi*]-fluoranthene	0.39	0.30	6.05	1.25				0.20 (0.97)
C_1-226 MW PAH			10.1	1.48				0.14 (0.97)
chrysene/triphenyline	0.61	0.43	7.70	1.50				0.34 (1.62)

TABLE 3C-2 (cont'd). PARTICULATE ORGANIC COMPOUND CONCENTRATIONS (in ng C/m^3) BASED ON STUDIES PUBLISHED AFTER 1990 AT SELECTED SITES

	Rogge et al. (1993)[a]		**Schauer and Cass (2000)**		**Veltkamp et al. (1996)**	**Khwaja (1995)**	**Allen et al. (1997)**	**Fraser et al. (1998)**
	Jan-Dec 1982		Dec 26-28, 1995		July 24-Aug 4, 1989	October 1991	Summer 1994	Sept 8-9, 1993
	(annual average)		(pollution episode)		no precut	(semiurban)	(urban)	(urban)
	$PM_{2.1}$		$PM_{2.5}$			no precut	$PM_{1.9}$	
	Los Angeles, CA	**Pasadena, CA**	**Fresno, CA**	**Bakersfield, CA**	**Niwot Ridge, CO**	**Schenectady, NY**	**Kenmore Square, Boston, MA**	**Los Angeles Basin, CA**
Polycyclic Aromatic Hydrocarbons (cont'd)								
C_1-228 MW PAH			17.6	5.35				0.34 (2.16)
C_2-228 MW PAH								0.09 (0.46)
benz[*e*]acephen-anthrylene								0.20 (1.00)
benzo[*k*]fluoranthene	1.15	1.20	8.69	2.13				0.22 (1.07)
benzo[*b*]fluoranthene	1.23	0.85	10.7	2.48				
benzo[*j*]fluoranthene			3.62	0.499				0.02 (0.10)
benzo[*e*]pyrene	0.97	0.93	7.20	1.98				0.22 (1.00)
benzo[*a*]pyrene	0.42	0.44	8.23	1.77				0.14 (0.80)
perylene			1.50	0.246				0.05 (0.51)
methyl-substituted 252 MW PAH								0.10 (0.88)
indeno[*1,2,3-cd*]-pyrene	0.37	0.42	6.84	2.56				0.29 (1.38)
indeno[*1,2,3-cd*]-fluoranthene	1.05	1.09	1.36	0.764				0.10 (0.46)
benzo[*ghi*]perylene	4.47	4.43	9.75	3.49				0.77 (4.23)
anthanthrene			0.180	0.131				
coronene								
Total polycyclic aromatic hydrocarbons	**11.66**	**11.10**	**139.57**	**34.40**				**3.77**
Oxygenated PAHs/ Polycyclic Aromatic Ketones/Quinones								
1,4-naphthoquinone								
1-acenaphthenone							0.26	
9-fluorenone							2.07	0.29 (1.04)
1,8-naphthalic anhydride							1.77	0.41 (1.65)
phenanthrenequinone							0.43	
phenalen-9-one								0.53 (2.23)
anthracene-9,10-dione								0.36 (1.14)
methylanthracene-9,10-dione								0.09 (0.24)
11H-benzo[*a*]fluoren-11-one							1.03	

TABLE 3C-2 (cont'd). PARTICULATE ORGANIC COMPOUND CONCENTRATIONS (in ng C/m^3) BASED ON STUDIES PUBLISHED AFTER 1990 AT SELECTED SITES

	Rogge et al. (1993)[a] Jan-Dec 1982 (annual average) $PM_{2.1}$		**Schauer and Cass (2000)** Dec 26-28, 1995 (pollution episode) $PM_{2.5}$		**Veltkamp et al. (1996)** July 24-Aug 4, 1989 no precut	**Khwaja (1995)** October 1991 (semiurban) no precut	**Allen et al. (1997)** Summer 1994 (urban) $PM_{1.9}$	**Fraser et al. (1998)** Sept 8-9, 1993 (urban)
	Los Angeles, CA	**Pasadena, CA**	**Fresno, CA**	**Bakersfield, CA**	**Niwot Ridge, CO**	**Schenectady, NY**	**Kenmore Square, Boston, MA**	**Los Angeles Basin, CA**
Oxygenated PAHs/ Polycyclic Aromatic Ketones/Quinones (cont'd)								
7H-benzo[*c*]fluoren-7-one							0.37	
11H-benzo[*b*]fluoren-11-one							0.85	
1H-phenalen-1-one			7.96	0.588				
benzanthrone							1.18	
5,12-naphthacene-quinone							0.32	
7H-benz[*de*]-anthracen-7-one	0.81	0.84	7.80	1.48				
benz[*de*]anthracene-7-dione								0.20 (1.00)
benz[*a*]anthracene-7,12-dione	0.21	0.25						0.09 (0.31)
cyclopenta[*def*]phen-anthrone								0.05 (0.14)
benzo[*cd*]pyren-6-one	0.80	1.24						0.54 (2.47)
6H-benzo[*cd*]pyrene-6-one							1.34	
benzo[*a*]pyrene-6,12-dione							0.096	
Total polycyclic aromatic ketones/quinones	**1.82**	**2.33**	**15.76**	**2.07**			**9.72**	**2.56**
Steroids								
cholesterol	**nd**	**1.9**						
Substituted Phenols								
p-benzenediol			3.46	nd				
m-benzenediol			7.59	nd				
hydroxybenzaldehydes			2.64	0.604				
Total substituted phenols			**13.69**	**0.604**				

TABLE 3C-2 (cont'd). PARTICULATE ORGANIC COMPOUND CONCENTRATIONS (in ng C/m^3) BASED ON STUDIES PUBLISHED AFTER 1990 AT SELECTED SITES

	Rogge et al. (1993)[a] Jan-Dec 1982 (annual average) PM$_{2.1}$		**Schauer and Cass (2000)** Dec 26-28, 1995 (pollution episode) PM$_{2.5}$		**Veltkamp et al. (1996)** July 24-Aug 4, 1989 no precut	**Khwaja (1995)** October 1991 (semiurban) no precut	**Allen et al. (1997)** Summer 1994 (urban) PM$_{1.9}$	**Fraser et al. (1998)** Sept 8-9, 1993 (urban)
	Los Angeles, CA	**Pasadena, CA**	**Fresno, CA**	**Bakersfield, CA**	**Niwot Ridge, CO**	**Schenectady, NY**	**Kenmore Square, Boston, MA**	**Los Angeles Basin, CA**
Guaiacol and Substituted Guaiacols								
guaiacol			0.889	0.832				
4-methylguaiacol			0.606	0.387				
trans-isoeugenol			1.45	1.04				
vanillin			26.8	6.05				
acetovanillone			3.23	0.705				
guaiacyl acetone			10.8	4.29				
coniferyl aldehyde			47.0	nd				
Total guaiacol and substituted guaiacols			**90.78**	**13.30**				
Syringol and Substituted Syringols								
syringol			1.16	0.845				
4-methylsyringol			1.72	1.77				
4-ethylsyringol			2.28	2.39				
4-propylsyringol			0.871	nd				
4-propenylsyringol			4.38	1.40				
syringaldehyde			135	44.5				
acetosyringone			171	55.7				
acetonylsyringol			406	68.1				
propionylsyringol			32.1	16.2				
butyrylsyringol			15.3	6.18				
sinapyl aldehyde			15.9					
Total syringol and substituted syringols			**785.7**	**197.1**				
Sugars								
levoglucosan			7590	1100				
other sugars			1070	171				
Total sugars			**8660**	**1271**				

TABLE 3C-2 (cont'd). PARTICULATE ORGANIC COMPOUND CONCENTRATIONS (in ng C/m^3) BASED ON STUDIES PUBLISHED AFTER 1990 AT SELECTED SITES

	Rogge et al. (1993)[a] Jan-Dec 1982 (annual average) PM$_{2.1}$		**Schauer and Cass (2000)** Dec 26-28, 1995 (pollution episode) PM$_{2.5}$		**Veltkamp et al. (1996)** July 24-Aug 4, 1989 no precut	**Khwaja (1995)** October 1991 (semiurban) no precut	**Allen et al. (1997)** Summer 1994 (urban) PM$_{1.9}$	**Fraser et al. (1998)** Sept 8-9, 1993 (urban)
	Los Angeles, CA	**Pasadena, CA**	**Fresno, CA**	**Bakersfield, CA**	**Niwot Ridge, CO**	**Schenectady, NY**	**Kenmore Square, Boston, MA**	**Los Angeles Basin, CA**
Other Compounds								
divanillyl			19.4	3.18				
divanillyl methane			2.39	nd				
vanillylmethylguaiacol			3.24	0.568				
Total other			**25.0**	**3.75**				
N-Containing Compounds								
3-methoxypyridine	0.86	1.4						
isoquinoline	1.1	1.1						
1-methoxypyridine	0.27	0.24						
1,2-dimethoxy-4-nitro-benzene	1.8	3.9						
dihydroxynitrobenzene								1.62 (10.52)
Total N-containing compounds	**4.03**	**6.64**						**1.62**
Total Quantified Organic Compound Mass	**789**	**764**	**11410**	**2075**	**267**	**487**	**10**	**8**
Total Organic Compound Mass			**55700**	**18700**				
Percent of Organic Mass Quantified	**8-15% (a)**	**8-15% (a)**	**20%**	**11%**		**<3%**		
Percent of Organic Mass Extractable and Elutable	**45-60% (a)**	**45-60% (a)**	**30%**	**21%**				

Mean values are provided with maximum concentrations in parentheses.

[a] Rogge et al. (1993) summarized these percentages for all four Los Angeles Basin sampling sites (West LA, Downtown LA, Pasadena, and Rubidoux). Only Downtown LA and Pasadena data are shown here.

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APPENDIX 3D

Composition of Particulate Matter Source Emissions

This appendix includes discussions of the elemental composition of emissions from various source categories discussed in Table 3-8. Discussions in this appendix incorporate material dealing with the inorganic components of source emissions from Chapter 5 of the 1996 PM AQCD (U. S. Environmental Protection Agency, 1996), updates to that material, and material describing the composition of organic components in source emissions. Primary emphasis is placed in the discussions on the composition of $PM_{2.5}$ sources.

Soil and Fugitive Dust

The compositions of soils and average crustal material are shown in Table 3D-1 (adapted from Warneck, 1988). Two entries are shown as representations of average crustal material. Differences from the mean soil composition shown can result from local geology and climate. Major elements in both soil and crustal profiles are Si, Al, and Fe, which are found in the form of various minerals. In addition, organic matter constitutes a few percent, on average, of soils. In general, the soil profile is similar to the crustal profiles, except for the depletion of soluble elements such as Ca, Mg, Na, and K. It should be noted that the composition of soils from specific locations can vary considerably from these global averages, especially for elements like Ca, Mg, Na, and K.

Fugitive dust emissions arise from paved and unpaved roads, building construction and demolition, parking lots, mining operations, storage piles, feed lots, grain handling, and agricultural tilling, in addition to wind erosion. Figure 3D-1 shows examples of size distributions in dust from paved and unpaved roads, agricultural soil, sand and gravel, and alkaline lake bed sediments, which were measured in a laboratory resuspension chamber as part of a study in California (Chow et al., 1994). This figure shows substantial variation in particle size among some of these fugitive dust sources. The $PM_{1.0}$ abundance (6.9%) in the total suspended PM (TSP) from alkaline lake bed dust is twice its abundance in paved and unpaved road dust. Approximately 10% of the TSP is in the $PM_{2.5}$ fraction and approximately 50% of

TABLE 3D-1. AVERAGE ABUNDANCES OF MAJOR ELEMENTS IN SOIL AND CRUSTAL ROCK

	Elemental Abundances (ppmw)		
	Soil	Crustal Rock	
Element	(1)	(2)	(3)
Si	330,000	277,200	311,000
Al	71,300	81,300	77,400
Fe	38,000	50,000	34,300
Ca	13,700	36,300	25,700
Mg	6,300	20,900	33,000
Na	6,300	28,300	31,900
K	13,600	25,900	29,500
Ti	4,600	4,400	4,400
Mn	850	950	670
Cr	200	100	48
V	100	135	98
Co	8	25	12

Source: (1) Vinogradov (1959); (2) Mason (1966); (3) Turekian (1971), Model A; as quoted in Warneck (1988).

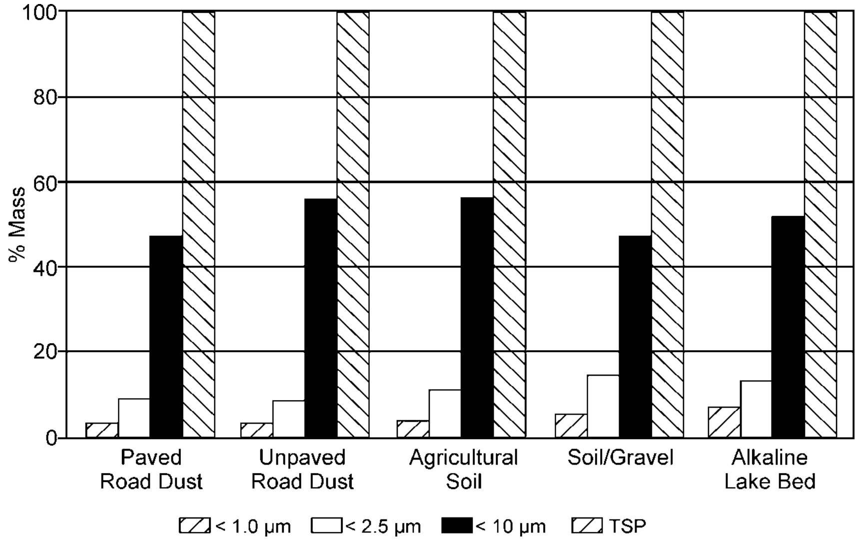

Figure 3D-1. Size distribution of particles generated in a laboratory resuspension chamber.

Source: Chow et al. (1994).

TSP is in the PM_{10} fraction. The sand/gravel dust sample shows that 65% of the mass is in particles larger than the PM_{10} fraction. The $PM_{2.5}$ fraction of TSP is approximately 30 to 40% higher in alkaline lake beds and sand/gravel than in the other soil types. The tests were performed after sieving and with a short (< 1 min) waiting period prior to sampling. It is expected that the fraction of $PM_{1.0}$ and $PM_{2.5}$ would increase with distance from a fugitive dust emitter, as the larger particles deposit to the surface faster than do the smaller particles.

The size distribution of samples of paved road dust obtained from a source characterization study in California is shown in Figure 3D-2. As might be expected, most of the emissions are in the coarse size mode. The chemical composition of paved road dust obtained in Denver, CO, during the winter of 1987-1988 is shown in Figure 3D-3. The chemical composition of paved road dust consists of a complex mixture of particulate matter from a wide variety of sources. Hopke et al. (1980) found that the inorganic composition of urban roadway dust in samples from Urbana, IL, could be described in terms of contributions from natural soil, automobile exhaust, rust, tire wear, and salt. Automobile contributions arose from exhaust emissions enriched in Pb; from rust as Fe; tire wear particles enriched in Zn; brake linings enriched in Cr, Ba, and Mn; and cement particles derived from roadways by abrasion. In addition to organic compounds from combustion and secondary sources, road dust also contains biological material such as pollen and fungal spores.

Very limited data exist for characterizing the composition in organic compounds found in resuspended paved road dust and soil dust. The only reported measurements are from Rogge et al. (1993a) and Schauer and Cass (2000), which consist of data for the fine particle fraction. The resuspended road dust sample analyzed by Rogge et al. (1993a) was collected in Pasadena, CA, during May of 1988. The sample analyzed by Schauer and Cass (2000) is a composite sample collected at several sites in the Central Valley of California in 1995. In both cases, road dust samples were resuspended in the laboratory. Samples were drawn through a $PM_{2.0}$ cyclone upstream of the collection substrate to remove particles with aerodynamic diameters greater than 2.0 μm. It is unclear if these samples are representative of road dust in other locations of the United States. Table 3D-2 summarizes the organic compounds measured in these road dust samples.

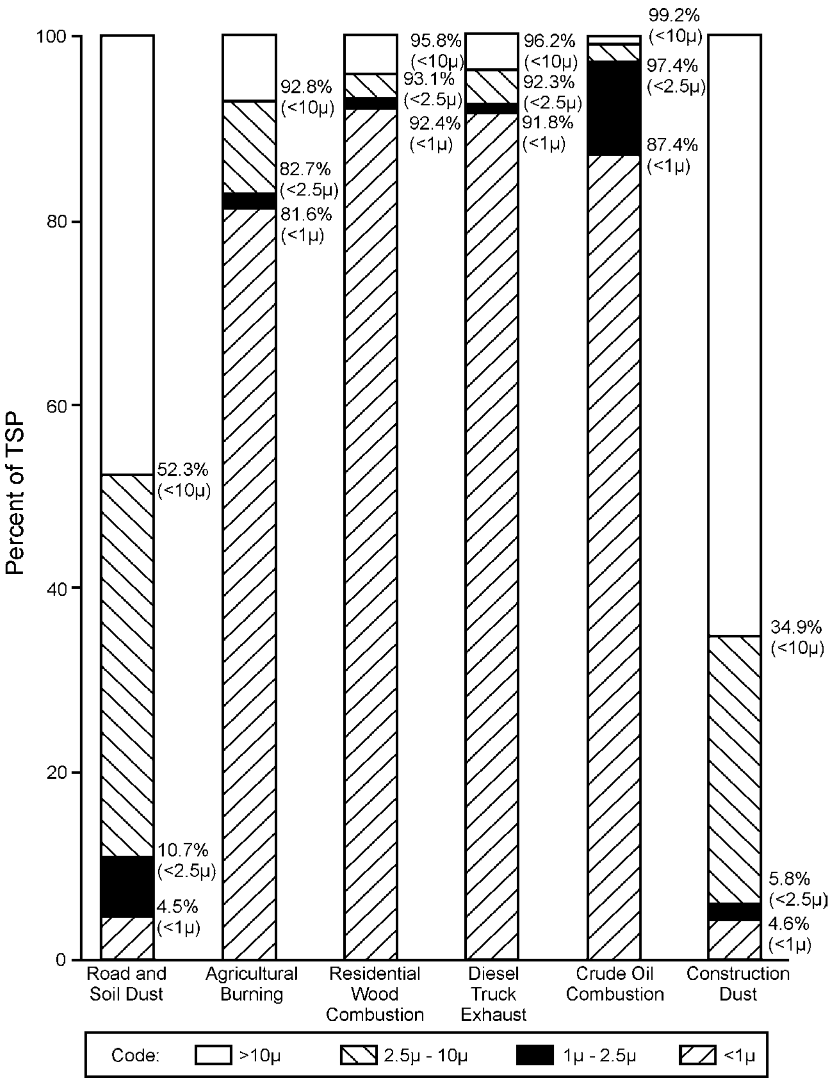

Figure 3D-2. Size distribution of California source emissions, 1986.

Source: Houck et al. (1989, 1990).

Stationary Sources

The elemental composition of primary particulate matter emitted in the fine fraction from a variety of power plants and industries in the Philadelphia area is shown in Table 3D-3 as a representative example of emissions from stationary fossil combustion sources (Olmez et al., 1988). Entries for the coal fired power plant show that Si and Al, followed by sulfate, are the major primary constituents produced by coal combustion; whereas fractional abundances of elemental carbon were much lower and organic carbon species were not detected. Sulfate is the

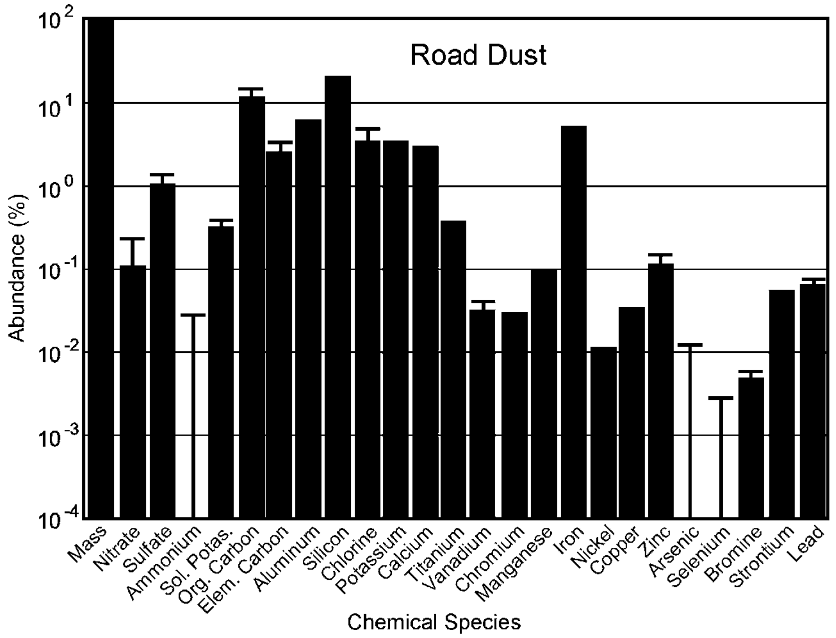

Figure 3D-3. Chemical abundances for $PM_{2.5}$ emissions from paved road dust in Denver, CO. Solid bars represent fractional abundances, and the error bars represent variability in species abundances. Error bars represent detection limits when there are no solid bars.

Source: Watson and Chow (1994).

TABLE 3D-2. SUMMARY OF PARTICLE-PHASE ORGANIC COMPOUNDS PRESENT IN FINE PARTICLE ROAD DUST SAMPLE

Source	Compound Class	Contribution to Particulate Mass (%)	Dominant Contributors to Emissions of Compound Class
Pasadena Road Dust (Rogge et al., 1993a)	n-Alkanes	0.13	C_{17}, C_{19}, C_{21}
	n-Alkanoic acids	0.37	Palmitic acid and stearic acid
	n-Alkenoic acids	0.028	Oleic acid and linoleic Acid
	Petroleum biomarkers	0.017	Hopanes and steranes
	PAH	0.0059	No dominant compounds
	n-Alkanals	0.046	Octacosanol and triacontanal
	n-Alkanols	0.021	Hexacosanol and octacosanol
San Joaquin Valley Road Dust (Schauer and Cass, 2000)	n-Alkanes	0.023	No dominant compounds
	n-Alkanoic acids	0.23	Palmitic acid and stearic acid
	n-Alkenoic acids	0.095	Oleic acid, linoleic acid, and hexadecenoic acid

TABLE 3D-3. COMPOSITION OF FINE PARTICLES RELEASED BY VARIOUS STATIONARY SOURCES IN THE PHILADELPHIA AREA

Species (Units)	Eddystone Coal-Fired Power Plant	N	Oil-Fired Power Plants				Secondary Al Plant	N	Fluid Cat. Cracker	N	Municipal Incinerator	N
			Eddystone	N	Schuylkill	N						
C-v (%)	ND		2.7 ± 1.2	3	0.75 ± 0.63	4	1.6 ± 1.5	2	ND		0.57 ± 0.26	4
C-e (%)	0.89 ± 0.12	3	7.7 ± 1.5	3	0.22 ± 0.17	4	0.18 ± 0.10	2	0.16 ± 0.05	3	3.5 ± 0.2	4
NH_4 (%)	1.89 ± 0.19	3	3.5 ± 1.6	3	3.7 ± 1.7	4	2.2 ± 0.9	2	0.43 ± 0.22	3	0.36 ± 0.07	4
Na (%)	0.31 ± 0.03	3	3.0 ± 0.8	3	3.3 ± 0.8	3	16.3 ± 0.8	1	0.38 ± 0.05	3	6.6 ± 3.5	3
Al (%)	14 ± 2	3	0.45 ± 0.09	3	0.94 ± 0.08	3	1.74 ± 0.09	1	6.8 ± 1.2	3	0.25 ± 0.10	3
Si (%)	21.8 ± 1.6	9	1.9 ± 0.6	9	2.6 ± 0.4	11	3.1 ± 2.2	2	9.8 ± 20.0	9	1.7 ± 0.3	10
P (%)	0.62 ± 0.10	9	1.5 ± 0.4	9	1.0 ± 0.2	11	0.45 ± 0.27	2	ND		0.63 ± 0.12	10
S (%)	3.4 ± 0.6	9	11 ± 2	9	13 ± 1	11	3 ± 4	2	4.2 ± 12.6	9	2.9 ± 0.8	10
SO_4 (%)	11.9 ± 1.2	3	40 ± 4	3	45 ± 7	4	5.9 ± 2	2	38 ± 4	3	6.8 ± 2.3	4
Cl (%)	0.022 ± 0.11	3	0.019 ± 0.009	2	ND		21 ± 4	1	ND		29 ± 5	3
K (%)	1.20 ± 0.09	9	0.16 ± 0.05	9	0.21 ± 0.03	11	10.9 ± 1.5	2	0.031 ± 0.005	9	7.6 ± 2.3	10
Ca (%)	1.4 ± 0.5	3	3.6 ± 1.0	3	2.3 ± 1.0	3	0.12 ± 0.09	2	0.030 ± 0.004	9	0.23 ± 0.10	10
Sc (ppm)	42 ± 2	3	0.17 ± 0.02	3	0.47 ± 0.02	3	0.092 ± 0.039	1	2.7 ± 0.4	3	0.11 ± 0.02	1
Ti (%)	1.1 ± 0.2	3	0.040 ± 0.044	9	0.12 ± 0.02	11	0.024 ± 0.003	2	0.38 ± 0.1	3	0.030 ± 0.015	10
V (ppm)	550 ± 170	3	11500 ± 3000	3	20,000 ± 3000	3	36 ± 7	1	250 ± 70	3	8.6 ± 5.3	2
Cr (ppm)	390 ± 120	3	235 ± 10	3	230 ± 70	3	410 ± 20	1	59 ± 8	3	99 ± 31	3
Mn (ppm)	290 ± 15	3	380 ± 40	3	210 ± 50	3	120 ± 15	1	14 ± 3	3	165 ± 40	3
Fe (%)	7.6 ± 0.4	3	1.6 ± 0.2	3	1.7 ± 0.4	3	0.31 ± 0.02	1	0.20 ± 0.03	9	0.22 ± 0.05	3
Co (ppm)	93 ± 10	3	790 ± 150	3	1100 ± 200	3	13 ± 2	1	15 ± 2	3	3.7 ± 0.8	3
Ni (ppm)	380 ± 50	9	15000 ± 5000	9	19000 ± 2000	11	300 ± 100	2	220 ± 30	9	290 ± 40	10

TABLE 3D-3 (cont'd). COMPOSITION OF FINE PARTICLES RELEASED BY VARIOUS STATIONARY SOURCES IN THE PHILADELPHIA AREA

Species (units)	Eddystone Coal-Fired Power Plant	N	Oil-Fired Power Plants: Eddystone	N	Oil-Fired Power Plants: Schuylkill	N	Secondary Al Plant	N	Fluid Cat. Cracker	N	Municipal Incinerator	N
Cu (ppm)	290 ± 20	9	980 ± 320	9	1100 ± 500	11	450 ± 200	2	14 ± 8	9	1300 ± 500	3
Zn (%)	0.041 ± 0.005	3	1.3 ± 0.3	3	0.78 ± 0.30	3	0.079 ± 0.006	1	0.0026 ± 0.0007	3	10.4 ± 0.5	3
As (ppm)	640 ± 80	3	33 ± 6	1	50 ± 16	3	15 ± 6	1	ND		64 ± 34	3
Se (ppm)	250 ± 20	3	26 ± 9	3	23 ± 7	3	66 ± 3	1	15 ± 1	3	42 ± 16	3
Br (ppm)	35 ± 8	3	90 ± 60	9	45 ± 17	11	630 ± 70	2	5.6 ± 1.8	9	2300 ± 800	10
Rb (ppm)	190 ± 80	1	ND		ND		97 ± 38	1	ND		230 ± 50	2
Sr (ppm)	1290 ± 60	9	160 ± 50	9	280 ± 70	11	ND		36 ± 6	9	87 ± 14	10
Zr (ppm)	490 ± 190	9	140 ± 180	9	100 ± 120	11	ND		130 ± 50	2	ND	
Mo (ppm)	170 ± 60	2	930 ± 210	3	1500 ± 300	3	ND		ND		240 ± 130	10
Ag (ppm)	ND		ND		ND		ND		ND		71 ± 15	3
Cd (ppm)	ND		ND		ND		ND		ND		1200 ± 700	3
In (ppm)	0.71 ± 0.04	2	ND		ND		ND		ND		4.9 ± 1.4	3
Sn (ppm)	ND		320 ± 230	9	200 ± 80	11	550 ± 540	2	ND		6700 ± 1900	10
Sb (ppm)	[a]		370 ± 410	3	1020 ± 90	3	6100 ± 300	1	7.7 ± 1.5	3	1300 ± 1000	3
Cs (ppm)	9.2 ± 0.9	2	ND		ND		ND		ND		5.9 ± 3.0	3
Ba (ppm)	ND		1960 ± 100	3	2000 ± 500	3	ND		290 ± 90	2	ND	
La (ppm)	120 ± 10	3	130 ± 30	3	450 ± 30	3	19 ± 2	1	3300 ± 500	3	1.1 ± 0.5	1
Ce (ppm)	180 ± 10	2	89 ± 23	3	360 ± 20	3	ND		2700 ± 400	3	ND	
Nd (ppm)	80 ± 26	3	28 ± 5	2	230 ± 20	3	ND		1800 ± 250	3	ND	
Sm (ppm)	23 ± 2	3	3.7 ± 0.7	3	20.5 ± 1.5	3	ND		170 ± 20	3	ND	

TABLE 3D-3 (cont'd). COMPOSITION OF FINE PARTICLES RELEASED BY VARIOUS STATIONARY SOURCES IN THE PHILADELPHIA AREA

Species (units)	Eddystone Coal-Fired Power Plant	N	Oil-Fired Power Plants				Secondary Al Plant	N	Fluid Cat. Cracker	N	Municipal Incinerator	N
			Eddystone	N	Schuylkill	N						
Eu (ppm)	5.1 ± 0.5	3	ND		0.65 ± 0.23	3	ND		4.9 ± 0.7	3	ND	
Gd (ppm)	ND		ND		ND		ND		71 ± 10	3	ND	
Tb (ppm)	3.3 ± 0.3	3	ND		0.90 ± 0.29	3	ND		8.9 ± 1.3	3	ND	
Yb (ppm)	10.3 ± 0.5	1	ND		ND		ND		3.7 ± 0.4	3	ND	
Lu (ppm)	ND		ND		ND		ND		0.59 ± 0.17	3	ND	
Hf (ppm)	5.8 ± 0.8	3	0.39 ± 0.07	1	ND		ND		0.99 ± 0.08	3	ND	
Ta (ppm)	ND		ND		ND		ND		0.56 ± 0.10	3	ND	
W (ppm)	20 ± 8	1	60 ± 5	2	ND		ND		ND		ND	
Au (ppm)	ND		0.054 ± 0.017	2	ND		ND		ND		0.56 ± 0.27	3
Pb (%)	0.041 ± 0.004	9	1.8 ± 0.6	9	1.0 ± 0.2	11	0.081 ± 0.014	2	0.0091 ± 0.0021	9	5.8 ± 1.2	10
Th (ppm)	24 ± 2	3	1.9 ± 0.5	2	ND		ND		6.2 ± 0.7	3	ND	
% mass	24 ± 2	6	93.5 ± 2.5	6	96 ± 2	6	81 ± 10	2	97 ± 2	7	89 ± 2	7

[a] Omitted because of sample contamination.

N = Number of samples.
ND = Not detected.
The "% mass" entries give the average percentage of the total emitted mass found in the fine fraction.
1 ppm = 10^{-4}%

Source: Adapted from Olmez et al. (1988).

major particulate constituent released by the oil fired power plants examined in this study; and, again, elemental and organic carbon are not among the major species emitted. Olmez et al. (1988) also compared their results to a number of similar studies and concluded that their data should have much wider applicability to receptor model studies in other areas with some of the same source types. The high temperature of combustion in power plants results in the almost complete oxidation of the carbon in the fuel to CO_2 and very small amounts of CO. Combustion conditions in smaller boilers and furnaces allow the emission of unburned carbon and sulfur in more reduced forms such as thiophenes and inorganic sulfides. A number of trace elements are greatly enriched over crustal abundances in different fuels, such as Se in coal and V, Zn, and Ni in oil. In fact, the higher V content of the fuel oil than in coal could help account for the higher sulfate seen in the profiles from the oil-fired power plant compared to the coal-fired power plant because V at combustion temperatures found in power plants is known to catalyze the oxidation of reduced sulfur species. During combustion at lower temperatures, the emission of reduced sulfur species also occurs. For example, Huffman et al. (2000) identified sulfur species emitted by the combustion of several residual fuels oil (RFO) in a fire tube package boiler that is meant to simulate conditions in small institutional and industrial boilers. They found that sulfur was emitted not only as sulfate (26 to 84%), but as thiophenes (13 to 39%) with smaller amounts of sulfides and elemental S. They also found that Ni, V, Fe, Cu, Zn, and Pb are present mainly as sulfates in emissions. Linak et al. (2000) found, when burning RFO, that the fire tube package boiler produced particles with a bimodal size distribution in which about 0.2% of the mass was associated with particles smaller than 0.1 μm AD, with the rest of the mass lying between 0.5 and 100 μm. Miller et al. (1998) found that larger particles consisted mainly of cenospheric carbon; whereas trace metals and sulfates were found concentrated in the smaller particles in a fire tube package boiler. In contrast, when RFO was burning in a refractory-lined combustor that is meant to simulate combustion conditions in a large utility residual oil fired boiler, Linak et al. (2000) found that particles were distributed essentially unimodally, with a mean diameter of about 0.1 μm.

Apart from emissions in the combustion of fossil fuels, trace elements are emitted as the result of various industrial processes such as steel and iron manufacturing and nonferrous metal production (e.g., for Pb, Cu, Ni, Zn, and Cd). As may be expected, emissions factors for the various trace elements are highly source-specific (Nriagu and Pacyna, 1988). Inspection of

Table 3D-3 reveals that the emissions from the catalytic cracker and the oil-fired power plant are greatly enriched in rare-earth elements (such as La) compared to other sources.

Emissions from municipal waste incinerators are heavily enriched in Cl, arising mainly from the combustion of plastics and metals that form volatile chlorides. The metals can originate from cans or other metallic objects, and some metals such as Zn and Cd are also additives in plastics or rubber. Many elements such as S, Cl, Zn, Br, Ag, Cd, Sn, In, Sb, and Pb are enormously enriched compared to their crustal abundances. A comparison of the trace elemental composition of incinerator emissions in Philadelphia, PA (shown in Table 3D-3) with those in Washington DC, and Chicago, IL (Olmez et al., 1988) shows agreement for most constituents to within less than a factor of two.

Very limited data exist for characterizing the chemical composition of organic compounds present in particulate emissions from industrial-scale stationary fuel combustion. Oros and Simoneit (2000) have presented the abundance and distribution of organic constituents in coal smokes that have been burned under laboratory conditions. This work provides the basis for further investigation addressing the emissions of coal fired boilers.

Rogge et al. (1997a) measured the composition of the organic constituents in the particulate matter emissions from a 50 billion kj/h boiler that was operating at 60% capacity and was burning number 2 distillate fuel oil. The fine carbon particulate matter emissions from this boiler over five tests were composed of an average of 14% organic carbon and 86% elemental carbon (Hildemann et al., 1991). Significant variability in the distribution of organic compounds present in the emissions from two separate tests was observed. Most of the identified organic mass consisted of n-alkanonic acids, aromatic acids, n-alkanes, PAH, oxygeanted PAH, and chlorinated compounds. It is unclear if these emissions are representative of typical fuel oil combustion units in the United States. Rogge et al. (1997b) measured the composition of hot asphalt roofing tar pots, and Rogge et al. (1993b) measured the composition of emissions from home appliances that use natural gas.

Motor Vehicles

Exhaust emissions of particulate matter from gasoline powered motor vehicles and diesel powered vehicles have changed significantly over the past 25 years (Sawyer and Johnson, 1995; Cadle et al., 1999). These changes have resulted from reformulation of fuels, the wide application of exhaust-gas treatment in gasoline-powered motor vehicles, and changes in engine design and operation. Because of these evolving tailpipe emissions, along with the wide variability of emissions between vehicles of the same class (Hildemann et al., 1991; Cadle et al., 1997; Sagebiel et al., 1997; Yanowitz et al., 2000), well-defined average emissions profiles for the major classes of motor vehicles have not been established. Two sampling strategies have been employed to obtain motor vehicle emissions profiles: (1) the measurement of exhaust emissions from vehicles operating on dynamometers and (2) the measurement of integrated emissions of motor vehicles driving through roadway tunnels. Dynamometer testing can be used to measure vehicle emissions operating over an integrated driving cycle and allows the measurement of emissions from individual vehicles. However, dynamometer testing requires considerable resources and usually precludes testing a very large number of vehicles. In contrast, a large number of vehicles can be readily sampled in tunnels; however, vehicles driving through tunnels operate over limited driving conditions, and the measurements represent contributions from a large number of vehicle types. As a result, except in a few cases, tunnel tests have not been effective at developing chemically speciated particulate matter emissions profiles for individual motor vehicle classes. Rather, several studies have measured the contribution of both organic and elemental carbon to the particulate matter emissions from different classes of motor vehicles operating on chassis dynamometers.

The principal components emitted by diesel and gasoline fueled vehicles are organic carbon (OC) and elemental carbon (EC) as shown in Tables 3D-4a and 4b. As can be seen, the variability among entries for an individual fuel type is large and overlaps that found between different fuel types. On average, the abundance of elemental carbon is larger than that of organic carbon in the exhaust of diesel vehicles; whereas organic carbon is the dominant species in the exhaust of gasoline fueled vehicles. Per vehicle mile, total carbon emissions from light and heavy duty diesel vehicles can range from 1 to 2 orders of magnitude higher than those from gasoline vehicles.

As might be expected, most of the PM emitted by motor vehicles is in the $PM_{2.5}$ size range. Particles in diesel exhaust are typically trimodal (consisting of a nuclei mode, an accumulation mode, and a coarse mode) and are log-normal in form (Kittelson, 1998). More than 90% of the total number of particles are in the nuclei mode, which contains only about 1 to 20% of the particle mass with a mass median diameter of about 0.02 μm; whereas the accumulation mode (with a mass median diameter of about 0.25 μm) contains most of the mass with a smaller

TABLE 3D-4a. ORGANIC AND ELEMENTAL CARBON FRACTIONS OF DIESEL AND GASOLINE ENGINE PARTICULATE MATTER EXHAUST

	Organic Carbon	Elemental Carbon
Heavy-duty diesel engines[a]	19 ± 8%	75 ± 10%
Heavy-duty diesel engines (SPECIATE)[b]	21 - 36%	52 - 54%
Light-duty diesel engines[c]	30 ± 9%	61 ± 16%
Light-duty diesel engines (SPECIATE)[b]	22 - 43%	51 - 64%
Gasoline engines (hot stabilized)[a]	56 ± 11%	25 ± 15%
Gasoline engines ("smoker" and "high emitter")[a,c]	76 ± 10%	7 ± 6%
Gasoline engines (cold start)[a]	46 ± 14%	42 ± 14%

[a] Fujita et al. (1998) and Watson et al. (1998).
[b] SPECIATE database (U.S. Environmental Protection Agency, 1999).
[c] Norbeck et al. (1998).

Source: U.S. Environmental Protection Agency (2002).

fraction (5 to 20%) contained in the coarse mode. Kerminin et al. (1997), Bagley et al. (1998), and Kleeman et al. (2000) also have shown that gasoline and diesel fueled vehicles produce particles that are mostly less than 2.0 μm in diameter. Cadle et al. (1999) found that 91% of PM emitted by in-use gasoline vehicles in the Denver area was in the $PM_{2.5}$ size range, which increased to 97% for "smokers" (i.e., light-duty vehicles with visible smoke emitted from their tailpipes) and 98% for light-duty diesels. Durbin et al. (1999) found that about 92% of the PM was smaller than 2.5 μm for smokers and diesels. The mass median diameter of the PM emitted by the gasoline vehicles sampled by Cadle et al. (1999) was about 0.12 μm and increased to 0.18 μm for smokers and diesels. Corresponding average emissions rates of $PM_{2.5}$ found by Cadle et al. (1999) were 552 mg/mile for diesels; 222 mg/mile for gasoline smokers; and 38 mg/mile for other gasoline vehicles. The values for gasoline smokers and for diesels appear to be somewhat lower than those given in Table 3D-5; whereas the value for other gasoline vehicles falls in the range given for low and medium gasoline vehicle emissions.

Examples of data for the trace elemental composition of the emissions from a number of vehicle classes obtained December 1997 in Colorado, as part of the North Frontal Range Air Quality Study (NFRAQS), are shown in Table 3D-5. As can be seen from Table 3D-5, emissions of total carbon (TC), which is equal to the sum of organic carbon (OC) and elemental

TABLE 3D-4b. CONTRIBUTION OF ORGANIC CARBON TO PARTICULATE MATTER CARBON EMISSIONS IN MOTOR VEHICLE EXHAUST COLLECTED FROM VEHICLES OPERATED ON CHASSIS DYNAMOMETERS

	Year of Tests	Test Cycle	Number of Vehicles	OC % of Total Carbon	Notes
GASOLINE POWERED VEHICLES					
Light-duty vehicles	1996-97	FTP	195[a]	70	A
High-CO/VOC-emitting smokers	1994	IM-240	7	91	B
High-CO/VOC-emitting nonsmokers	1994	IM-240	15	76	B
Catalyst-equipped vehicles	Mid-1980s	FTP	7	69	C
Noncatalyst vehicles	Mid-1980s	FTP	6	89	C
DIESEL VEHICLES					
Light-duty diesel vehicles	1996-1997	FTP	195[a]	40	A
Medium-duty diesel vehicles	1996	FTP	2	50[b]	D
Heavy-duty diesel vehicles	1992	[c]	6	42	E
Heavy-duty diesel vehicles	Mid-1980s	[c]	2	45	C

Notes:
A. From Cadle et al. (1999). Average of summer and winter cold start emissions.
B. From Sagebiel et al. (1997). Hot start testing of vehicles identified as either high emitters of carbon monoxide or volatile organic compounds (VOCs).
C. From Hildemann et al. (1991). Cold start tests.
D. From Schauer et al. (1999). Hot start tests of medium duty vehicles operating on an FTP cycle.
E. From Lowenthal et al. (1994). Only includes measurement of vehicles powered by diesel fuel operated without an exhaust particulate trap.

[a] A total of 195 light duty vehicles were tested that include both gasoline powered vehicles and diesel powered vehicles.

[b] Fraction of particulate matter consisting of organic carbon was measured with and without an organics denuder upstream of particulate filter. Results reported here represent measurement without an organics denuder for consistency with other measurements. Using an organics denuder, the organic carbon comprised 39% of the particulate matter carbon.

[c] Driving cycle comprised of multiple idle, steady acceleration, constant speed, deceleration steps (see reference for more details).

carbon (EC), from gasoline vehicles are highly variable. Gillies and Gertler (2000) point out that there is greater variability in the concentrations of trace elements and ionic species than for OC and EC among different source profiles (e.g., SPECIATE [U.S. Environmental Protection Agency, 1999], Lawson and Smith [1998], Norbeck et al. [1998]). They suggest that this may arise because emissions of trace elements are not related only to the combustion process, but also

TABLE 3D-5. EMISSION RATES (mg/mi) FOR CONSTITUENTS OF PARTICULATE MATTER FROM GASOLINE AND DIESEL VEHICLES

	Gasoline Vehicles				Diesel Vehicles	
	Low	Medium	High	Smoker	Light Duty	Heavy Duty
TC	9.07 ± 0.75	41.30 ± 1.68	207.44 ± 7.29	456.38 ± 16.80	373.43 ± 13.75	1570.69 ± 58.24
OC	6.35 ± 0.54	26.02 ± 1.31	95.25 ± 4.28	350.24 ± 15.27	132.01 ± 5.82	253.94 ± 16.12
EC	2.72 ± 0.52	15.28 ± 0.99	112.19 ± 5.82	106.14 ± 5.42	241.42 ± 12.11	1316.75 ± 55.33
NO_3^-	0.039 ± 0.027	0.057 ± 0.028	0.141 ± 0.031	0.964 ± 0.051	1.474 ± 0.071	1.833 ± 1.285
$SO_4^=$	0.158 ± 0.036	0.518 ± 0.043	0.651 ± 0.052	2.160 ± 0.137	2.902 ± 0.165	3.830 ± 1.286
Na	0.060 ± 0.063	0.023 ± 0.111	0.052 ± 0.092	0.000 ± 0.000	0.000 ± 0.000	1.288 ± 2.160
Mg	0.036 ± 0.022	0.068 ± 0.027	0.041 ± 0.033	0.000 ± 0.000	0.000 ± 0.000	1.061 ± 0.729
Al	0.083 ± 0.016	0.078 ± 0.016	0.057 ± 0.014	0.000 ± 0.000	0.000 ± 0.000	0.321 ± 0.543
Si	0.066 ± 0.008	0.279 ± 0.011	0.714 ± 0.012	0.000 ± 0.000	0.000 ± 0.000	8.018 ± 0.221
P	0.035 ± 0.004	0.152 ± 0.007	0.113 ± 0.007	0.000 ± 0.000	0.000 ± 0.000	0.407 ± 0.136
S	0.085 ± 0.006	0.442 ± 0.009	0.822 ± 0.022	2.515 ± 0.116	2.458 ± 0.124	3.717 ± 0.111
Cl	0.024 ± 0.012	0.038 ± 0.012	0.081 ± 0.020	0.140 ± 0.117	0.228 ± 0.114	0.881 ± 0.221
K	0.010 ± 0.009	0.019 ± 0.009	0.031 ± 0.035	0.033 ± 0.386	0.000 ± 0.426	0.064 ± 0.248
Ca	0.060 ± 0.010	0.212 ± 0.011	0.210 ± 0.030	0.362 ± 0.250	0.150 ± 0.304	0.716 ± 0.107
Fe	0.143 ± 0.004	0.756 ± 0.005	1.047 ± 0.010	2.438 ± 0.054	0.515 ± 0.057	0.376 ± 0.055
Ni	0.001 ± 0.004	0.005 ± 0.004	0.011 ± 0.005	0.008 ± 0.017	0.014 ± 0.018	0.002 ± 0.057
Cu	0.002 ± 0.004	0.016 ± 0.003	0.021 ± 0.005	0.071 ± 0.018	0.024 ± 0.021	0.001 ± 0.062
Zn	0.048 ± 0.003	0.251 ± 0.004	0.265 ± 0.023	0.188 ± 0.272	0.000 ± 0.299	0.707 ± 0.032
Br	0.001 ± 0.002	0.016 ± 0.002	0.079 ± 0.003	0.047 ± 0.012	0.003 ± 0.014	0.012 ± 0.050
Ba	0.013 ± 0.136	0.009 ± 0.138	0.011 ± 0.299	0.380 ± 2.175	0.428 ± 2.390	0.493 ± 3.108
Pb	0.007 ± 0.006	0.085 ± 0.005	0.255 ± 0.008	0.345 ± 0.032	0.153 ± 0.033	0.008 ± 0.154

Source: Lawson and Smith (1998).

to their abundances in different fuels and lubricants and to wear and tear during vehicle operation. Emissions from gasoline smokers are comparable to those from light-duty diesel vehicles. Thus, older, poorly maintained gasoline vehicles could be significant sources of $PM_{2.5}$ (Sagebiel et al., 1997; Lawson and Smith, 1998), in addition to being significant sources of gaseous pollutants (e.g., Calvert et al., 1993). Durbin et al. (1999) point out that although smokers constitute only 1.1 to 1.7% of the light-duty fleet in the South Coast Air Quality Management District in California, they contribute roughly 20% of the total PM emissions from the light-duty fleet. In general, motor vehicles that are high emitters of hydrocarbons and carbon monoxide also will tend to be high emitters of PM (Sagebiel et al.,1997; Cadle et al., 1997). Particle emission rates, even in newer vehicles, also are correlated with vehicle acceleration; and emissions occur predominantly during periods of heavy acceleration (Maricq et al., 1999).

Although the data shown in Table 3D-5 indicate that S (mainly in the form of sulfate) is a minor component of $PM_{2.5}$ emissions, S may be the major component of the ultrafine particles that are emitted by either diesel or internal combustion engines (Gertler et al., 2000). It is not clear what the source of the small amount of Pb seen in the auto exhaust profile is. It is extremely difficult to find suitable tracers for automotive exhaust because Pb has been removed from gasoline. However, it also should be remembered that restrictions in the use of leaded gasoline have resulted in a dramatic lowering of ambient Pb levels.

Several tunnel studies have measured the distribution of organic and elemental carbon in the integrated exhaust of motor vehicle fleets comprising several classes of motor vehicles (Pierson and Brachaczek, 1983; Weingartner et al., 1997a; Fraser et al., 1998a). The study by Fraser et al. (1998a) found that organic carbon constituted 46% of the carbonaceous PM emissions from the vehicles operating in the Van Nuys tunnel in Southern California in the Summer of 1993. Although diesel vehicles constituted only 2.8% of the vehicles measured by Fraser et al. (1998a), the contribution of the organic carbon to the total particulate carbon emissions obtained in the Van Nuys tunnels is in reasonable agreement with the dynamometer measurements shown in Table 3D-4b.

Very few studies have reported comprehensive analyses of the organic composition of motor vehicle exhaust. The measurements by Rogge et al. (1993c) are the most comprehensive but are not expected to be the best representation of current motor vehicle emissions because these measurements were made in the mid-1980s. Measurements reported by Fraser et al. (1999) were made in a tunnel study conducted in 1993 and represent integrated diesel and gasoline powered vehicle emissions. In addition, exhaust emissions from two medium-duty diesel vehicles operating over an FTP cycle were analyzed by Schauer et al. (1999). A unique feature of both the measurements by Faser et al. (1999) and Schauer et al. (1999) is that they include the quantification of unresolved complex mixture (UCM), which comprises aliphatic and cyclic hydrocarbons that cannot be resolved by gas chromatography (Schauer et al., 1999).

Schauer et al. (1999) have shown that all of the organic compound mass in their diesel exhaust samples could be extracted and eluted by CG/MS techniques even though not all of the organic compound mass can identified on a single compound basis. Table 3D-6 summarizes the composition of motor vehicle exhaust measured by Fraser et al. (1999) and Schauer et al. (1999).

TABLE 3D-6. SUMMARY OF PARTICLE-PHASE ORGANIC COMPOUNDS EMITTED FROM MOTOR VEHICLES

Source	Compound Class	Contribution to Particulate Mass (%)	Dominant Contributors to Emissions of Compound Class
Gasoline and diesel-powered vehicles driving through the Van Nuys Tunnel (Fraser et al., 1999)[a]	n-Alkanes	0.009	C_{21} through C_{29}
	Petroleum biomarkers	0.078	Hopanes and steranes
	PAH	0.38	No dominant compound
	Aromatic acids	0.29	Benzenedicarboxylic acids
	Aliphatic acids	0.21	Palmitic and stearic acids
	Substituted aromatic	0.042	No dominant compound
	UCM[b]	23.0	
Medium-duty diesel vehicles operated over an FTP Cycle (Schauer et al., 1999)	n-Alkanes	0.22	C_{20} through C_{28}
	Petroleum biomarkers	0.027	Hopanes and steranes
	PAH	0.54	No dominant compound
	Aliphatic acids	0.24	n-Octadecanoic acid
	Aromatic acids	0.014	Methylbenzoic acid
	Saturated cycloalkanes	0.037	C_{21} through C_{25}
	UCM[b]	22.2	

[a] Includes emissions of brake wear, tire wear, and resuspension of road dust associated with motor vehicle traffic.
[b] Unresolved complex mixture.

Several studies have measured the distribution of polycyclic aromatic hydrocarbons (PAHs) in motor vehicles exhaust from on-road vehicles (Westerholm et al., 1991; Lowenthal et al., 1994; Venkataraman et al., 1994; Westerholm and Egeback, 1994; Reilly et al., 1998; Cadle et al., 1999, Weingartner et al., 1997b; Marr et al., 1999). Cadle et al. (1999) found high molecular weight PAHs (PAHs with molecular weights greater than or equal to 202 g/mole) constitute 0.1 to 7.0% of the particulate matter emissions from gasoline powered and diesel powered light duty vehicles. It is important to note, however, that PAHs with molecular weights of 202 (fluoranthene, acephenanthrylene, and pyrene), 226 (benzo[ghi]fluoranthene and cyclopenta[cd]pyrene), and 228 (benz[*a*]anthracene, chrysene, and triphenylene) exist in both the gas-phase and particle-phase at atmospheric conditions (Fraser et al., 1998b) although those with molecular weight of 228 are predominantly associated with particles, with only traces in the gas-phase (Arey et al., 1987). Excluding these semivolatile PAHs, the contribution of nonvolatile PAHs to the particulate matter emitted from the light-duty vehicles sampled by Cadle et al. (1999) ranges from 0.013 to 0.18%. These measurements are in good agreement with the tunnel study conducted by Fraser et al. (1999) and the heavy-duty diesel truck and bus exhaust measurements by Lowenthal et al. (1994), except that the nonvolatile PAH emissions from the heavy duty diesel vehicles tested by Lowenthal et al. (1994) were moderately higher, making up approximately 0.30% of the particulate matter mass emissions.

Biomass Burning

In contrast to the mobile and stationary sources discussed earlier, emissions from biomass burning in wood stoves and forest fires are strongly seasonal and can be highly episodic within their peak emissions seasons. The burning of fuelwood is confined mainly to the winter months and is acknowledged to be a major source of ambient air particulate matter in the northwestern United States during the heating season. Forest fires occur primarily during the driest seasons of the year in different areas of the country and are especially prevalent during prolonged droughts. PM produced by biomass burning outside the United States (e.g., in Central America during the spring of 1988) also can affect ambient air quality in the United States.

An example of the composition of fine particles ($PM_{2.5}$) produced by wood stoves is shown in Figure 3D-4. These data were obtained in Denver during the winter of 1987-1988 (Watson and Chow, 1994). As was the case for motor vehicle emissions, organic and elemental carbon are the major components of particulate emissions from wood burning. It should be remembered that the relative amounts shown for organic carbon and elemental carbon vary with the type of stove, the stage of combustion, and the type and condition of the fuelwood. Fine particles are dominant in smoke studies of wood burning emissions. For instance, the mass median diameter

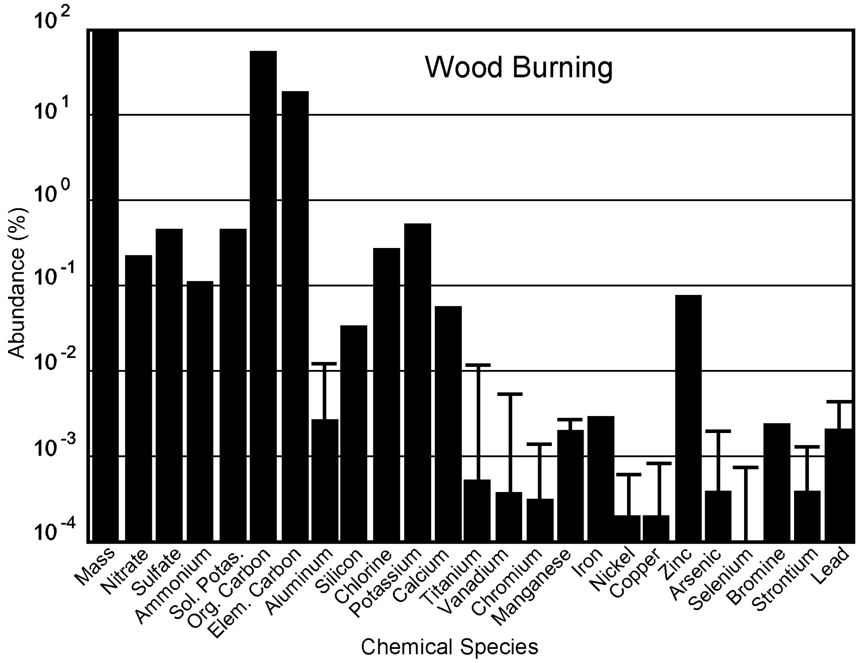

Figure 3D-4. Chemical abundances for $PM_{2.5}$ emissions from wood burning in Denver, CO. Solid bars represent fractional abundances, and the error bars represent variability in species abundances. Error bars represent detection limits when there are no solid bars.

Source: Watson and Chow (1994).

of wood particles was found to be about 0.17 μm in a study of the emissions from burning hardwood, softwood, and synthetic logs (Dasch, 1982).

Kleeman et al. (1999) showed that the particles emitted by the combustion of wood in fireplaces are predominately less than 1.0 μm in diameter, such that the composition of fine PM ($PM_{2.5}$) emitted from fireplace combustion of wood is representative of the total particulate matter emissions from this source. Hildemann et al. (1991) and McDonald et al. (2000) reported that smoke from fireplace and wood stove combustion consists of 48% to 71% OC and 2.9% to 15% EC. Average elemental and organic carbon contents for these measurements are shown in Table 3D-7. It should be noted that the two methods used for the measurements shown in Table 3D-7 have been reported to produce different relative amounts of OC and EC for wood smoke samples but show good agreement for total carbon (OC + EC) measurements (Chow et al., 1993).

TABLE 3D-7. MASS EMISSIONS, ORGANIC CARBON, AND ELEMENTAL CARBON EMISSIONS FROM RESIDENTIAL COMBUSTION OF WOOD

Wood Type	Combustion Type	Average Mass Emission Rate (g kg^{-1} of wood burned)	Number of Tests	Percent Organic Carbon[a]	Percent Elemental Carbon[a]	References
Softwood	Fireplace	13.0	2	48.4	5.2	Hildemann et al. (1991)
Softwood	Fireplace	5.14	5	58.5	15.0	McDonald et al. (2000)
Hardwood	Fireplace	5.28	3	48.4	2.9	Hildemann et al. (1991)
Hardwood	Fireplace	5.66	5	63.2	7.0	McDonald et al. (2000)
Hardwood	Wood Stove	3.96	8	71.2	9.0	McDonald et al. (2000)

[a] Hildemann et al. (1991) used the method described by Birch and Cary (1996) to measure EC and McDonald et al. (2000) used the method reported by Chow et al. (1993) to measure OC.

Hawthorne et al. (1988) and Hawthorne et al. (1989) measured gas-phase and particle-phase derivatives of guaiacol (2-methoxyphenol), syringol (2,6-dimethoxyphenol), phenol, and catechol (1,2-benzenediol) in the downwind plume of 28 residential wood stoves and fireplaces. Rogge et al. (1998) reported a broad range of particle-phase organic compounds in the wood smoke samples collected by Hildemann et al. (1991), which include n-alkanes, n-alkanoic acids, n-alkenoic acids, dicarboxylic acids, resin acids, phytosterols, polycyclic aromatic hydrocarbons (PAH), and the compounds reported by Hawthorne et al. (1989). Supplementing these measurements, McDonald et al. (2000) reported the combined gas-phase and particle-phase emissions of PAH and the compounds quantified by Hawthorne et al. (1989). The measurements by Rogge et al. (1998), which represent a comprehensive data set of the organic compounds present in wood smoke aerosol, are summarized in Table 3D-8. It should be noted, however, that these nearly 200 compounds account for only approximately 15 to 25% of the organic carbon particle mass emitted from the residential combustion of wood. Simoneit et al. (1999) have shown that levoglucosan constitutes a noticeable portion of the organic compound mass not identified by Rogge et al. (1998). In addition, Elias et al. (1999) used high-temperature gas chromatography/mass spectrometry (HTGC-MS) to measure high-molecular-weight organic compounds in smoke from South American leaf and stem litter biomass burning. These compounds cannot be measured by the analytical techniques employed by Rogge et al. (1998) and, therefore, are strong candidates to make up some of the unidentified organic mass in the

TABLE 3D-8. SUMMARY OF PARTICLE-PHASE ORGANIC COMPOUNDS EMITTED FROM THE COMBUSTION OF WOOD IN FIREPLACES*

Biomass Type	Compound Class	Contribution to Particulate Mass (%)	Dominant Contributors to Emissions of Compound Class
Fireplace combustion of softwood	n-Alkanes	0.039	C_{21} through C_{31}
	n-Alkanoic acids	0.45	C_{16}, C_{18}, C_{20}, C_{21}, C_{22}, C_{24}
	n-Alkenoic acids	0.12	Oleic and linoleic acid
	Dicarboxylic acids	0.36	Malonic acid
	Resin acids	1.28	Abietic, dehydroabietic, isopimaric, pimaric, and sandaracopimaric acids
	Substituted phenols	3.30	Benzenediols and guaiacols
	Phytosterols	0.37	β-Sitosterol
	PAH	0.092	Fluoranthene and pyrene
	Oxygenated PAH	0.019	1H-phenalen-1-one
Fireplace combustion of hardwood	n-Alkanes	0.044	C_{21} through C_{29}
	n-Alkanoic acids	1.33	C_{16}, C_{22}, C_{24}, C_{26}
	n-Alkenoic acids	0.049	Oleic and linoleic acid
	Dicarboxylic acids	0.42	Succinic acid
	Resin acids	0.11	Dehydroabietic acid
	Substituted phenols	8.23	Benzediols, guaiacols, and syringols
	Phytosterols	0.21	β-sitosterol
	PAH	0.13	No dominant compounds
	Oxygenated PAH	0.020	1H-phenalen-1-one

*Note: Measurements were made using a dilution sampler and no semivolatile organic compound sorbent.

Source: Rogge et al. (1998).

wood smoke samples analyzed by Rogge et al. (1998). These compounds, which include triterpenyl fatty acid esters, wax esters, triglycerides, and high-molecular-weight n-alkan-2-ones,are expected to be present in North American biomass smoke originating from agricultural burning, forest fires, grassland fires, and wood stove/fireplace smoke.

Measurements of aerosol composition, size distributions, and aerosol emissions factors have been made in biomass burning plumes, either on towers (Susott et al., 1991) or aloft on fixed-wing aircraft (e.g., Radke et al., 1991) or on helicopters (e.g., Cofer et al., 1988). As was found for wood stove emissions, the composition of biomass burning emissions is strongly dependent on the stage of combustion (i.e., flaming, smoldering, or mixed), and the type of vegetation (e.g., forest, grassland, scrub). Over 90% of the dry mass in particulate biomass burning emissions is composed of organic carbon (Mazurek et al., 1991). Ratios of organic carbon to elemental carbon are highly variable, ranging from 10:1 to 95:1, with the highest ratio found for smoldering conditions and the lowest for flaming conditions. Emissions factors for total particulate emissions increase by factors of two to four in going from flaming to smoldering stages in the individual fires studied by Susott et al. (1991).

Particles in biomass burning plumes from a number of different fires were found to have three distinguishable size modes: (1) a nucleation mode, (2) an accumulation mode, and (3) a coarse mode (Radke et al., 1991). Based on an average of 81 samples, approximately 70% of the mass was found in particles <3.5 μm in aerodynamic diameter. The fine particle composition was found to be dominated by tarlike, condensed hydrocarbons; and the particles were usually spherical in shape. Additional information for the size distribution of particles produced by vegetation burning is shown in Figure 3D-2.

An example of ambient data for the composition of $PM_{2.5}$ collected at a tropical site that was heavily affected by biomass burning is shown in Table 3D-9. The samples were collected during November of 1997 on the campus of Sriwijaya University, which is located in a rural setting on the island of Sumatra in Indonesia (Pinto et al., 1998). The site was subjected routinely to levels of $PM_{2.5}$ well in excess of the U.S. NAAQS as a result of the Indonesian biomass fires from the summer of 1997 through the spring of 1998. As can be seen from a comparison of the data shown in Table 3D-9 with those shown in Figure 3D-4, there are a number of similarities and differences (especially with regard to the heavy metal content) in the abundances of many species. The abundances of some crustal elements (e.g., Si, Fe) are higher in Table 3D-9 than in Figure 3D-4, perhaps reflecting additional contributions of entrained soil dust.

Limited emissions data that include organic compound speciation information have been reported for agricultural burning (Jenkins et al., 1996), forest fires (Simoneit, 1985), and grassland burning (Standley and Simoneit, 1987). Jenkins et al. (1996) present PAH emissions

TABLE 3D-9. MEAN AEROSOL COMPOSITION AT TROPICAL SITE (SRIWIJAYA UNIVERSITY, SUMATRA, INDONESIA) AFFECTED HEAVILY BY BIOMASS BURNING EMISSIONS[a]

Component	Abundance (%)	Component	Abundance (%)
OC	76	Cr	BD[b]
EC	1.2	Mn	BD[b]
SO_4^{-2}	11	Fe	3.9×10^{-2}
Al	BD[b]	Ni	$< 3.8 \times 10^{-5}$
Si	9.3×10^{-2}	Cu	4.8×10^{-4}
Cl	4.4	Zn	3.1×10^{-3}
K	0.7	As	6.4×10^{-4}
Ca	4.5×10^{-2}	Se	2.8×10^{-4}
Ti	4.2×10^{-3}	Br	3.6×10^{-2}
V	BD[b]	Pb	3.1×10^{-3}

[a] The mean $PM_{2.5}$ concentration during the sampling period (November 5 through 11, 1997) was 264 μg/m^3.
[b] Beneath detection limit.

Source: Pinto et al. (1998).

factors for the combustion of cereals (barley, corn, rice, and wheat), along with PAH emissions factors for wood burning. Profiles of organic compounds in emissions from meat cooking (Rogge et al., 1991) and cigarette smoke (Rogge et al., 1994) also have been obtained.

Natural Sources

Although sea-salt aerosol production is confined to salt water bodies, it is included here because many marine aerosols can exert a strong influence on the composition of the ambient aerosol in coastal areas. In some respects, the production of sea-salt aerosols is like that of windblown dust, in that both are produced by wind agitation of the surface. The difference between the two categories arises because sea-salt particles are produced from the bursting of air bubbles rising to the sea surface. Air bubbles are formed by the entrainment of air into the water by breaking waves. The surface energy of a collapsing bubble is converted to kinetic energy in the form of a jet of water that can eject drops above the sea surface. The mean diameter of the jet drops is about 15% of the bubble diameter (Wu, 1979). Bubbles in breaking waves range in size from a few µm to several mm in diameter. Field measurements by Johnson and Cooke (1979) of bubble size spectra show maxima in diameters at around 100 µm, with the bubble size distribution varying as $(d/d_0)^{-5}$ with $d_0 = 100$ µm.

Because sea-salt particles receive water from the surface layer, which is enriched in organic compounds, aerosol drops are composed of this organic material in addition to sea salt (about 3.5% by weight in seawater). Na^+ (30.7%), Cl^- (55.0%), SO_4^{-2} (7.7%), Mg^{2+} (3.6%), Ca^{2+} (1.2%), K^+ (1.1%), HCO_3^- (0.4%), and Br^- (0.2%) are the major ionic species by mass in seawater (Wilson, 1975). The composition of the marine aerosol also reflects the occurrence of displacement reactions that enrich sea-salt particles in SO_4^{-2} and NO_3^- while depleting them of Cl^- and Br^-.

Sea salt is concentrated in the coarse size mode with a mass median diameter of about 7 µm for samples collected in Florida, the Canary Islands, and Barbados (Savoie and Prospero, 1982). The size distribution of sulfate is distinctly bimodal. Sulfate in the coarse mode is derived from sea water, but sulfate in the submicron aerosol arises from the oxidation of dimethyl sulfide (CH_3SCH_3) or DMS. DMS is produced during the decomposition of marine micro-organisms. DMS is oxidized to methane sulfonic acid (MSA), a large fraction of which is oxidized to sulfate (e.g., Hertel et al., 1994).

Apart from sea spray, other natural sources of particles include the suspension of organic debris and volcanism. Profiles of organic compounds in vegetative detritus have been obtained by Rogge et al. (1993d). Particles are released from plants in the form of seeds, pollen, spores, leaf waxes, and resins, ranging in size from 1 to 250 µm (Warneck, 1988). Fungal spores and animal debris, such as insect fragments, also are to be found in ambient aerosol samples in this size range. Although material from all the foregoing categories may exist as individual particles, bacteria usually are found attached to other dust particles (Warneck, 1988). Smaller bioaerosol particles include viruses, individual bacteria, protozoa, and algae (Matthias-Maser and Jaenicke, 1994). In addition to natural sources, other sources of bioaerosol include industry (e.g., textile mills), agriculture, and municipal waste disposal (Spendlove, 1974). The size distribution of bioaerosols has not been characterized as well as it has for other categories of airborne particles.

Trace metals are emitted to the atmosphere from a variety of sources such as sea spray, wind-blown dust, volcanoes, wildfires and biotic sources (Nriagu, 1989). Biologically mediated volatilization processes (e.g., biomethylation) are estimated to account for 30 to 50% of the worldwide total Hg, As, and Se emitted annually; whereas other metals are derived principally from pollens, spores, waxes, plant fragments, fungi, and algae. It is not clear, however, how much of the biomethylated species are remobilized from anthropogenic inputs. Median ratios of the natural contribution to globally averaged total sources for trace metals are estimated to be 0.39 (As), 0.15 (Cd), 0.59 (Cr), 0.44 (Cu), 0.41 (Hg), 0.35 (Ni), 0.04 (Pb), 0.41 (Sb), 0.58 (Se), 0.25 (V), and 0.34 (Zn), suggesting a significant natural source for many trace elements. It should be noted, however, that these estimates are based on emissions estimates that have uncertainty ranges of an order of magnitude.

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APPENDIX 3E

Variability Observed in $PM_{2.5}$ and $PM_{10-2.5}$ Concentrations at IMPROVE Sites

In this appendix, the temporal variability of $PM_{2.5}$, $PM_{10-2.5}$ and PM_{10} concentrations is characterized on various time scales based on daily values in the PM data set obtained at 18 sites in the IMPROVE network. The purpose of these analyses is to provide concentrations of $PM_{2.5}$ and $PM_{10-2.5}$ that could be used for characterizing human and ecosystem exposures to PM under the least polluted conditions that are found in the United States and to provide limits on policy relevant background PM concentrations (cf., Section 3.3.3). This is accomplished by analyzing $PM_{2.5}$ and $PM_{10-2.5}$ concentrations and their variability at relatively remote monitoring sites that are not obviously influenced by local pollution sources in the United States. The potential for receiving contributions from anthropogenic sources exists at every monitoring site. However, we are interested in characterizing data obtained at the sites with lowest concentrations. Only those sites in which anthropogenic sources do not contribute extensively to the observations are considered. These sites will be referred to as relatively remote monitoring sites (RRMS). Thus, virtually all sites in the eastern United States would not fit into this definition. Data from these sites are included to permit comparison with sites in the West. More detailed analyses of the data are available in Lefohn et al. (2004).

Data stored in the IMPROVE database as of December 4, 2002 from 18 IMPROVE network sites were downloaded from the following internet address: (http://vista.cira.colostate.edu/IMPROVE/Data/IMPROVE/IMPLoctable_Data.asp?SortColumn=Site_Code). The locations of the sites chosen are shown in Figure 3E-1. Data at many sites are available from 1989, data at other sites are available for shorter periods of time. In addition, sites have been relocated within various national parks. The monitoring site in Yellowstone National Park was relocated in 1996; thus, the designations for the two locations are Yellowstone National Park1 and Yellowstone National Park2. The Voyageurs National Park site was also relocated. The designations for the two locations are similar to those used for Yellowstone National Park. The 24-hour average data were summarized on seasonal and annual

Figure 3E-1. Locations of the rural PM IMPROVE sites selected for the study.

bases. The data capture requirement for the annual analysis required that there had to be at least 13 valid days of data for a particular constituent for each quarter of a calendar year in order for the information to be included. For the seasonal analysis, all 24-hour average data were used. The percentile information was organized by minimum, 10th percentile concentration (P10), 25th percentile concentration (P25), 50th percentile concentration (P50), 75th percentile concentration (P75), 90th percentile concentration (P90), 95th percentile concentration (P95), 99th percentile concentration (P99), and maximum concentration.

Information about the range of annual mean $PM_{2.5}$, $PM_{10-2.5}$ and PM_{10} concentrations is summarized in Table 3E-1, and the range of 90th percentile concentrations is summarized in Table 3E-2. As can be seen from Table 3E-1, the lowest average annual mean $PM_{2.5}$ concentrations among all sites examined were recorded at Denali National Park (AK), with concentrations there ranging from an annual mean of 1.15 $\mu g/m^3$ to 3.14 $\mu g/m^3$. On the other hand, the highest annual mean $PM_{2.5}$ concentrations in the 12 western sites studied were observed in Glacier National Park (MT); values there ranged from 4.92 to 6.36 $\mu g/m^3$. The highest average annual mean $PM_{2.5}$ concentrations in the continental United States were observed at Dolly Sods/Otter Creek Wilderness (WV), those ranging from 10.03 $\mu g/m^3$ to 14.24 $\mu g/m^3$. In general, the lowest average annual mean $PM_{2.5}$ concentration increased in going

TABLE 3E-1. THE RANGE OF ANNUAL MEAN $PM_{2.5}$, $PM_{10-2.5}$, AND PM_{10} CONCENTRATIONS AT IMPROVE PARTICULATE MATTER MONITORING SITES (all units in µg/m^3)

Site Name	$PM_{2.5}$	$PM_{10-2.5}$	PM_{10}
*Denali National Park, AK	1.15 - 3.14	1.09 - 5.37	2.36 - 8.19
*Glacier National Park, MT	4.92 - 6.36	4.31 - 9.66	9.89 - 15.25
*Bridger Wilderness, WY	2.15 - 3.05	2.36 - 4.75	4.22 - 7.39
*Yellowstone National Park1, WY	2.79 - 4.68	3.98 - 7.72	6.80 - 10.55
*Yellowstone National Park2, WY	2.33 - 3.15	1.91 - 2.81	4.21 - 5.71
*Bryce Canyon National Park, UT	2.68 - 3.65	2.48 - 5.74	5.23 - 8.66
*Canyonlands National Park, UT	2.73 - 4.03	3.25 - 8.05	6.12 - 11.79
*Lone Peak Wilderness, UT	4.13 - 5.81	3.25 - 6.19	7.37 - 11.60
*Three Sisters Wilderness, OR	2.63 - 4.19	1.92 - 4.43	4.57 - 7.74
*Redwood National Park, CA	3.62 - 5.43	3.33 - 6.50	7.20 - 12.19
*Lassen Volcanic National Park, CA	2.10 - 5.47	1.86 - 6.47	4.42 - 8.68
*Gila Wilderness, NM	3.46 - 4.86	2.55 - 4.94	5.91 - 9.17
Boundary Waters Canoe Area, MN	4.28 - 5.88	2.24 - 3.72	7.19 - 9.35
Voyageurs National Park1, MN	5.01 - 6.60	3.98 - 4.22	10.08 - 13.25
Voyageurs National Park2, MN	4.48 - 7.82	2.71 - 3.03	6.93 - 7.14
Dolly Sods/Otter Creek Wilderness, WV	10.03 - 14.24	2.29 - 5.3	13.26 - 18.92
Acadia National Park, ME	4.23 - 8.50	1.84 - 6.04	7.28 - 15.03
Lye Brook Wilderness, VT	5.33 - 8.43	1.58 - 4.88	6.84 - 13.16
Brigantine National Wildlife Refuge, NJ	10.20 - 12.63	7.90 - 14.87	18.49 - 26.63

* Western monitoring sites

to the midwestern and then to the eastern United States, and the range of annual average concentrations tends to be lower at western than at eastern sites. Over the period of the observational record, a substantial range in annual mean concentrations in all three size ranges is observed, indicating the importance of examining a number of years in attempting to characterize long term averages. Inspection of Table 3E-1 shows that the range in annual average $PM_{10-2.5}$ concentrations was generally larger than for $PM_{2.5}$. However, it should be noted that $PM_{10-2.5}$ concentrations are obtained by a difference technique and so is more strongly affected by errors in the determination of both $PM_{2.5}$ and PM_{10}.

TABLE 3E-2. THE RANGE OF 24-HOUR $PM_{2.5}$, $PM_{10-2.5}$, AND PM_{10} AVERAGE CONCENTRATIONS AT THE 90TH PERCENTILE LEVEL AT IMPROVE PARTICULATE MATTER MONITORING SITES (all units in µg/m^3)

Site Name	$PM_{2.5}$	$PM_{10-2.5}$	PM_{10}
*Denali National Park, AK	2.18 - 7.44	1.92 - 11.65	4.31 - 17.94
*Glacier National Park, MT	8.05 - 11.00	8.36 - 27.60	17.66 - 36.82
*Bridger Wilderness, WY	3.94 - 5.77	4.80 - 12.26	8.32 - 15.14
*Yellowstone National Park1, WY	4.67 - 6.58	8.78 - 16.53	12.34 - 21.34
*Yellowstone National Park2, WY	4.06 - 6.04	4.22 - 5.94	7.42 – 10.82
*Bryce Canyon National Park, UT	4.40 - 5.92	5.03 - 11.99	8.93 - 13.60
*Canyonlands National Park, UT	4.48 - 6.38	6.30 - 14.68	10.89 - 18.46
*Lone Peak Wilderness, UT	6.74 - 11.07	6.55 - 10.87	13.42 - 21.52
*Three Sisters Wilderness, OR	5.82 - 9.97	3.97 - 9.63	8.51 - 16.47
*Redwood National Park, CA	6.25 - 9.93	5.94 - 12.97	13.21 - 23.73
*Lassen Volcanic National Park, CA	4.00 - 9.05	3.74 - 14.73	8.54 - 15.95
*Gila Wilderness, NM	5.58 - 10.57	4.22 - 9.66	10.25 - 18.84
Boundary Waters Canoe Area, MN	8.11 - 12.14	4.77 - 8.84	13.64 - 18.85
Voyageurs National Park1, MN	7.72 - 13.57	9.04 - 17.38	17.89 - 26.46
Dolly Sods/Otter Creek Wilderness, WV	15.57 - 29.04	4.35 - 9.20	21.30 - 34.63
Acadia National Park, ME	8.80 - 17.13	3.58 - 12.02	12.74 - 26.04
Lye Brook Wilderness, VT	11.44 - 16.46	3.31 - 5.85	15.66 - 22.88
Brigantine National Wildlife Refuge, NJ	16.20 - 22.72	13.60 - 32.19	31.37 - 45.28

*Western monitoring sites.

As can be seen from Table 3E-2, concentrations of PM in all three size fractions at the 90th percentile level are often several times higher than the mean concentrations at all sites. In addition, the range of values at the 90th percentile level is much greater than that at lower levels. These findings indicate that extreme events are important for shaping the frequency distribution of PM that is observed. Wildfires play a major role in defining the year-to-year variability at specific sites, especially in the West. Notable examples include the massive forest fire in 1988 in Yellowstone National Park and those that occurred in 2000 in many western states. Dust storms also play a role in arid climates. The variability in annual average $PM_{10-2.5}$ concentrations is again related to several factors. Variability in factors that govern the production of soil dust from the surface and the production of primary biological aerosol particles may be largely responsible. Wildfires also produce PM in this size range (cf., Appendix 3D).

The interannual variability in the percentile distributions of $PM_{2.5}$ concentrations for 1997 through 2001 is shown in Figures 3E-2(a-d) for four sites. The corresponding interannual variability in $PM_{10-2.5}$ concentrations at these sites is shown in Figures 3E-3(a-d). As can be seen, at concentrations less than the P90 level, year-to-year differences can be less than 1 $\mu g/m^3$ at sites such as Bridger, WY. Differences at the P90 level are much larger, both on an absolute and on a relative basis at eastern sites.

Percentile distributions by season are shown in Figure 3E-4(a-d) for $PM_{2.5}$ and Figures 3E-5(a-d) for $PM_{10-2.5}$. For most sites, the variability in concentrations on a quarterly basis increases substantially beyond the 90th percentile level, as can be seen from inspection of Figures 3E-4(a-d) for $PM_{2.5}$ and Figures 3E-5(a-d) for $PM_{10-2.5}$. Perhaps the most striking features seen in Figures 3E-4(a-d) and Figures 3E-5(a-d) are the concentration changes associated with the P_{95} and P_{99} events, which represent extreme value events. Most of these events occur in the third calendar quarter; however, at some sites high concentrations occur during the second and fourth calendar quarters. If locally derived climatologic seasons were used instead of calendar quarters, a more accurate depiction of the seasonal variability of these events may have been obtained. In most cases, there is consistency in the behavior of $PM_{2.5}$ and PM_{10}, which suggests that the episodes of higher concentrations could be associated with sources that produce mainly $PM_{2.5}$ such as wildfires and/or anthropogenic combustion sources. Wildfires are limited to hotter and drier times of the year, but anthropogenic sources can contribute to high concentrations during other seasons. Additional factors which would tend to produce a 3rd quarter maximum include: the enhanced production of secondary particulate matter from anthropogenic and biogenic precursors during summer months; wildfires that are located in the East or elsewhere during summer; and surface dust produced locally and/or in northern Africa.

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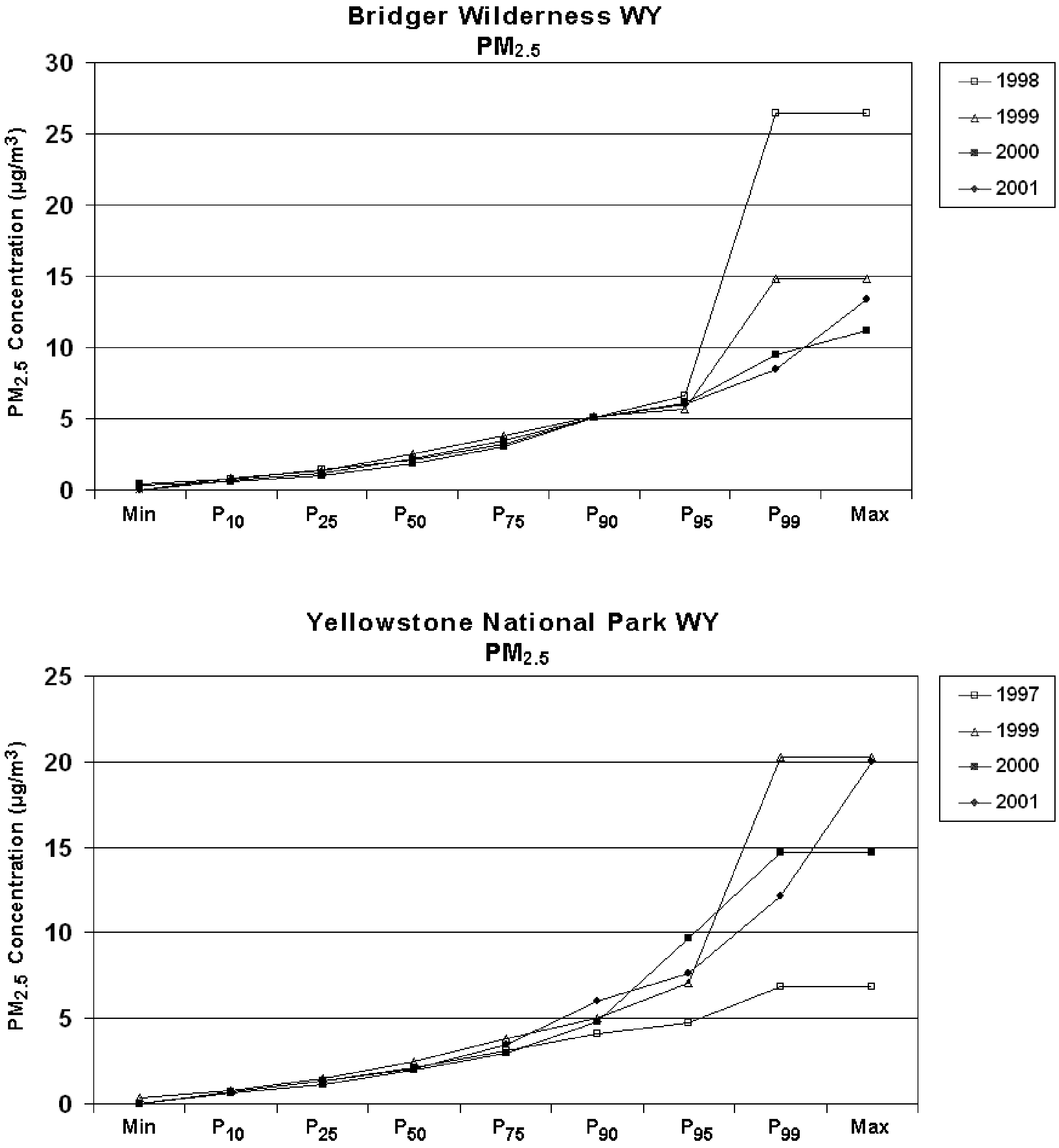
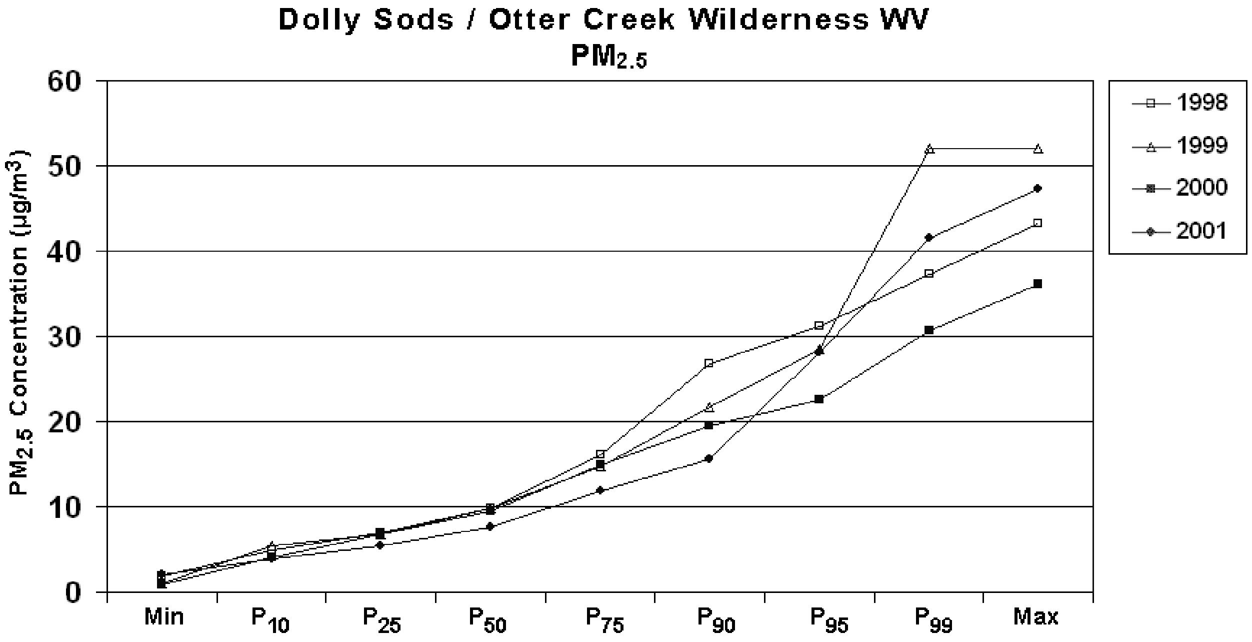


Figure 3E-2a,b. Interannual variability in 24-h average $PM_{2.5}$ concentrations observed at selected IMPROVE sites: (a) Bridger Wilderness, WY; (b) Yellowstone National Park, WY; (c) Dolly Sods/Otter Creek Wilderness, WV; and (d) Brigantine National Wildlife Refuge, NJ.



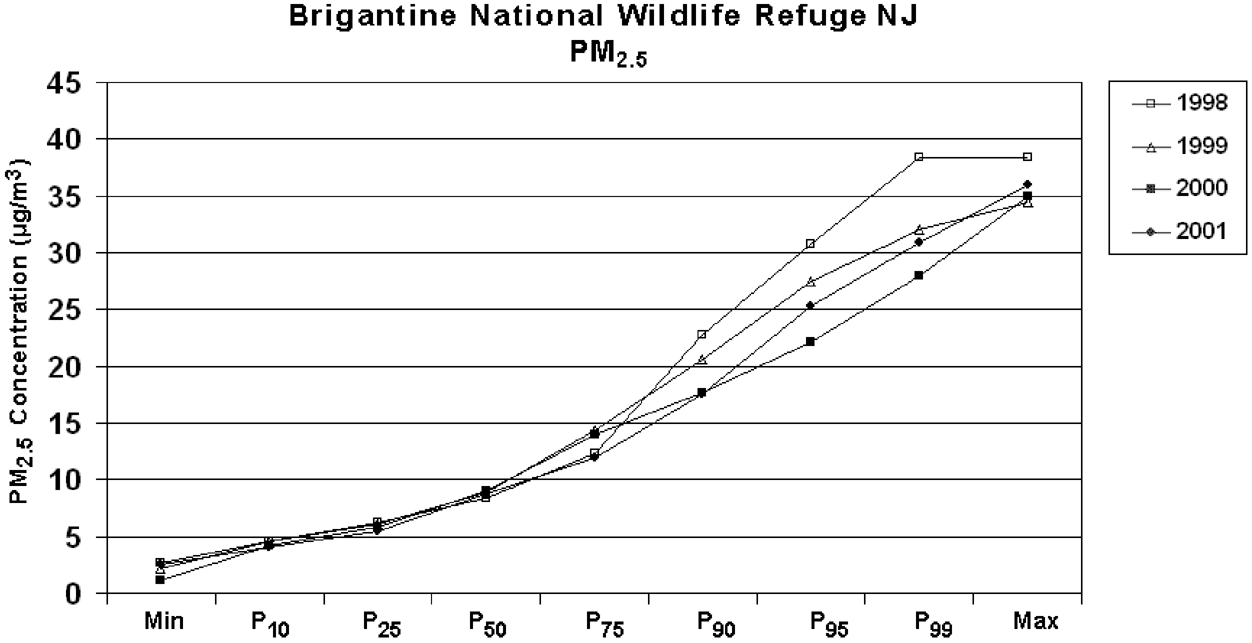
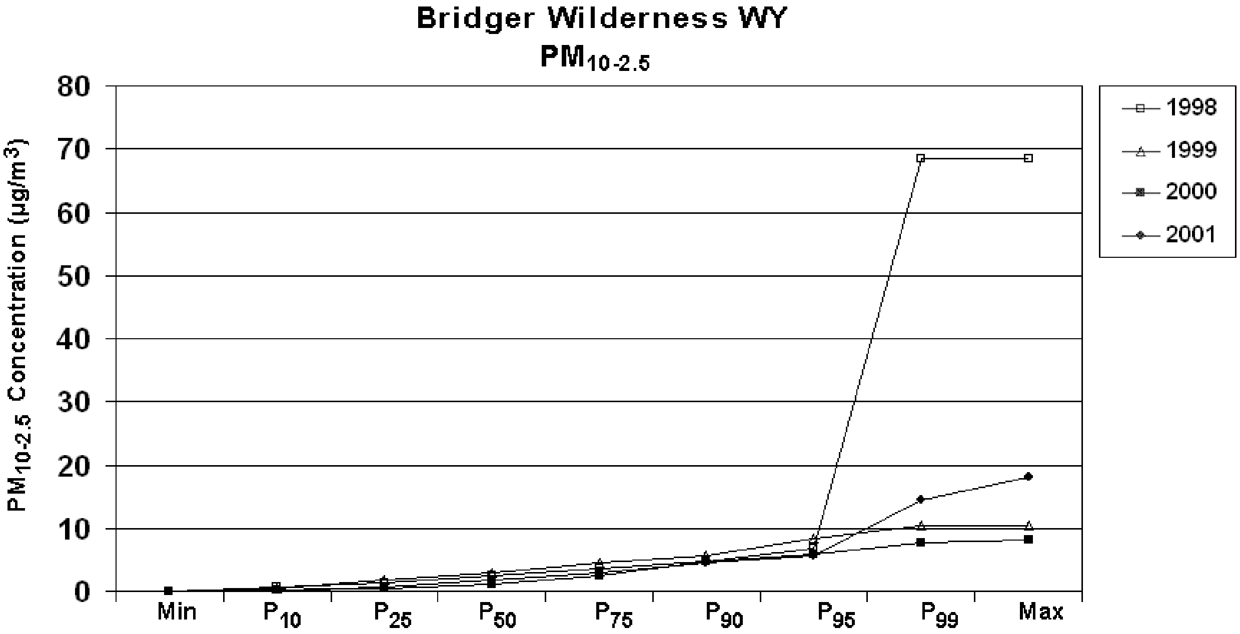


Figure 3E-2c,d. **Interannual variability in 24-h average $PM_{2.5}$ concentrations observed at selected IMPROVE sites: (a) Bridger Wilderness, WY; (b) Yellowstone National Park, WY; (c) Dolly Sods/Otter Creek Wilderness, WV; and (d) Brigantine National Wildlife Refuge, NJ.**



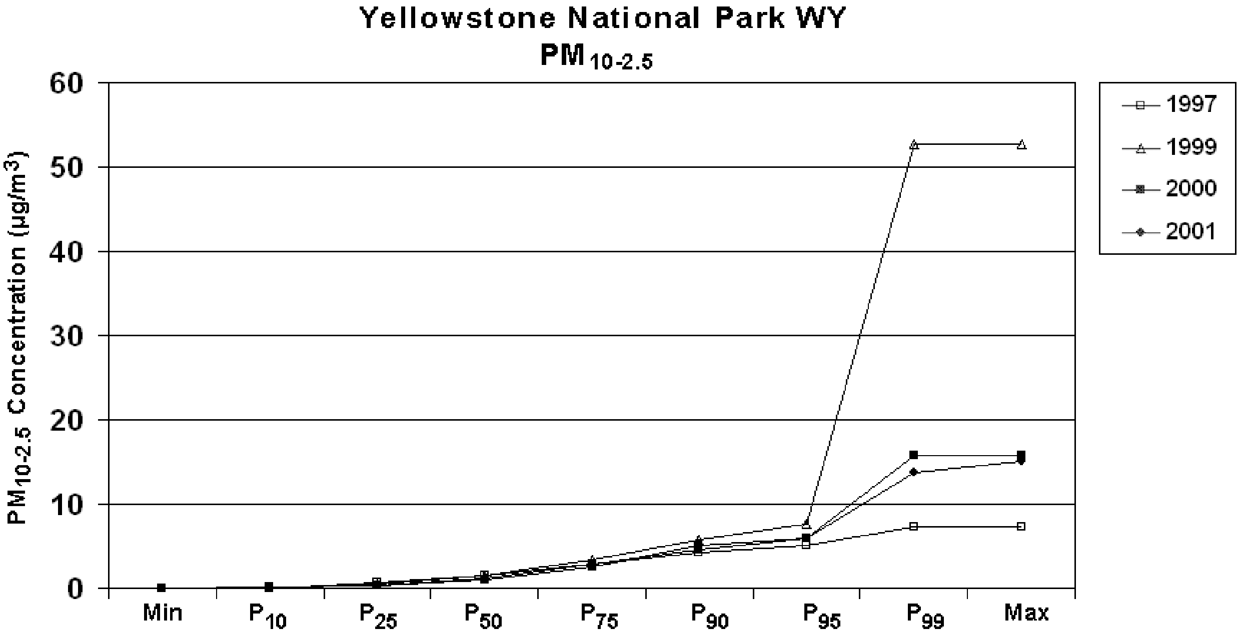
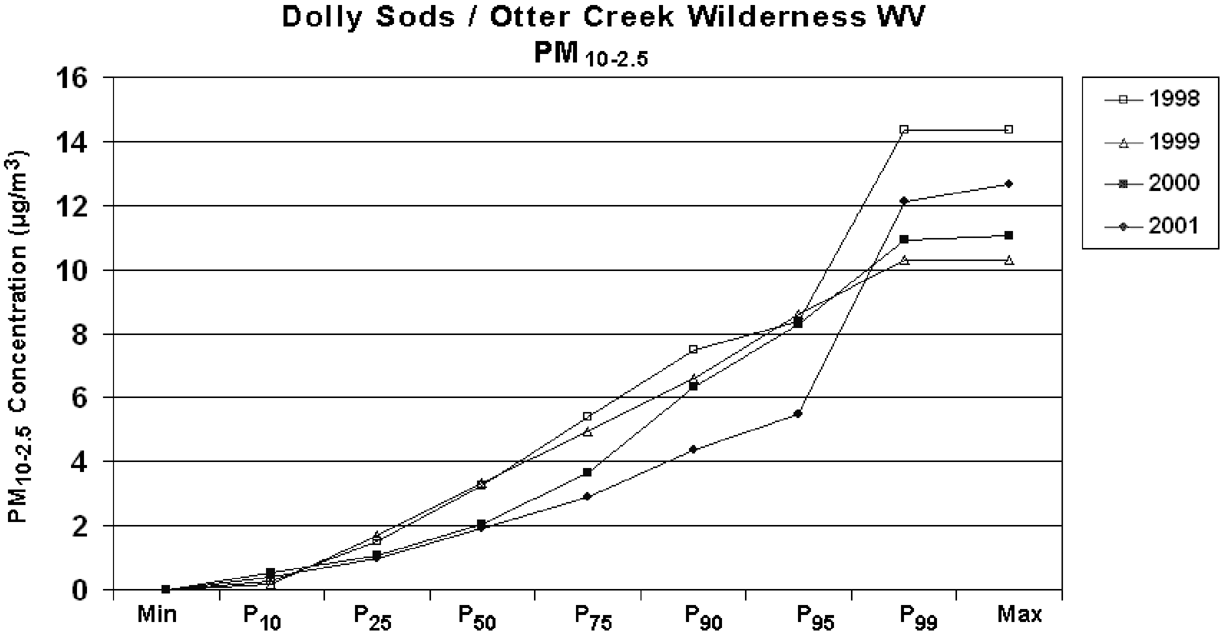


Figure 3E-3a,b. **Interannual variability in 24-h average $PM_{10\text{-}2.5}$ concentrations observed at selected IMPROVE sites: (a) Bridger Wilderness, WY; (b) Yellowstone National Park, WY; (c) Dolly Sods/Otter Creek Wilderness, WV; and (d) Brigantine National Wildlife Refuge, NJ.**



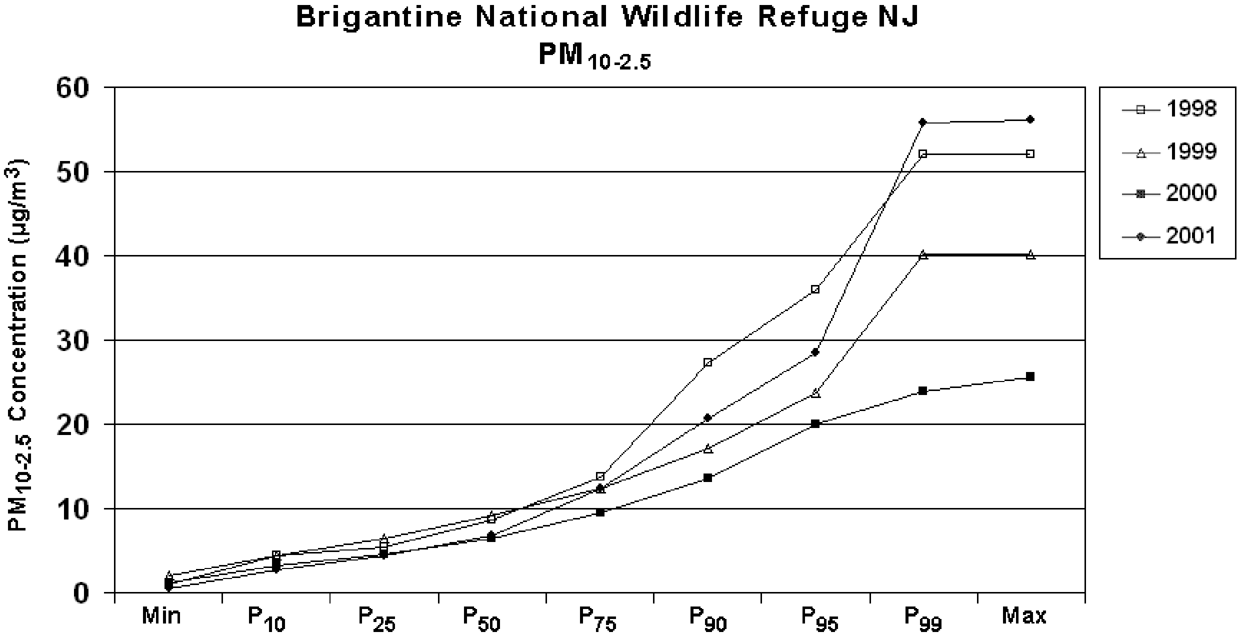
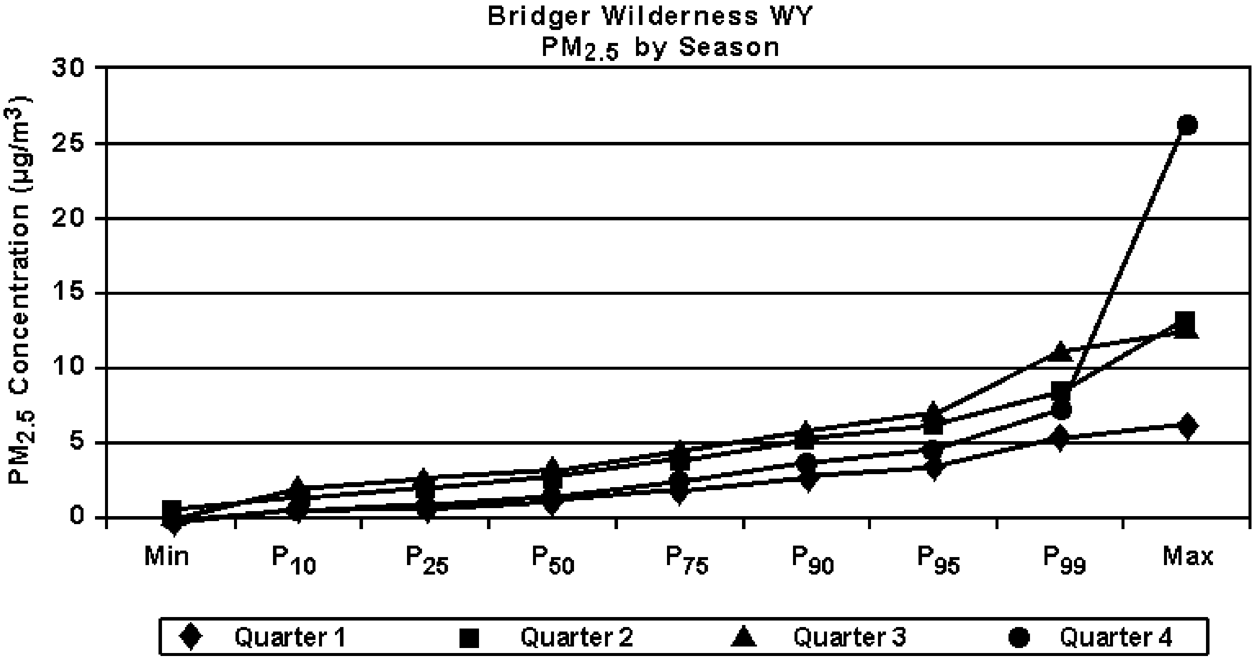


Figure 3E-3c,d. **Interannual variability in 24-h average $PM_{10-2.5}$ concentrations observed at selected IMPROVE sites: (a) Bridger Wilderness, WY; (b) Yellowstone National Park, WY; (c) Dolly Sods/Otter Creek Wilderness, WV; and (d) Brigantine National Wildlife Refuge, NJ.**



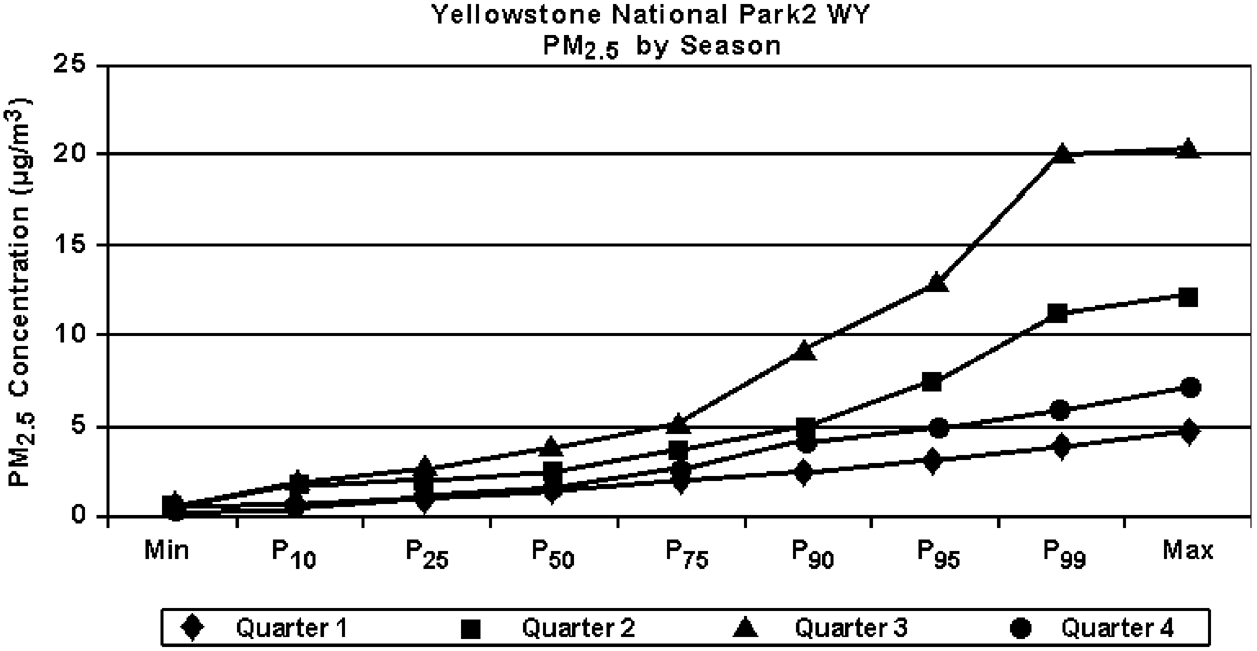


Figure 3E-4a,b. **Seasonal variability in 24-h average $PM_{2.5}$ concentrations observed at selected IMPROVE sites: (a) Bridger Wilderness, WY; (b) Yellowstone National Park, WY; (c) Dolly Sods/Otter Creek Wilderness, WV; and (d) Brigantine National Wildlife Refuge, NJ.**

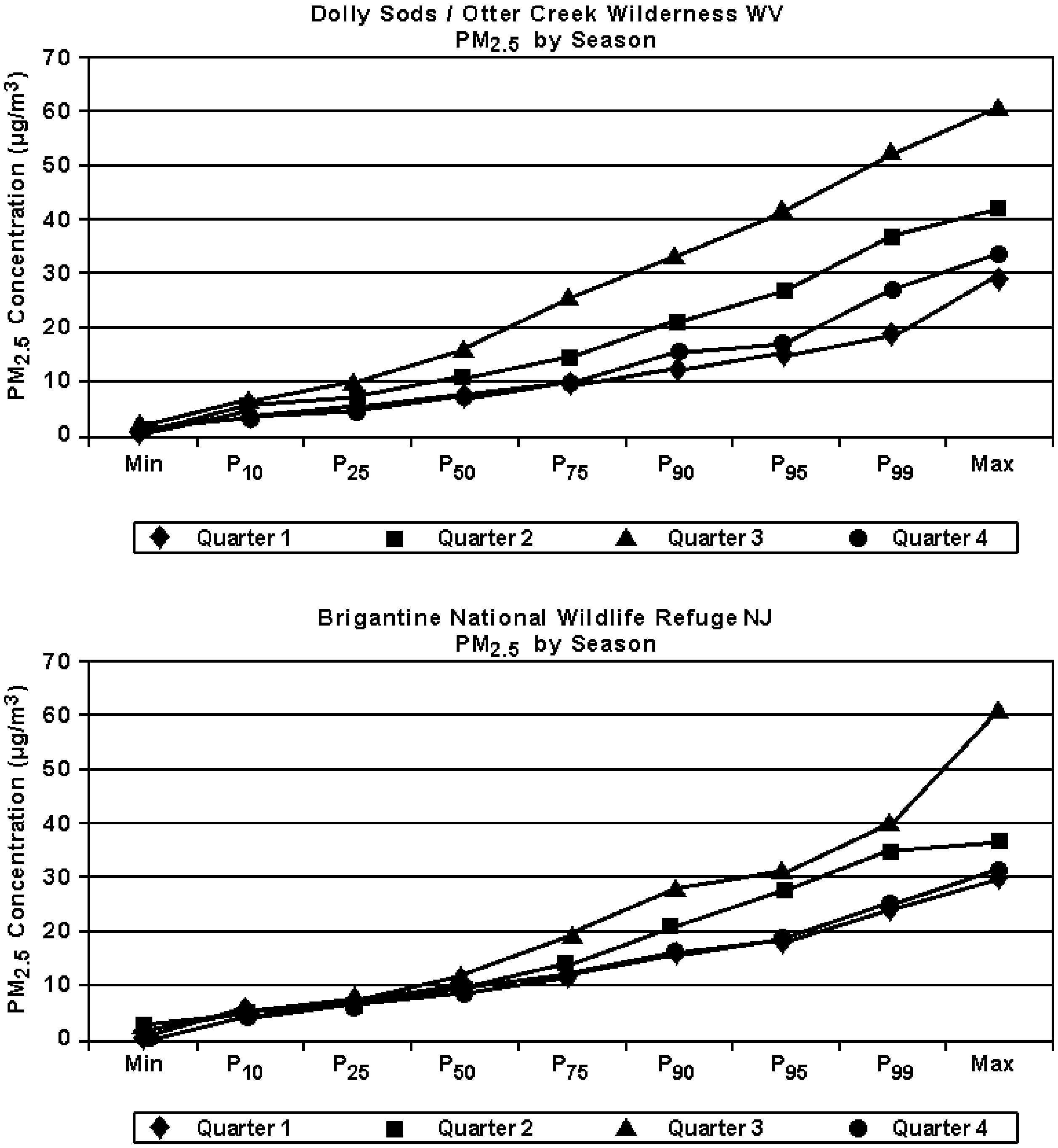
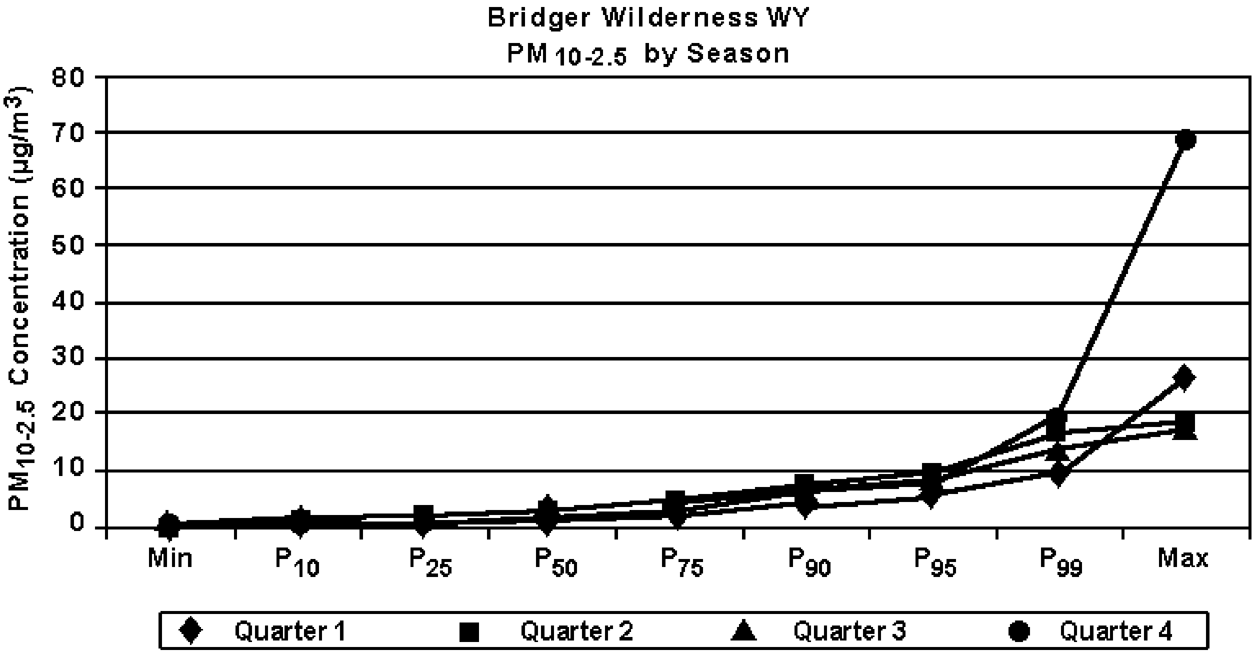


Figure 3E-4c,d. Seasonal variability in 24-h average $PM_{2.5}$ concentrations observed at selected IMPROVE sites: (a) Bridger Wilderness, WY; (b) Yellowstone National Park, WY; (c) Dolly Sods/Otter Creek Wilderness, WV and (d) Brigantine National Wildlife Refuge, NJ.



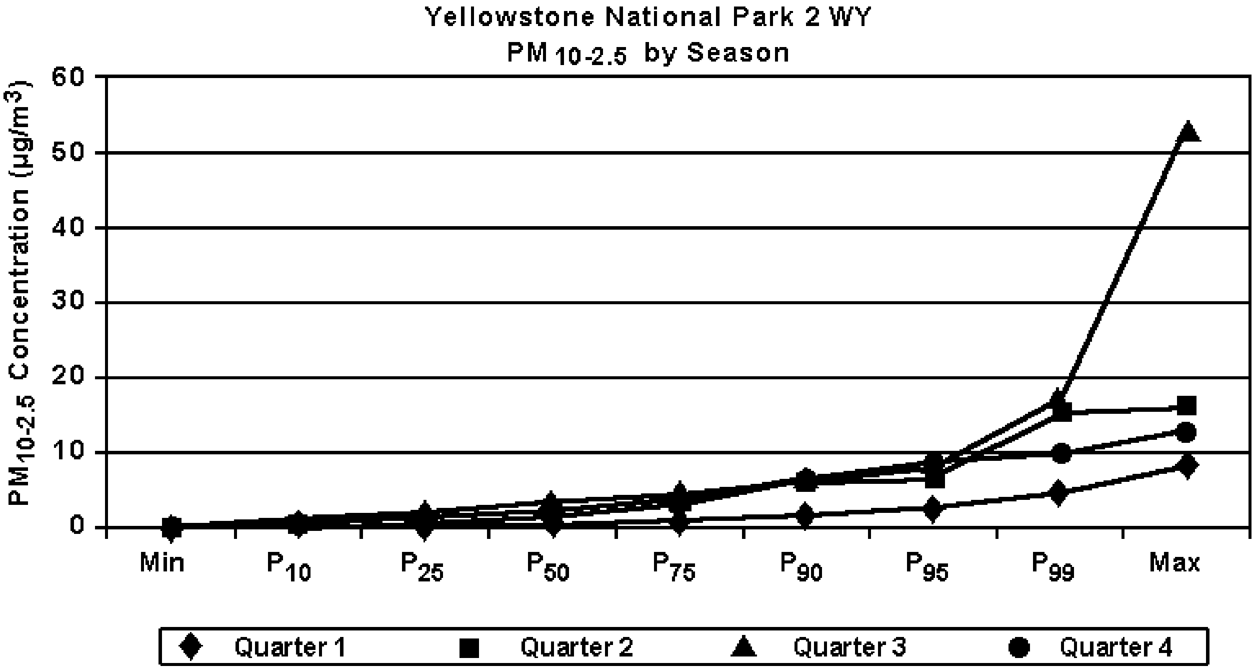
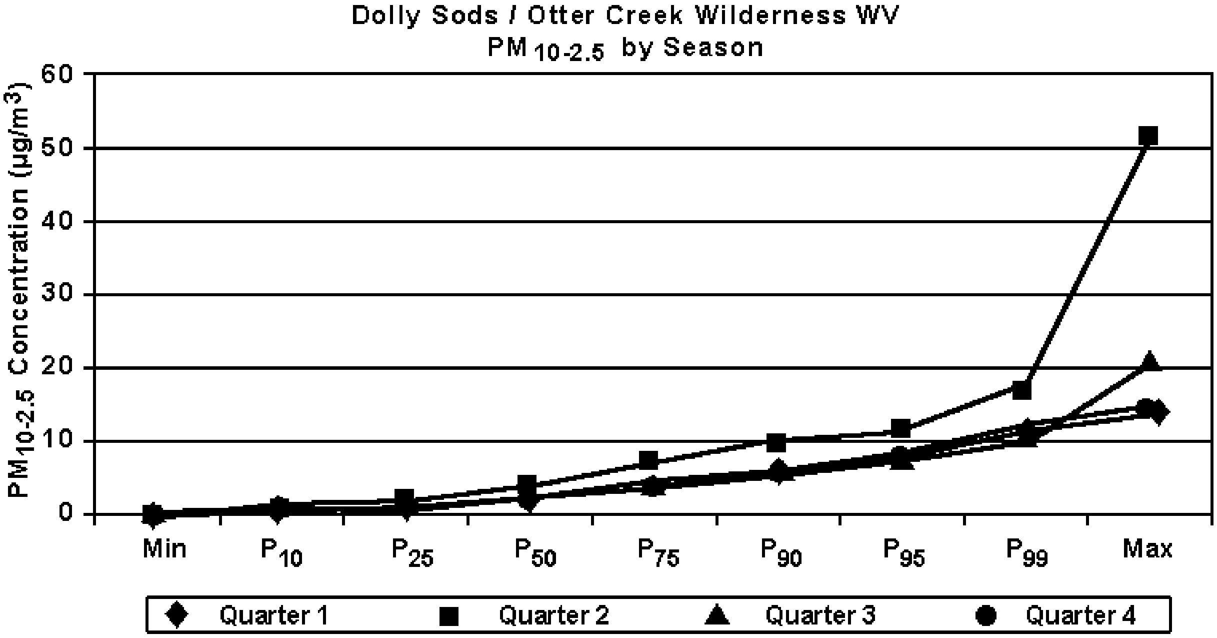


Figure 3E-5a,b. **Seasonal variability in 24-h average $PM_{10-2.5}$ concentrations observed at selected IMPROVE sites: (a) Bridger Wilderness, WY; (b) Yellowstone National Park, WY; (c) Dolly Sods/Otter Creek Wilderness, WV; and (d) Brigantine National Wildlife Refuge, NJ.**



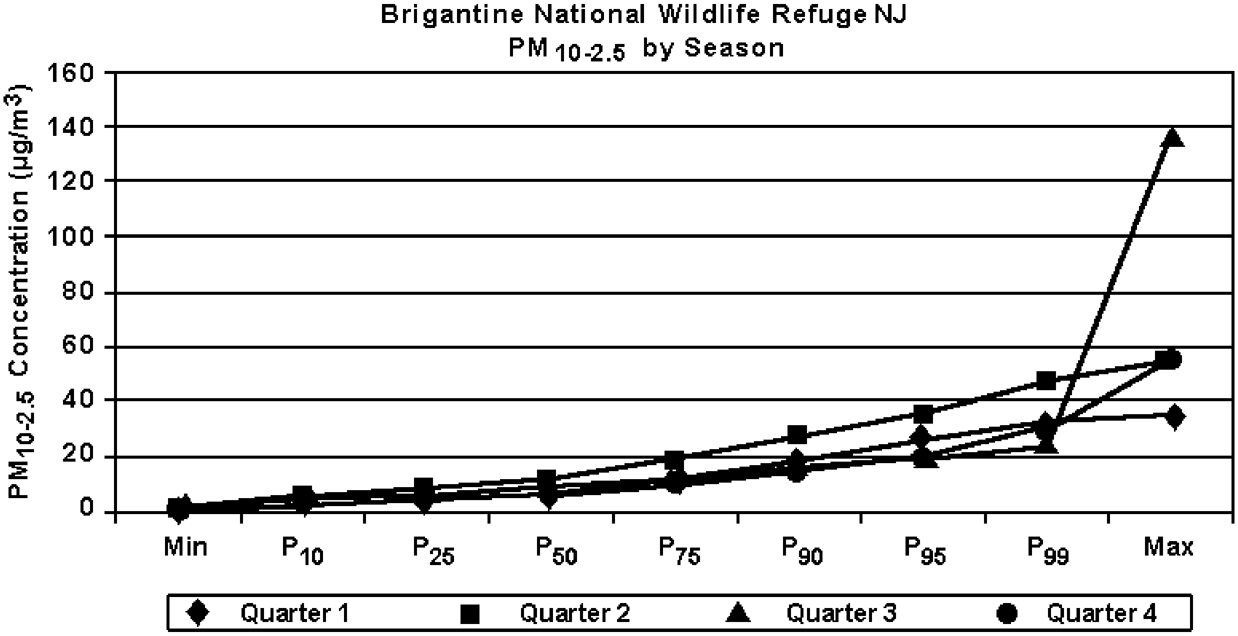


Figure 3E-5c,d. Seasonal variability in 24-h average $PM_{10-2.5}$ concentrations observed at selected IMPROVE sites: (a) Bridger Wilderness, WY; (b) Yellowstone National Park, WY; (c) Dolly Sods/Otter Creek Wilderness, WV; and (d) Brigantine National Wildlife Refuge, NJ.

4. ENVIRONMENTAL EFFECTS OF AIRBORNE PARTICULATE MATTER

4.1 INTRODUCTION

This chapter assesses information providing inputs to U.S. EPA decision making on secondary National Ambient Air Quality Standards (NAAQS) aimed at protecting against welfare effects of ambient airborne particulate matter (PM). Specifically, it assesses the effects of atmospheric PM on the environment, including: (a) direct and indirect effects on vegetation and natural ecosystem integrity; (b) effects on visibility; and (c) effects on man-made materials, as well as (d) relationships of atmospheric PM to climate change processes. The 1997 EPA revisions to the U.S. PM NAAQS, discussed in Chapter 1 (Introduction), included establishment of $PM_{2.5}$ secondary standards identical to the primary $PM_{2.5}$ NAAQS set at that time. The 1997 FR notice promulgating these standards noted “The new secondary standards, in conjunction with a regional haze program, will provide appropriate protection against PM-related public welfare effects including soiling, material damage, and visibility impairment.”

4.2 EFFECTS OF AMBIENT AIRBORNE PM ON VEGETATION AND NATURAL ECOSYSTEMS

Introduction

The effects of airborne particles are manifested via physical and chemical effects exerted at the individual plant level. However, plants are key members of ecosystems, structurally complex communities comprised of populations of plants, animals (including humans), insects, and microorganisms that interact with one another and with their non-living (abiotic) chemical and physical environment in which they exist (Odum, 1989; U.S. Environmental Protection Agency, 1993). All life on Earth is dependent on chemical energy in the form of carbon compounds to sustain their life processes. Terrestrial vegetation, via the process of photosynthesis, provides approximately half of the carbon that annually cycles between the Earth and the atmosphere (Chapin and Ruess, 2001).

Ecosystems respond to stresses through their constituent organisms. The responses of plant species and populations to environmental perturbations (such as those caused by atmospheric PM) depend on their genetic constitution (genotype), their life cycles, and the microhabitats in which they are growing. Stresses that produce changes in their physical and chemical environment apply selection pressures on individual organisms (Treshow, 1980). The changes that occur within populations and plant communities reflect these new and different pressures. A common response in a community under stress is the elimination of the more sensitive populations and an increase in abundance of species that tolerate or are favored by stress (Woodwell, 1970, Guderian et al., 1985).

The present section is organized to discuss: (1) factors affecting deposition of airborne PM on plants and ecosystems and then (2) the effects of PM deposition on individual plants, plant populations, forest trees and terrestrial ecosystems. As such, the section is organized to follow, in rough outline, the Framework for Assessing and Reporting on Ecological Condition recommended in a report by the Ecological Processes and Effects Committee (EPEC) of EPA's Science Advisory Board (Science Advisory Board, 2002), which states "The purpose of this report is to provide the Agency with a sample framework that may serve as a guide for designing a system to assess, and then report on, ecological condition at local, regional, or national scale. The sample framework is intended as an organizing tool that may help the Agency decide what ecological attributes to measure and how to aggregate those measurements into an understandable picture of ecological integrity." This framework is not actually a risk assessment per se, but it can be used to "construct a report of ecological condition" that characterizes the ecological integrity of an ecosystem based on "the relationship between common anthropogenic stressors and one or more of the six Essential Ecological Attributes." It nevertheless does provide a useful approach for organizing discussions of stressor effects on ecosystem components at successive levels of complexity.

4.2.1 Ecological Attributes

The EPEC Framework provides a checklist of generic ecological attributes that should be considered when evaluating the integrity of ecological systems (see Table 4-1). The six generic ecological attributes, termed Essential Ecological Attributes (EEA), represent groups of related ecological characteristics (Science Advisory Board, 2002; Harwell et al., 1999) and include:

TABLE 4-1. ESSENTIAL ECOLOGICAL ATTRIBUTES AND REPORTING CATEGORIES

Landscape Condition

- Extent of Ecological System/Habitat Types
- Landscape Composition
- Landscape Pattern and Structure

Biotic Condition

- Ecosystems and Communities
  - Community Extent
  - Community Composition
  - Trophic Structure
  - Community Dynamics
  - Physical Structure
- Species and Populations
  - Population Size
  - Genetic Diversity
  - Population Structure
  - Population Dynamics
  - Habitat Suitability
- Organism Condition
  - Physiological Status
  - Symptoms of Disease or Trauma
  - Signs of Disease

Chemical and Physical Characteristics (Water, Air, Soil, and Sediment)

- Nutrient Concentrations
  - Nitrogen
  - Phosphorus
  - Other Nutrients
- Trace Inorganic and Organic Chemicals
  - Metals
  - Other Trace Elements
  - Organic Compounds
- Other Chemical Parameters
  - pH
  - Dissolved Oxygen
  - Salinity
  - Organic Matter
  - Other
- Physical Parameters

Ecological Processes

- Energy Flow
  - Primary Production
  - Net Ecosystem Production
  - Growth Efficiency
- Material Flow
  - Organic Carbon Cycling
  - Nitrogen and Phosphorus Cycling
  - Other Nutrient Cycling

Hydrology and Geomorphology

- Surface and Groundwater flows
  - Pattern of Surface flows
  - Hydrodynamics
  - Pattern of Groundwater flows
  - Salinity Patterns
  - Water Storage
- Dynamic Structural Characteristics
  - Channel/Shoreline Morphology, Complexity
  - Extent/Distribution of Connected Floodplain
  - Aquatic Physical Habitat Complexity
- Sediment and Material Transport
  - Sediment Supply/Movement
  - Particle Size Distribution Patterns
  - Other Material Flux

Natural Disturbance Regimes

- Frequency
- Intensity
- Extent
- Duration

Source: Science Advisory Board (2002).

Chemical and Physical Characteristics; Biotic Conditions; Landscape Conditions; Ecological Processes; Hydrology and Geomorphology; and Natural Disturbance Regimes. All of the EEAs are interrelated (i.e., changes in one EEA may directly or indirectly affect other EEAs).

The first three ecological attributes listed in Table 4-1 are primarily “patterns,” whereas the last three are “processes.” Ecological science has used “patterns” and “processes” as terms to describe features of ecological systems for many years (e.g., Bormann and Likens, 1979). Of main concern in this chapter are relationships between a certain class of diverse airborne stressors from anthropogenic sources, termed particulate matter (PM), and one or more of the EEAs. Changes in patterns resulting from responses of vegetation and ecosystems to the effects of fine and coarse PM deposition, along with known or possible effects on ecological processes associated with changes in the patterns, are discussed in the subsections that follow.

The reader is also referred to several other sources for more detailed discussions of several topics only briefly alluded to or addressed here. For example, an extensive discussion of various types of effects of acidic deposition is presented in the U.S. National Acid Precipitation Assessment Program (NAPAP) Biennial Report to Congress: An Integrated Assessment Program (National Scientific and Technology Council, 1998). Additionally, ecological effects of acidic precipitation and nitrate deposition on aquatic systems are discussed in the EPA Air Quality Criteria Document for Nitrogen Oxides (U.S. Environmental Protection Agency, 1993); and sulfate deposition and effects, as related to wetlands and aquatic habitats, are discussed in U.S. Environmental Protection Agency (1982). Effects of lead on crops, vegetation, and ecosystems are assessed in the EPA document, Air Quality Criteria for Lead (U.S. Environmental Protection Agency, 1986). Lastly, effects of “certain pesticides, metal compounds, chlorinated organic compounds, and nitrogen compounds” are discussed in Deposition of Air Pollutants to the Great Waters, Third Report to Congress (U.S. Environmental Protection Agency, 2000a).

4.2.2 Ecosystem Exposures – Particle Deposition

Airborne particles, their precursors, and their transformation products are removed from the atmosphere by wet and dry deposition processes. This atmospheric cleansing process fortunately lowers the long-term buildup of lethal concentrations of these pollutants in the air and moderates the potential for direct human health effects caused by their inhalation. Unfortunately, these deposition processes also mediate the transfer of PM pollutants to other environmental media where they can and do alter the structure, function, diversity, and sustainability of complex ecosystems.

The potential effects of PM deposition on vegetation and ecosystems encompass the full range, scales, and properties of biological organization listed under Biotic Condition, Table 4-1. Exposure to a given mass concentration of airborne PM, however, may lead to widely differing responses, depending on the particular mix of deposited particles**.** Particulate matter is not a single pollutant, but rather a heterogeneous mixture of particles differing in size, origin, and chemical composition. This heterogeneity exists across individual particles within samples from individual sites and, to an even greater extent, between samples from different sites. Thus far, atmospheric PM has been defined, for regulatory purposes, mainly by size fractions and less clearly so in terms of chemical nature, structure, or source. While size is related to the mode and magnitude of deposition to vegetated landscapes and may be a useful surrogate for chemical constitution, PM size classes do not necessarily have specific differential relevance for vegetation effects (Whitby, 1978; U.S. Environmental Protection Agency, 1996a); that is, both fine- and coarse-mode particles may affect plants. Much of the burden of sulfates, nitrates, ammonium salts, and hydrogen ions resides in the atmosphere either dissolved in fog water or as liquid or solid aerosols. Therefore, assessment of atmospheric PM deposition and effects on vegetation unavoidably include discussion of nitrates and sulfates and associated compounds involved in acidic and acidifying deposition. Other important issues relate to trace elements and heavy metals often found in ambient airborne PM.

4.2.2.1 Fine and Coarse Particulate Matter

Particulate matter in current U.S. regulatory standards is classified as fine PM ($PM_{2.5}$; $\leq$ 2.5 µm aerodynamic diameter) and coarse PM (2.5–10 µm). These combined fractions constitute PM_{10} (U.S. Environmental Protection Agency, 1996a,b).

Fine and coarse PM have a number of contrasting properties that affect their impact on vegetated systems (see Chapter 2, Table 2-1 of this document). The model results of Wiman and Agren (1985) and the measurements of Lovett and Lindberg (1993) addressing the complexity of deposition processes in patchy forested landscapes and vertical stratification within canopies reveal clear distinctions between the deposition behavior of fine and coarse particles. For one, coarse particles settle nearer their site of formation than do fine particles. Also, the chemical constitution of individual particles is strongly correlated with size (i.e., most S and much N is present on fine particles, whereas much of the base cation and heavy metal burden is present on coarse particles) and influences the predicted landscape loading of specific elements. Atmospheric PM may also act as a carrier for other directly phytotoxic materials (e.g., herbicides). Fine PM dominates the surface area of particles suspended in the atmosphere, while coarse PM dominates the mass of such airborne particles. Surface area may become more central to ecological impact assessment as recognition of the oxidizing capacity of fine particles, their interactions with other pollutants such as ozone, and their adsorption of phytoactive organic compounds such as herbicides become more fully appreciated. Fine and coarse particles respond to changes in atmospheric humidity, precipitation, and wind through different mechanisms, differentially altering their deposition characteristics.

Fine PM may exhibit similar mass concentrations at different sites (Figure 4-1) and yet be composed of very different constituents. In eastern North America, sulfate typically is the major component of this fraction, in contrast to the West where nitrate is a key component (Figure 4-1; cf., the eastern Appalachian site and the western California site). On the other hand, in the urban center of Mexico City (Hidy et al., 2000), an environment more similar to the western than eastern U.S., concentrations of fine PM of about 300 $\mu g\ m^{-3}$ are found, and sulfate concentrations are 3 times that of nitrate. In contrast to sulfur and nitrogen, the contributions of organic and elemental carbon to the eastern and western U.S. sites were similar (Figure 4-1); soil-derived geologic material was greater at the more arid western site.

Fine PM is typically more diverse than coarse PM and is secondary in nature, having condensed from the vapor phase or been formed by chemical reaction from gaseous precursors in the atmosphere (see Chapter 2). Fine PM derives from atmospheric gas-to-particle conversion reactions involving nucleation, condensation, and coagulation, and from evaporation of water from contaminated fog and cloud droplets. Sulfur and nitrogen oxides (SO_x and NO_x) are often oxidized to their respective acids and neutralized with ammonium cations as particulate salts. Fine PM may also contain condensates of volatile organic compounds, volatilized metals, and products of incomplete combustion (see Chapter 3).

Coarse PM, in contrast, is mainly primary in nature, having been emitted from area or point sources as fully formed particles derived from abrasion and crushing processes, soil disturbances, desiccation of marine aerosol from bursting bubbles, hygroscopic fine PM expanding with humidity to coarse mode, and/or gas condensation directly onto pre-existing coarse particles (see Chapters 2 and 3). Suspended primary coarse PM may contain iron, silica,

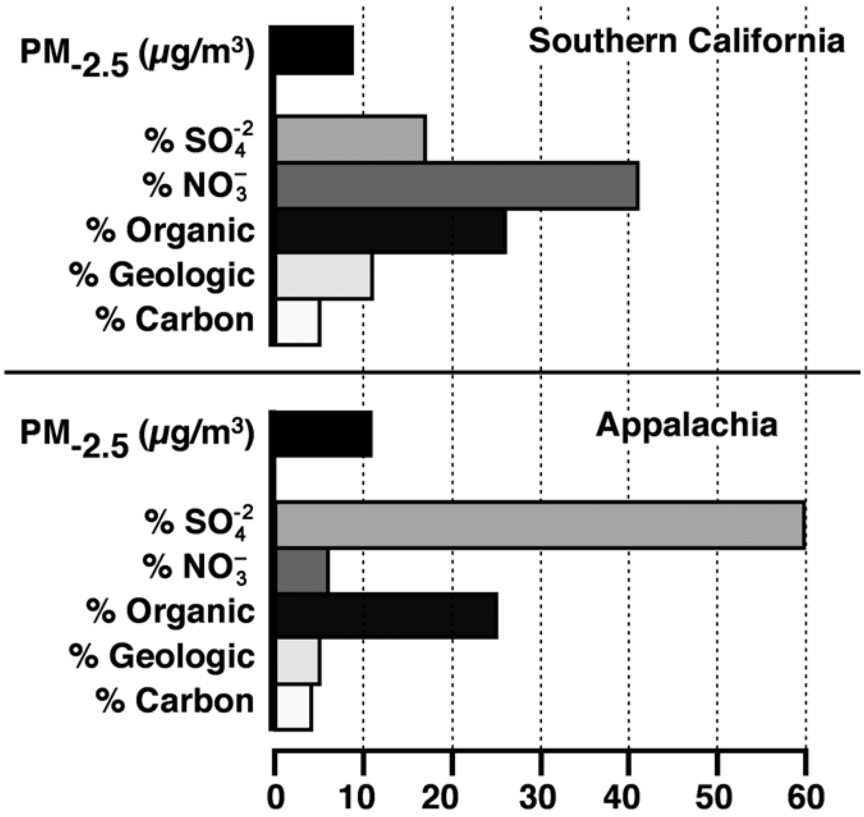


Figure 4-1. The diversity of fine PM from sites in the western and eastern U.S.

Modified from Sisler and Malm (2000).

aluminum, and base cations from soil, plant and insect fragments, pollen, fungal spores, bacteria, and viruses, as well as fly ash, brake linings, debris, and automobile tire fragments. Coarse-mode particles can be altered by chemical reactions and/or physical interactions with gaseous or liquid contaminants.

The coating of coarse particles with semivolatile materials can substantially affect their deposition and potential for biological effects. For example, nitrogen exhibits a strongly bimodal size distribution: the peak above 1 µm can be attributed to HNO_3 adsorption onto coarse alkaline particles; and that below 1 µm can be attributed to gas phase condensation of ammonia with either sulfuric or nitric acid yielding either $(NH_4)_2SO_4$ or NH_4NO_3 aerosol. HNO_3 has an extremely high deposition velocity, nearly independent of the physiology of the surface.

Therefore, formation of ammonium nitrate reduces nitrogen deposition, because the deposition velocity of these particles is much less than that of HNO_3 gas.

Similarly, anthropogenic emissions of sulfur are mostly as sulfur dioxide (SO_2), which is hydrophilic, rapidly hydrated, and subsequently oxidized to sulfate (SO_4^{-2}), which is about 30-fold less phytotoxic than SO_2. The ratio of SO_4^{-2}: SO_2 increases with aging of the air mass and, therefore, with distance from the source. Sulfate is thus a widespread regional/global pollutant and is sufficiently hygroscopic, that in humid air it exists significantly in the coarse PM fraction. It is unusual for injurious levels of particulate sulfate to be deposited upon vegetation, while direct injury due to SO_2 is commonly observed near uncontrolled point sources. Gas-to-particle conversion in this case is of benefit to vegetation. The chemical composition of gaseous precursors of particulate matter and the formation of sulfates and nitrates is discussed in Section 2.1.3 of Chapter 2.

Since enactment of the 1990 Clean Air Act Amendments, the atmospheric mix of PM precursors in the United States has changed substantially. That is, as emissions of SO_2 have declined, emissions of oxides of nitrogen (NO_x) have remained about the same, but emissions of cations have increased. This is almost certainly due to increased suspension of wind-borne geologic material from exposed soils.

For characterization of tropospheric chemistry, deposition of O_3, NO_x, peroxides, and ammonia are first-order problems, followed by deposition of organics, SO_2, and particulate sulfate and nitrate (Wesely and Hicks, 2000). For impact on vegetation, however, the order may be different and may include different species — notably SO_2, fluoride where it still exists as a problem, particulate heavy metals, base cations, sulfate and nitrate. In spite of the current regulatory focus on non-speciated PM, exposure to a given mass concentration of PM may lead to widely differing phytotoxic outcomes depending upon the particular mix of PM constituents involved. This variability has not been characterized adequately. Though effects of specific chemical fractions of PM have been described, there has been relatively little research aimed at defining the effects of unspeciated PM on plants or ecosystems.

4.2.2.2 Diversity of Deposition Modes

Atmospheric deposition of particles to ecosystems takes place via both wet and dry processes, through three major routes: (1) wet, by precipitation scavenging in which particles are deposited in rain and snow; (2) much slower dry deposition; and (3) occult deposition (so named because it was hidden from measurements which determined the previous two types of deposition) by fog, cloud-water, and mist interception (Table 4-2). Unlike gaseous dry deposition, neither the solubility of the particle nor the physiological activity of the surface are likely to be of first order importance in determining particulate dry deposition velocity (V_d). Factors that contribute to surface wetness or stickiness may be critical determinants of deposition efficiency. Available tabulations of deposition velocity are highly variable and suspect. Recent evidence indicates that all three modes of deposition (wet, occult, and dry) must be considered in determining inputs to watersheds or ecosystems because each may dominate over specific intervals of time or space and ultimately, by interception and impaction onto vegetation or other rough elements in the landscape.

The distribution of deposition between wet, dry, and occult modes varies substantially between locations for both nitrogen and sulfur (Figure 4-2). Clearly, rainfall and snowfall will determine the magnitude of wet deposition. Precipitation events clean the air so that dry deposition is eliminated or reduced during subsequent dry periods. Occult deposition depends upon landscape interception of the cloud base (Cape, 1993). This may occur at high elevation sites, in coastal areas subject to onshore advection, or in low-lying interior areas subject to radiation fogs. Thus, ecosystem exposure is determined by the mode, and to some extent the magnitude, of deposition. Total deposition particularly for nitrogen, among mountain sites is related to the magnitude of the occult deposition, particularly for nitrogen (Figure 4-2). Topography and vegetation characteristics influence the deposition modes differently (Table 4-3). In general, dry deposition is the most sensitive and wet deposition is the least sensitive to features of the vegetated surface.

Comparison of micrometeorological and other methods for estimating particle deposition velocity (Erisman et al., 1997) suggests that there is little discrepancy between contrasting methodologies for estimating particle deposition and that this conclusion holds for both anions and cations, with the exception of nitrogenous species, which appear to interact with foliage in more complex ways. These comprehensive studies in the Speulder forest in the Netherlands indicated that aerosol deposition represents a considerable fraction of total deposition to the landscape. At this location, occult deposition was relatively insignificant, but dry deposition accounted for about one-fourth of alkaline-earth cation deposition.

TABLE 4-2. TYPES AND DETERMINANTS OF PARTICULATE DEPOSITION AND IMPACT TO VEGETATION

Type of Deposition	Determinant of Deposition	Quantifiable Factors
Dry Deposition	Ambient Concentration	Distance from Source Emission Strength
	Atmospheric Conditions	Wind Speed Stability Mixing Height Temperature Humidity Dew Formation
	Aerosol Properties	Chemical Reactivity Particle Solubility Aerodynamic Diameter Biological Availability Hygroscopicity
	Surface Roughness	Terrain Discontinuity Leaf Pubescence Leaf Shape Plant Density Branch Spacing Tissue Flexibility
	Vegetation Condition	Surface Wetness Salt Exudates Organic Exudates Insect Excreta
Wet Deposition	Ambient Concentration	Distance from Source Emission Strength
	Atmospheric Conditions	Mixing Height Timing of Precipitation Intensity of Precipitation Duration of Precipitation
	Aerosol Properties	Chemical Reactivity Particle Solubility Biological Availability
	Surface Roughness	Terrain Discontinuity Leaf Pubescence Leaf Area Index Nature of Exposed Bark and Stem
Occult Deposition	As Above	Combination of Above Factors

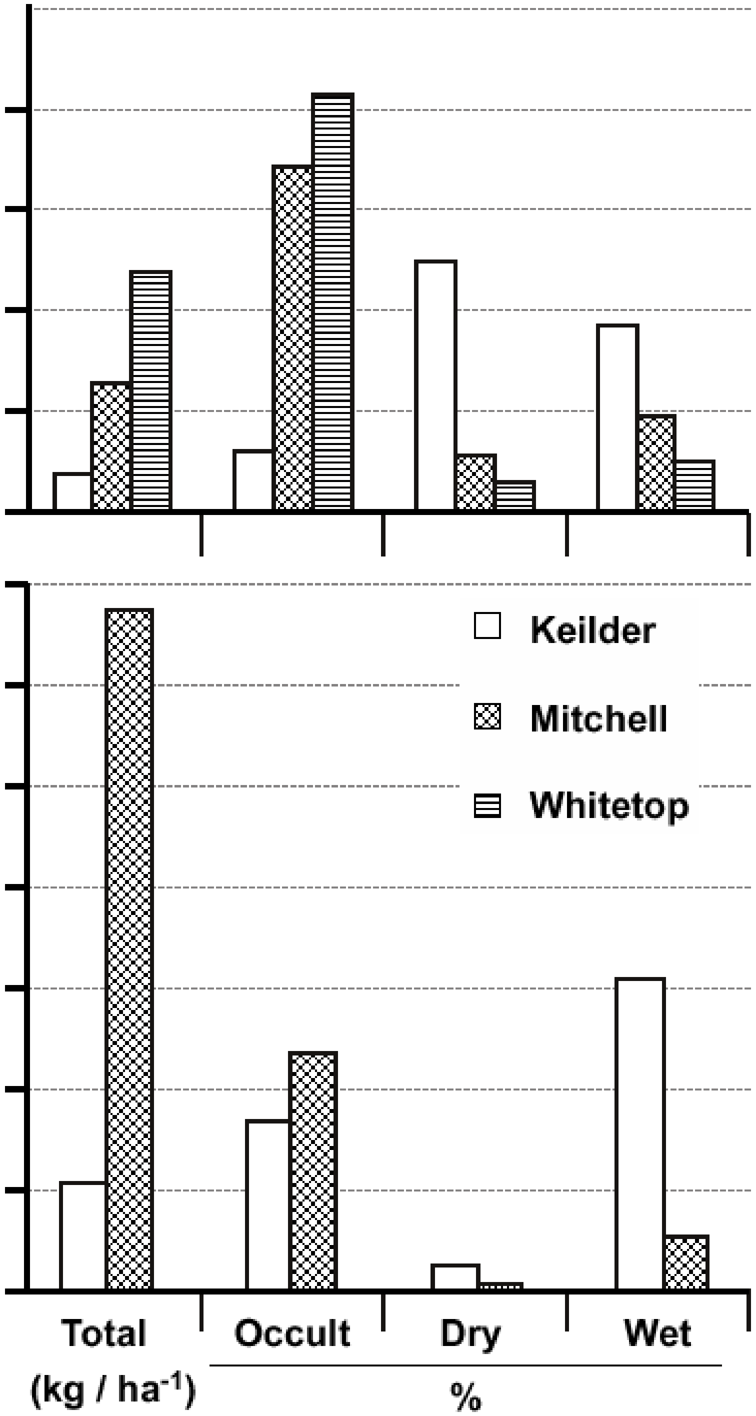


Figure 4-2. Relative importance of three modes of deposition of nitrate (A) and sulfate (B) at high elevation sites (Unsworth and Wilshaw, 1989; Fowler et al., 1989; Mueller, 1988; Aneja and Murthy, 1994).

TABLE 4-3. RELATIVE IMPORTANCE OF WET, DRY, PARTICULATE, AND TOTAL DEPOSITION TO THREE FOREST SITES[a]

	Deposition							
	Total Nitrogen[b]				Total Sulfur[c]			
Site	Wet (%)	Dry (%)	Particle (%)	Total (kg ha^{-1})	Wet (%)	Dry (%)	Particle (%)	Total (kg ha^{-1})
Duke Forest	75	25	0.11	9.87	64	33	2.7	17.20
Cary Forest	71	20	0.94	5.80	76	20	4.2	7.60
Austin Forest	71	29	0.58	6.57	83	13	4.3	7.79

[a] Data from Allen et al. (1994). Sampling was by triple filter pack so that fine-mode particles could be sampled preferentially. An average particle deposition velocity of 0.9 cm s^{-1} was derived as in Hicks et al. (1987).

[b] Wet nitrogen consists of NO_3^- and NH_4^+; dry nitrogen consists of vapor phase HNO_3 and NO_2; and particulate nitrogen consists of NO_3^-.

[c] Wet sulfur consists of SO_4^{-2}, dry sulfur consists of vapor phase SO_2, and particulate sulfur consists of $pSO_4^{-2.}$

Wet Deposition

Wet deposition results from the incorporation of atmospheric particles and gases into cloud droplets and their subsequent precipitation as rain or snow, or from the scavenging of particles and gases by raindrops or snowflakes as they fall (Lovett, 1994). Precipitation scavenging, in which particles are incorporated in hydrometers and deposited in the resulting rain and snow, includes rainout (within-cloud incorporation by nucleation) and washout (below-cloud scavenging by impaction). Wet deposition generally is confounded by fewer factors than dry or occult deposition and has been easier to quantify. Total inputs from wet deposition to vegetative canopies can be significant (Table 4-3), although not all wet deposition involves particle scavenging because gaseous pollutants also dissolve in raindrops during precipitation events (Lovett, 1994). This contribution is obscured during measurements because wet deposition is measured simply by chemical analysis of total precipitation collected in clean, non-reactive buckets. Exclusion of dry deposited material (as opposed to dissolved gaseous species) requires closure or covering of the vessels except during precipitation.

Wet deposition is largely a function of precipitation amount and ambient pollutant concentrations. It is not affected by surface properties (Table 4-2) as much as dry or occult deposition although leaves (depending on their surface properties of wettability, exposure, and roughness) retain liquid and solubilized PM. Extensive vegetative canopies typically develop leaf area indices (LAI; ratio of projected leaf area to ground area) much greater than 1. Thus any material deposited via precipitation to the upper stratum of foliage likely will be intercepted by several foliar surfaces before reaching the soil.

Landscape characteristics may also be important. Forested hillsides receive four- to six-fold greater inputs of wet deposition than short vegetation in nearby valleys. This is due to a variety of orographic effects (Unsworth and Wilshaw, 1989) and closer aerodynamic coupling to the atmosphere of tall forest canopies than of the shorter canopies in the valleys. This leads to more rapid foliar drying, which reduces the residence time but concentrates the solubilized particulate materials available for foliar uptake on the cuticular surface more quickly; and concentration increases the thermodynamic driving force for foliar uptake (Fowler et al., 1991; Unsworth, 1984; Schönherr and Huber, 1977). Following wet deposition, humidity and temperature conditions strongly influence the extent of biological effects, because of the competing effects of drying versus concentrating the solutions, and influence the rate of metabolic uptake of surface solutes (Swietlik and Faust, 1984). The net consequence of these factors on direct physical effects of wet deposited PM on leaves is not known.

Rainfall both introduces new wet deposition and redistributes throughout the canopy previously dry-deposited particulate material, particularly coarse particles which are preferentially deposited in the upper foliage (Peters and Eiden, 1992). Both effects scale the likelihood of foliar contact and potential direct PM effects on vegetation nearly linearly with canopy leaf area. The concentrations of suspended and dissolved materials are typically highest at the onset and decline with duration of individual precipitation events (Lindberg and McLaughlin, 1986; Hansen et al., 1994). Sustained rainfall removes much of the accumulation of dry-deposited PM from foliar surfaces, reducing direct foliar effects and combining the associated chemical burden with the wet-deposited material (Lovett and Lindberg, 1984; Lovett, 1994) for transfer to the soil. Intense rainfall may contribute substantial total particulate inputs to vegetated land surfaces, mostly via the soil, but is less effective as a source of directly bioavailable or injurious pollutants to foliar surfaces. This washing effect, combined with differential foliar uptake and foliar leaching of different chemical constituents of PM alters the composition of the rainwater that reaches the soil. Low intensity precipitation events, in contrast, may deposit significantly more particulate pollutants to foliar-surfaces than high intensity precipitation events. Because of the short duration and limited atmospheric cleansing, the concentration of PM in the final precipitation that remains in contact with foliar surfaces may be high. Additionally, such events may facilitate foliar uptake by hydrating some previously dry-deposited particles without removing them. This combination of dry deposition to foliage and subsequent wet removal increases the potential for PM to exert effects via soil pathways: first by enhancing dry deposition relative to adjacent unvegetated surfaces; and second by accelerating passage along with wet deposited material of the deposited PM by throughfall and stemflow to the soil. In the soil, PM may affect important ecosystem-level biogeochemical cycles of major, minor, and trace elements.

Dry Deposition

Dry deposition of atmospheric particles to plant and soil is a much slower process than wet or occult deposition, but it acts nearly continuously and affects all exposed surfaces (Hicks, 1986). In dry deposition, particles at the large end of the spectrum (i.e., > 5 µm diameter) are deposited mainly by gravitational sedimentation and inertial impaction. Smaller particles, especially those with diameters between ≈ 0.2 and 2 µm, are not readily dry-deposited and tend to travel long distances in the atmosphere until their eventual deposition, most likely by incorporation into precipitation. This long-distance transport of fine aerosols is largely responsible for the regional nature of acid deposition (Lovett, 1994). A major conclusion from atmospheric deposition research is the realization that dry deposition is usually a significant and, in some cases, a dominant portion of total atmospheric deposition to an ecosystem (Lovett, 1994). Plant parts of all types, including those not currently physiologically active, along with exposed soil and water surfaces, receive steady deposits of dry dusts, elemental carbon encrustations, grease films, tarry acidic coatings, and heterogeneous secondary particles formed from gaseous precursors (U.S. Environmental Protection Agency, 1982). The range of particle sizes, the diversity of canopy surfaces, and the variety of chemical constituents in airborne PM have slowed progress in both prediction and measurement of dry particulate deposition. Particulate deposition is a complex, poorly characterized process controlled primarily by atmospheric stability, macro- and micro-surface roughness, particle diameter, and surface characteristics (Table 4-2; Hosker and Lindberg, 1982). Deposition of particles suspended regionally and throughout the full depth of the planetary boundary layer (PBL) is controlled by different mechanisms within the three distinct atmospheric transport zones above the surface.

In the lower atmosphere, fine particles are transported by turbulent eddies of mechanical and convective origin. In the relatively unstirred, laminar boundary layer surrounding individual surface elements, Brownian diffusion dominates. Near the surface, actual deposition and contact with the surface is mediated by impaction (El-Shobokshy, 1985).

Deposition fluxes may be calculated from measurements, estimates, or modeled values of mass concentration (C) at a specified measurement height and the total conductance or deposition velocity (V_d) from this height to the surface (Eq. 4-1; Hicks et al., 1987). These modeling techniques are closely allied with the micrometeorological techniques used to measure such fluxes. The flux (F) may be inferred as:

$$F = V_d * (C_z - C_o), \tag{4-1}$$

where F is flux to the surface, C_z is the particle concentration at measurement height z, C_o is the particle concentration at receptor sites in the canopy (usually assumed equal to 0), and V_d is the overall deposition velocity. The flux is controlled by V_d and C_z.

Vertical transport of particles through the lower atmosphere to the vicinity of the vegetation elements is by turbulence and sedimentation, such that:

$$V_d = V_t + V_s \tag{4-2}$$

in which V_t (inner, left hand pathway of Figure 4-3) is a turbulent diffusion term, and V_s is a sedimentation term that dominates deposition of very coarse particles (Figure 4-4) and increases with particle size (Figure 4-5; dotted line). Sedimentation may be considered a pathway parallel to turbulent transport (Figure 4-4), but this is an over simplification. V_s affects the concentration of particles near the surface where eddy transport may occur and also governs the redeposition of some fraction of the particles lost to resuspension or rebound following deposition by impaction. For this reason, V_s is included (Figure 4-3) in the composite surface resistance term ($R_aR_{cp}V_s$) as well as in the parallel sedimentation term.

For submicron particles for which sedimentation is negligible (Hicks et al., 1987; Monteith and Unsworth, 1990; Wesely, 1989), the Ohm's Law Analogy (resistance catena) analogous to that used to describe transport of heat, momentum, or gases may be adequate, as:

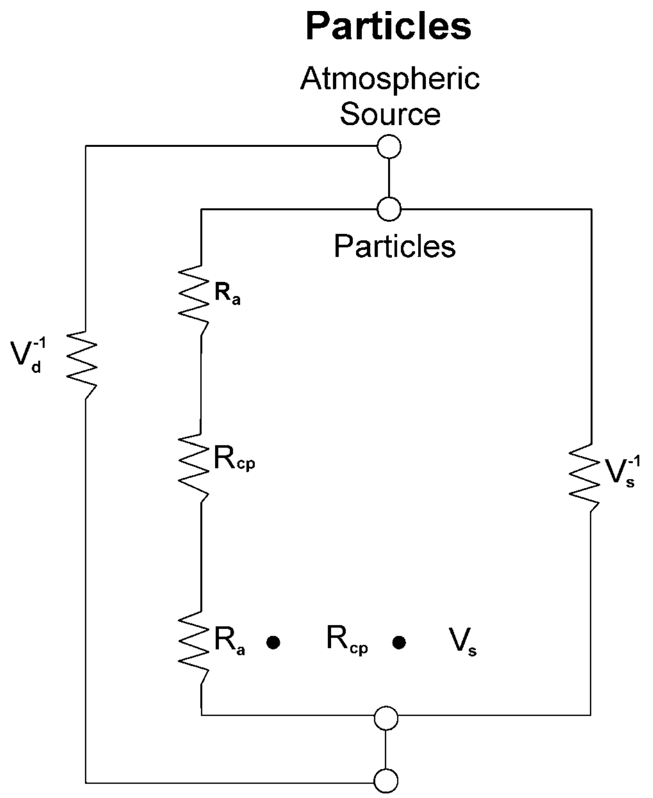


Figure 4-3. A simplified resistance catena representing the factors controlling deposition of particles to the surface. Vegetation-specific parameters are not explicitly considered. Modified after Hicks et al. (1987).

$$V_d = V_t = [r_a + r_b + r_c]^{-1}, \tag{4-3}$$

where V_t is the deposition velocity due to turbulent transport of particles or other entities through the atmosphere; r_a is aerodynamic resistance (inverse of conductance or velocity) associated with the efficiency of turbulent transport above the canopy; r_b is the boundary layer resistance associated with diffusional transport through the still air layer immediately adjacent to canopy elements; and r_c is canopy resistance associated with physiological control of leaf porosity via stomata in the leaf surface. Significant departures from the analogy arise near the surface (Chamberlain, 1975; Sehmel, 1980), as particles that were transported efficiently by turbulent eddies are slowed substantially in the laminar boundary layer that reduces the efficiency of impaction. The preservation of momentum in this zone declines with decreasing diameter;

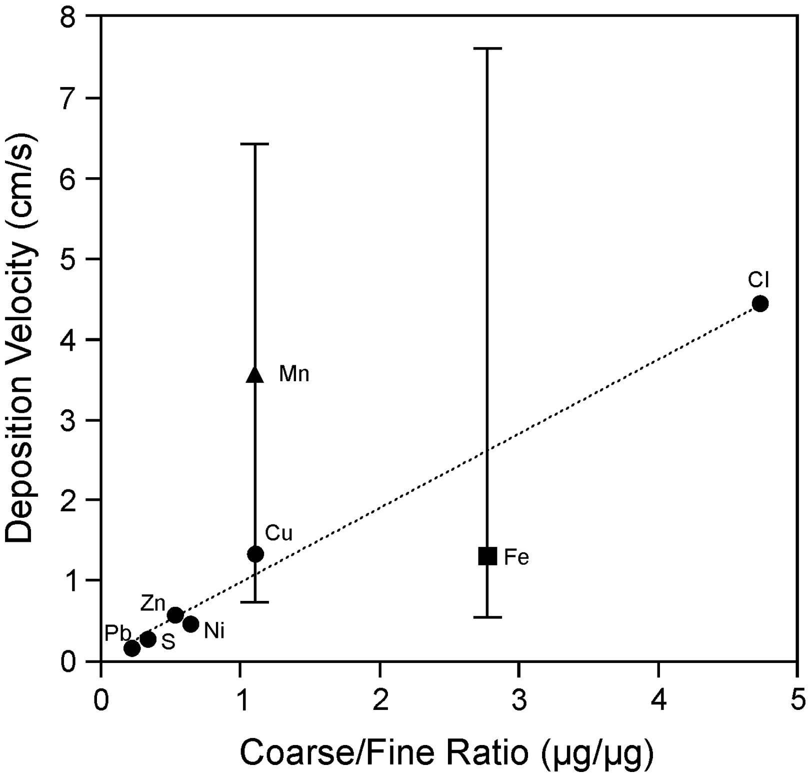


Figure 4-4. The relationship between deposition velocity of selected particulate materials and the distribution of the material between the coarse- and fine-aerosol fractions. Data from Foltescu et al. (1994). Ranges for Mn and Fe are from Davidson and Wu (1989).

however, this is offset by an increase in Brownian diffusivity with decreasing diameter (Figure 4-3). Aerodynamic streamlines are parallel to the surface of each roughness element, so that deposition ultimately depends on diffusion to the surface. The transition from impaction to diffusion is likely blurred in the presence of leaf pubescence extending beyond the boundary layer. These conflicting trends lead to a broad range over which empirical measurements of V_d and particle size are relatively independent (Figure 4-3), further demonstrating the importance of the quasilaminar boundary layer (Lamaud et al., 1994; Shinn, 1978).

The aerodynamic term (r_a) decreases with increasing wind speed, turbulence, and friction velocity and increases with measurement height and atmospheric stability. It describes the capacity of turbulent eddies to transport material, momentum, and heat between the measurement height and the roughness height of the surface. Coarse particles may not be carried efficiently by the high frequency eddies near the surface and may fall more rapidly than they

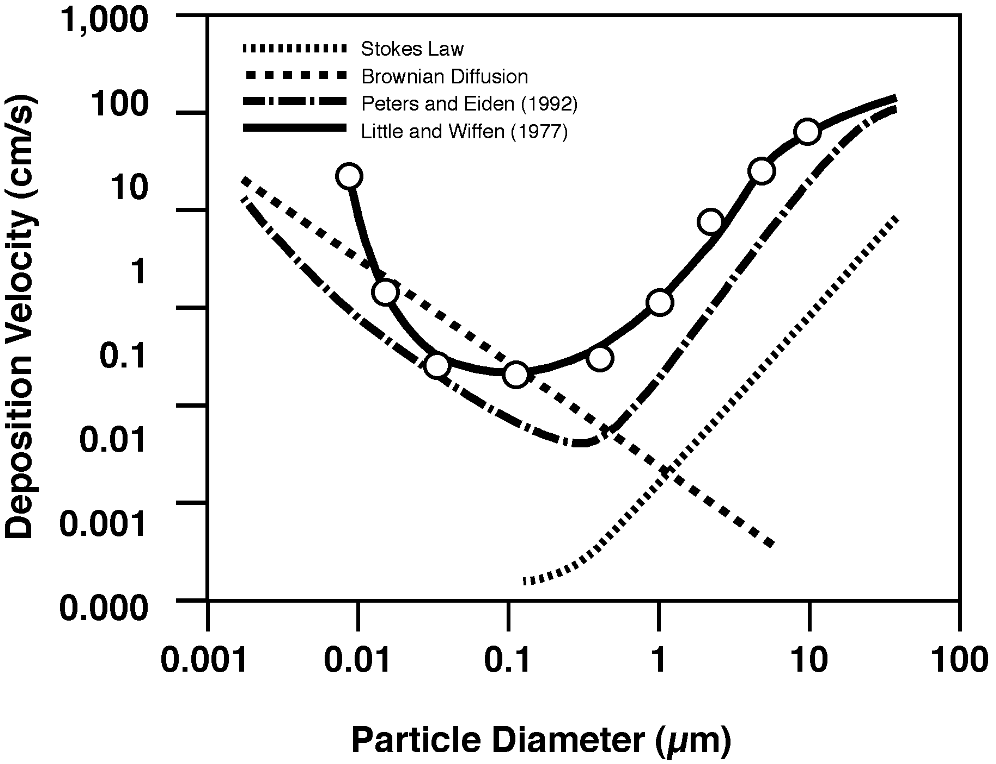


Figure 4-5. The relationship between particle diameter and deposition velocity for particles. Values measured in wind tunnels by Little and Wiffen (1977) over short grass with wind speed of 2.5 m s^{-1} closely approximate the theoretical distribution determined by Peters and Eiden (1992) for a tall spruce forest. These distributions reflect the interaction of Brownian diffusivity (descending dashed line), which decreases with particle size and sedimentation velocity (ascending dotted line from Stokes Law), which increases with particle size. Intermediate-sized particles (≈0.1 to 1.0 μm) are influenced strongly by both, and deposition is independent of size.

diffuse by either Brownian or turbulent processes. Thus, the relevance of r_a breaks down as V_s increases. Indeed because V_s (Eq. 4-2) is independent of a concentration gradient, the electrical analogy is a theoretically flawed approximate approach (Venkatram and Pleim, 1999).

Deposition Velocity

Because the final stage of deposition for particles involves either impaction following deceleration through a quasi-laminar boundary layer or diffusion through this boundary layer, its effective depth is a critical determinant of V_d (Wiman et al., 1985; Peters and Eiden, 1992). The term corresponding to the boundary layer resistance for gases (r_b; equation 4-3) incorporates the absence of form drag for gases. This parameter decreases with increasing turbulence and particle diffusivity but is poorly characterized for gases, depending critically on canopy morphology, vertical wind profiles, and gust penetration, and is of extremely limited usefulness for particles.

Once delivered by turbulent transport or sedimentation to the vicinity of vegetative surface elements, a variety of particle size-dependent mechanisms come into play, some differing substantially from those governing gaseous deposition. The concepts of r_b (the still air or boundary layer resistance) and r_c (the canopy or surface resistance) are not generally applicable to deposition of polydisperse particles. Because of the roles of momentum and bounce-off and complication by reentrainment back into the airstream following deposition of a particle to the surface, the factors determining the effective r_b and r_c for particle deposition are not as independent as for gases. They are replaced in some resistance formulations (e.g., Hicks et al., 1987) by the term, r_{cp}, that combines near-surface and surface effects and by a mathematically derived composite term, $R_aR_{cp}V_s$, that combines atmospheric, surface, and sedimentation effects (Figure 4-4). This latter term was insignificant for the submicron sulfate component considered originally in its derivation (Hicks et al., 1987), but it scales with the square of particle diameter, so that its general applicability to polydisperse particles is unclear. In general, transport between the turbulent air column and the leaf surface through the laminar boundary layer remains difficult to describe (Lindberg and McLaughlin, 1986).

Current estimates of regional particulate dry deposition (e.g., Edgerton et al., 1992; Brook et al., 1999) infer fluxes from the product of (variable and uncertain) measured or modeled particulate concentrations and (even more variable and uncertain) measured or modeled estimates of dry deposition velocity parameterized for a variety of specific surfaces (e.g., Brook et al., 1999). However, even for specific sites and well defined particles, uncertainties in F are largest in the values of V_d, which are typically characterized by the large ranges and variances described in other sources (e.g., Bytnerowicz et al., 1987a,b, Hanson and Lindberg, 1991, for nitrogen-containing particles; McMahon and Denison, 1979, Hicks et al., 1987, for general treatment). The nature of the vegetative cover to which particulate deposition occurs has a moderate to substantial effect on the components of V_d. The surface resistance (Hicks et al.,

1987) is a significant and highly site-specific component of total resistance that is difficult to predict along with site, seasonal, and diurnal effects on the atmospheric components of total resistance.

Early models of dry particulate deposition to vegetation (e.g., U.S. Environmental Protection Agency, 1982; Chamberlain, 1975; Davidson and Friedlander, 1978; Garland, 1978; Little and Wiffen, 1977; McMahon and Denison, 1979; Sehmel, 1980; Sehmel and Hodgson, 1976; and Slinn, 1977, 1978) used this paradigm (e.g., Eq. 4-3) to deal with transport to the near-surface regime explicitly including conventional micrometeorological and particle size considerations. Alternative modeling treatments have attempted to parameterize the geometry of vegetative receptor surfaces and within-canopy micrometeorology (Wiman and Ågren, 1985; Peters and Eiden, 1992). Chemical reactivity, particle shape and density, rates of physiological sequestration, and reentrainment by gusts of wind remain to be addressed. Modeling the deposition of particles to vegetation is at a relatively early stage of development, and it is not currently possible to identify a best or most generally applicable modeling approach. These approaches have been further elaborated with canopy-specific choices among the available models and with specific incorporation of capture efficiencies by Brook et al. (1999).

Methods of Measuring Dry Deposition

Methods of measuring dry deposition of particles are more restricted than for gaseous species and fall into two major categories (Davidson and Wu, 1990). Surface extraction or washing methods characterize the accumulation of particles on natural receptor surfaces of interest or on experimental surrogate surfaces. These techniques rely on methods designed specifically to remove only surface-deposited material (Lindberg and Lovett, 1985). Total surface rinsate may be equated to accumulated deposition or to the difference in concentrations in rinsate between exposed and control (sheltered) surfaces and may be used to refine estimates of deposition (John et al., 1985; Dasch, 1987). In either case, foliar extraction techniques may underestimate deposition to leaves because of uptake and translocation processes that remove pollutants from the leaf surface (Taylor et al., 1988; Garten and Hanson, 1990). Foliar extraction methods also cannot distinguish sources of chemicals (e.g., N) deposited as gases from those deposited as particles (e.g., nitric acid [HNO_3] or nitrate [NO_3^-] from nitrogen dioxide [NO_2], or ammonia [NH_3] from ammonium [NH_4^+]; Bytnerowicz et al., 1987a,b; Dasch, 1987; Lindberg and Lovett, 1985; Van Aalst, 1982). Despite these limitations, these methods are often used in the development of in-canopy deposition models (McCartney and Aylor, 1987).

Deposition of pollutants by wet deposition is relatively straightforward to determine through analysis of precipitation samples. Dry deposition of pollutants, on the other hand, is more difficult to measure. A significant limitation on current capacity to estimate regional impacts of PM is inadequate knowledge of the mechanism and factors governing particle dry deposition to diverse surfaces. This has hindered efforts to develop robust measurement techniques for particle deposition (distinct from atmospheric concentration) and has compromised efforts to develop generally applicable deposition models for particles. The National Dry Deposition Network (NDDN) was established in 1986 to document the magnitude, spatial variability, and trends in dry deposition across the United States. Currently, the network operates as a component of the Clean Air Status and Trends Network (CASTNet; Clarke et al., 1997).

Dry deposition is not measured directly, but is determined by a inferential approach (i.e., fluxes are calculated as the product of measured ambient concentration and a modeled deposition velocity). This method is appealing and widely used because atmospheric concentrations are relatively easy to measure when compared to dry deposition fluxes, and models have been developed to calculate deposition velocities (Lovett, 1994). Ambient pollutant concentrations, meteorological conditions, and land use data required for the inferential model are routinely collected at CASTnet dry deposition sites. Monitored chemical species include ozone, sulfate, nitrate, ammonium, sulfur dioxide, and nitric acid. The temporal resolution for the ambient concentration measurements and dry deposition flux calculations is hourly for ozone and weekly for the other chemical substances (Clarke et al., 1997). Isotopic labeling of dry deposited PM (e.g., sulfate with ^{35}S) prior to experimental surface exposures and extractions (Garten et al., 1988) can provide more precise differentiation between the deposition rates of related chemical species (e.g., sulfate [SO_4^{-2}] from sulfur dioxide [SO_2]).

At the whole-canopy level, natural surface washing by rainfall may be used to estimate dry deposition of PM and gases during the preceeding dry period (Cape et al., 1992; Davidson and Wu, 1990; Draaijers and Erisman, 1993; Erisman, 1993; Fahey et al., 1988; Lindberg and Lovett, 1992; Lovett and Lindberg, 1993; Reiners and Olson, 1984; Sievering, 1987). Collection and analysis of stem flow and throughfall provides useful estimates of particulate deposition when compared to directly sampled precipitation. The method is most precise for strictly PM deposition when gaseous deposition is a small component of the total dry deposition and when leaching or uptake of compounds of interest out of or into the foliage (i.e., N, S, base cations) is not a significant fraction of the total depositional flux (Davidson and Wu, 1990; Draaijers and Erisman, 1993; Lindberg and Lovett, 1992; Lovett and Lindberg, 1993). Throughfall sampling of sulfate deposition (Garten et al., 1988; Lindberg and Garten, 1988; Lindberg et al., 1990) often suggests substantial foliar exchange. Other throughfall studies (e.g., Erisman, 1993; Fahey et al., 1988) may lack sufficient specificity for dry particle deposition.

Careful timing of throughfall and stemflow measurements after prolonged dry periods, with simultaneous direct measurement of (unchanged) precipitation, can be used to determine the magnitude of dry deposition between precipitation events. Indeed, this foliar washing technique, whether using subsequent precipitation or experimental lavage, is one of the best currently available methods to determine dry deposition of PM to vegetated ecosystems. Major limitations are the extreme site specificity of the measurements, the substantial labor requirement that normally precludes regional coverage, and the restriction to elements that are conserved within the vegetative system (thereby excluding semivolatile organics, ammonium salts, and gases such as ozone).

Deposition to surrogate surfaces deployed in extensive plant canopies provides a measure of particle deposition to the surrounding foliage or soil surfaces. For example, a uniform population of 0.8 μm gold colloid particles were deposited similarly to leaves of *Phaseolus vulgaris* and to upward facing inert surfaces (Klepper and Craig, 1975). However, comparison of dry deposition of particles to foliage and to inert surrogate surfaces (polycarbonate Petri dishes) in a deciduous forest demonstrated greater accumulation on the inert surfaces; with both surfaces having accumulated particles of a similar range of sizes (Lindberg and Lovett, 1985). These differences in deposition/accumulation remain to be fully characterized and hinder efforts to use these surrogate techniques to provide quantitative estimates of deposition. Surrogate surfaces have not been found that can adequately replicate essential features of natural surfaces; and therefore the surfaces currently used do not produce reliable estimates of particle deposition to the landscape.

Micrometeorological methods employ an eddy covariance, eddy accumulation, or flux gradient protocol in contrast to washing or extracting of receptor surfaces to quantify dry deposition. These techniques require measurements of PM concentrations and of atmospheric transport processes. They are currently well developed for ideal conditions of flat, homogeneous, and extensive landscapes and for chemical species for which accurate and rapid sensors are available. Additional studies have expanded the range of such species and extended these techniques to more complex terrain (McMillen, 1988; Hicks et al., 1984; Wesely and Hicks, 1977).

The eddy covariance technique measures vertical fluxes of gases and fine particles directly from calculations of the mean covariance between the vertical component of wind velocity and pollutant concentration (Wesely et al., 1982). It is particularly limited by a requirement for sensors capable of acquiring concentration data at 5-20 Hz. For the flux-gradient or profile techniques, vertical fluxes are calculated from a concentration difference and an eddy exchange coefficient determined at discrete heights (Erisman et al., 1988; Huebert et al., 1988). Businger (1986), Baldocchi (1988), and Wesely and Hicks (1977) evaluate the benefits and pitfalls of these micrometeorological flux measurements for gases. Most measurements of eddy transport of PM have used chemical sensors (rather than mass or particle counting) to focus on specific PM components. These techniques have not been well developed for generalized particles and may be less suitable for coarse PM_{10} transported efficiently in high frequency eddies (Gallagher et al., 1988) for the same reasons that limit mathematical description of particle deposition.

Factors Affecting Dry Deposition

Ambient Concentration. The ambient concentration of particles (C_z; Eq. 4-1), the parameter for which there is the most data (for example, see Chapter 3, this document), is at best an indicator of exposure. However, it is the amount of PM actually entering the immediate plant environment that determines the biological effect. The linkage between ambient concentration and delivery to vegetation is the deposition velocity (V_d; Eq. 4-1). C_z is determined by regional and local emission sources, regional circulation, and weather. It may be locally sensitive to removal from the atmosphere by deposition, but the effect is generally small. Average annual concentrations for NO_3^- exhibit much more variability than SO_4^{-2} and a definite pattern of higher concentrations in the midwest than elsewhere. The highest concentrations are observed (i.e, > 2 $\mu g\ m^{-3}$) in the agricultural areas of the midwest, while the lowest are seen at forested sites in New England and the southern Appalachian Mountains. Annual average concentrations SO_4^{-2} of

5.0 μg m^{-3} are observed over nearly the entire eastern U.S. from New York and Michigan to northern Mississippi and Alabama (Edgerton et al., 1992).

Deposition increases linearly with the concentration of many materials over a broad range. This allows atmospheric cleansing to take place and accounts for the greater surface impact of pollutants during pollution episodes. A serious limitation of the V_d formulation used to infer deposition of specific chemical species that exist in a range of particle sizes is an appropriate specification of their concentration. Most sulfur emissions are readily oxidized to sulfite, bisulfite, and sulfate. In the presence of atmospheric ammonia, particulate ammonium sulfate is formed. However, this material is hygroscopic and will increase in mass and diameter in the presence of high humidity and alter its deposition behavior. Similarly, coalescence of small particles into larger aggregates and adsorption of gaseous pollutants onto existing coarse particles complicate the association of particle size with concentration of individual chemical species.

Distance and the resulting residence time in the atmosphere control the relative concentrations of surface reactive materials (NO, SO_2) of secondary particles that take some time to form in the atmosphere and of coarse particles that exhibit high rates of deposition by sedimentation near the source. These interacting processes affect the time required for the formation of secondary particles by gas-to-particle conversion reactions and result in a greater ratio of dry to wet deposition near emission sources where gaseous sulfur dioxide (gSO_2) deposition predominates than at greater distances where rainout of particulate SO_4^{-2} (pSO_4^{-2}) may dominate (Barrie et al., 1984) and where dry deposition of pSO_4^{-2} may be greater than that of gSO_2. The effect of gas-to-particle conversion on dry deposition of a specific chemical species can be substantial because V_d for SO_2 is approximately 0.33 ± 0.17 cm s^{-1}; whereas it is approximately 0.16 ± 0.08 cm s^{-1} for SO_4^{-2}. These phase conversions affect both C_z and the effective V_d which together control dry depositional fluxes (Eq. 4-1). The neutralization of acidic gaseous and particulate species by alkaline coarse particles has been described in arid regions, but it may be more prevalent in urban New York where coarse particles are observed to be neutral because alkaline cations approximately balance gaseous acidic species (Lovett et al., 2000). The deposition of the acidic materials in the urban environment is likely enhanced by incorporation into these previously formed coarse particles.

Similarly, the ratio of coarse to fine particle concentrations determines the effective V_d for chemically speciated particles (Figure 4-4). This reflects the size-dependent deposition processes that govern delivery of PM to receptor surfaces (Fig. 4-5). For example, SO_4^{-2} was found predominantly on fine submicron particles; whereas potassium ion (K^+), calcium (Ca^{+2}), and nitrate (NO_3^-) were associated most often with coarse particles larger than 2 μm (Lindberg and Lovett, 1985). However, concentrations of particulate S and K^+ within a coniferous canopy were strongly correlated (Wiman and Lannefors, 1985), suggesting a primary source of coarse-mode sulfur particles. However, many researchers reported mass-size distributions of NO_3^- were bimodal with one peak in the fine mode and the other peak in coarse mode (Wu and Okada, 1994). The behavior of NO_3^- in ambient aerosols depends not only on the concentrations of gaseous nitric acid and ammonia, but also on the chemical composition of the particles and atmospheric conditions (Tang, 1980). When sea-salt particles were transported from the Pacific Ocean in the Nagoya, Japan, area, the amount of nitrate in the coarse particle size range increased. Coarse particle formation on sea salt under these conditions becomes a major pathway for nitrate. The heterogeneous reaction of NaCl with gaseous HNO_3 is considered to be the dominating path (Wu and Okada, 1994). As a result, marine and continental particle size spectra for both N and S differ substantially: a peak in the coarse mode is generally apparent near marine sources (Milford and Davidson, 1987). The issue for NO_3^- is further confounded by uncertain discrimination between gaseous and particulate species in current sampling methods. The substantial effect of particle size on V_d (Figure 4-5) implies a need for size resolution as well as chemically speciated ambient particulate concentrations even within the PM_{10} fraction.

Particle Effects on V_d. Particle size is a key determinant of V_d as noted above; but, unfortunately, the size spectra may be quite complex. The particles in the study of Lindberg and Lovett (1985) at Walker Branch Watershed had median diameters ranging from 3 to 5 μm; but approximately 25% of the particles had diameters less than 1 μm (0.2 to 0.3 μm), and 5 to 20% of the particles were much larger aggregates. The aggregated particles are significant in that chemically they reflect their fine particle origins, but physically they behave like large particles and deposit by sedimentation. Direct observations with SEM demonstrate that particle morphology can be highly variable. Many submicron particles can be observed on trichomes (leaf hairs), although most particles are in the 5 to 50 μm diameter range. Large aggregated particles in excess of 100 µm also are seen, and carbonaceous aggregate particles are especially common (Smith, 1990a). Trichomes are efficient particle receptors; however, they are reduced in size by "weathering" and occasionally are completely broken off during the growing season.

In the size range around 0.1 to 1.0 µm, where V_d is relatively independent of particle diameter (Fig. 4-5), deposition is controlled by macroscopic roughness properties of the surface and by the stability and turbulence of the atmospheric surface layer. The resistance catena (Figure 4-3) is less useful in this size range and, in some treatments, has been abandoned entirely (e.g., Erisman et al., 1994; Eq. 4-4). Impaction and interception dominate over diffusion, and the V_d is considerably (up to two orders of magnitude; Figure 4-2) lower than for particles either smaller or larger (Shinn, 1978). The deposition velocity may be parameterized in this size range as a function of friction velocity,

$$V_d = (a/b)u^*, \tag{4-4}$$

where a depends on atmospheric stability and b depends on surface roughness (Wesely et al., 1985; Erisman et al., 1994). Similar formulations have been presented in terms of turbulence (standard deviation of wind direction) and wind speed (e.g., Wesely et al., 1983), both determinants of u*.

Deposition of particles between 1 and 10 µm diameter, including the coarse mode of PM_{10}, is strongly dependent on particle size (Shinn, 1978). Larger particles within this size range are collected more efficiently at typical wind speeds than are smaller particles (Clough, 1975), suggesting the importance of impaction. Impaction is related to wind speed, the square of particle diameter, and the inverse of receptor diameter as a depositing particle fails to follow the streamlines of the air in which it is suspended around the receptor. When particle trajectory favors a collision, increasing wind speed or ratio of particle size to receptor cross section makes collision nearly certain; and, as these parameters become very small, the probability of collision becomes negligible. However, the shape parameter for the more common range of situations between these extremes remains poorly characterized (Peters and Eiden, 1992; Wiman and Ågren, 1985).

As particle size increases above 1 µm, deposition is governed increasingly by sedimentation (Figure 4-5) and decreasingly by turbulence and impaction. Particles between

~10 and 24 µm (Gallagher et al., 1988) are both small enough to be transported efficiently by turbulent eddies to the surface and large enough to impact with sufficient momentum to overcome boundary layer effects. These particles deposit highly efficiently and relatively independently of particle size. Deposition of the largest suspended particles (e.g., > 50 µm) is governed, through sedimentation and the corresponding terminal settling velocity (V_s), almost entirely by size. These particles are not transported efficiently by small-scale eddies near the surface.

Theoretically based models for predicting particle deposition velocities have been published by Bache (1979a,b), Davidson et al. (1982), Noll and Fang (1989), Slinn (1982), and Wiman (1985). These models deal primarily with low canopies or individual elements of canopy surfaces. Wiman and Ågren (1985) have developed an aerosol deposition model that specifically treats the problem of particle deposition to forests where turbulence plays a particularly important role, especially at roughness transitions such as forest edges. They found that deposition of supermicron particles is controlled by complex interactions among particle size and concentration, forest structure, and aerodynamics; whereas deposition of fine particles (submicron) is controlled by particle concentration and forest structure.

At the present time, empirical measurements of V_d for fine particles under wind tunnel and field conditions are often several-fold greater than predicted by available theory (Unsworth and Wilshaw, 1989). A large number of transport phenomena, including streamlining of foliar obstacles, turbulence structure near surfaces, and various phoretic transport mechanisms remain poorly parameterized in current models. The discrepancy between measured and predicted values of V_d may reflect such model limitations or experimental limitations in specification of the effective size and number of receptor obstacles, as suggested by Slinn (1982).

Available reviews (Davidson and Wu, 1990; McMahon and Denison, 1979; Nicholson, 1988; Sehmel, 1980; Slinn, 1982; U.S. Environmental Protection Agency, 1982, 1996a) suggest the following generalizations: (1) particles larger than 10 µm exhibit a variable V_d between ≈0.5 and 1.1 cm s^{-1} depending on friction velocities; whereas a minimum particle V_d of 0.03 cm s^{-1} exists for particles in the size range 0.1 to 1.0 µm; (2) the V_d of particles is approximately a linear function of friction velocity; and (3) deposition of particles from the atmosphere to a forest canopy is from 2 to 16 times greater than deposition in adjacent open terrain (i.e., grasslands or other vegetation of low stature).

Leaf Surface Effects on V_d. The term r_c (Equation 4-3) reflects the chemical, physical, or physiological characteristics of the surface that govern its ability to capture, denature, or otherwise remove particulate material from the atmospheric surface layer. For gases, relevant surface properties involve the physiological state of the vegetation, including stomatal opening and mesophyll antioxidant activity, and the chemical reactivity of the exposed surface with the specific gas. For particles, relevant surface properties involve stickiness, microscale roughness, and cross-sectional area. These properties determine the probability of impaction and bounce (e.g., Shinn, 1978). The chemical composition of PM is not usually a primary determinant of deposition velocity. At the microscopic scale where Van der Waals forces may determine particle bounce and reentrainment, the chemical properties of both surface and particle may be significant but remain poorly understood.

Stickiness may itself depend on previous deposition of deliquescent particles that prolong leaf wetness, on the wettability of foliar surfaces, and on the presence of sticky residues such as honeydew deposited by aphids. These factors increase deposition by decreasing bounce-off, wind reentrainment, and, to some extent, wash-off by precipitation.

The distribution of particles on and the efficiency of deposition to vegetation also varies based on leaf shape and plant part. Particles are more prevalent on the adaxial (upper facing of the twig) surface than on the abaxial (lower away from the twig) surface. Peripheral leaf areas tend to be the cleanest most particles accumulate in the midvein, central portion of leaves. The rough area surrounding the stomatal pores was not found to be a preferential site for particle deposition or retention (Smith and Staskawicz, 1977). Most particles were located near veins with smaller particles localized on the trichomes. The greatest particulate loading on dicotyledonous leaves is frequently on the adaxial (upper) surface at the base of the blade, just above the petiole junction. It is probable that precipitation washing plays an important role in this distribution pattern. Lead particles accumulated to a larger extent on older than younger needles and twigs of white pine, indicating that wind and rain were insufficient to fully wash the foliage. Fungal mycelia (derived from windborne spores) were frequently observed in intimate contact with other particles on other leaves (Smith and Staskawicz, 1977), which may reflect shelter by the particles minimizing reentrainment of the spores, mycelia development near sources of soluble nutrients provided by the particles, or codeposition. This pattern is significant and could yield further insight into deposition mechanisms.

Leaves with complex shapes collect more particles than those with regular shapes. Conifer needles are more effective than broad leaves in accumulating particles. The edge to area ratio (Woodcock, 1953) is also a key determinant of salt deposition to individual artificial leaves. A strong negative correlation was observed under wind tunnel conditions between the area of individual leaves and deposition of coarse particles (Little, 1977). Small twigs and branches were more effective particle collectors than were large branches and trunks of trees (Smith, 1984). Lead particles accumulated 20-fold more on woody stems than on leaves of white pine (*Pinus strobus*), even though leaves displayed a 10-fold greater total area (Heichel and Hankin, 1976). Deposition is heaviest at tips of individual leaves.

Rough, pubescent broadleaf discs collected coarse (5.0-µm) particles up to sevenfold more efficiently than glabrous leaf discs (Little, 1977). Laminae, petioles, and stems, all differed in collection efficiency. Pubescent leaves of sunflower (*Helianthus annuus*) collected coarse particles nearly an order of magnitude more efficiently than the glabrous leaves of tulip poplar (*Liriodendron tulipifera*) under wind tunnel conditions (Wedding et al., 1975). Rough pubescent leaves of nettle (*Urtica dioica*) were more effective in capturing coarse PM_{10} than were the densely tomentose leaves of poplar (*Populus alba*) or smooth leaves of beech (*Fagus sylvatica*).

Conifer needles are more efficient than broad leaves in collecting particles by impaction. This reflects the small cross section of the needles relative to larger leaf laminae of broadleaves and the greater penetration of wind into conifer than broadleaf canopies. Conifers were more effective in removing coarse (≈20 µm) particles of ragweed pollen from the atmosphere than were broadleaf trees (Steubing and Klee, 1970) and in intercepting the even coarser particles of rain (Smith, 1984). Conifers are also more effective in retaining and accumulating particles against reentrainment by wind and removal by rain, particularly on foliar surfaces where they are likely to be most biologically active. Seedlings of white pine (*Pinus strobus*) and oak (*Quercus rubra*) initially retained between a quarter (pine) and a third (oak) of very coarse (88 to 175 µm) ^{134}Cs-tagged quartz particles applied under field conditions (Witherspoon and Taylor, 1971). After 1 h, the pine retained over 20% of the ^{134}Cs-tagged particles; whereas the oak retained only approximately 3%. Long-term retention of the particles was concentrated at the base of the fascicles in pine and near the surface roughness caused by the vascular system on leaves of oak. The sheltered locations available in the conifer foliage contribute substantially to greater retention of particles. For similar reasons, grasses also are efficient particle collectors (Smith and Staskawicz, 1977) with long-term retention mostly in the ligule and leaf sheath.

Because of the strong relationship between particle size and deposition, the sharply increasing humidity gradient near transpiring foliar surfaces may cause hygroscopic particles to behave, at the immediate surface, as larger particles than reflected in ambient measurements at reference heights. This needs to be further considered (Wesely and Hicks, 2000). Recent deposition models (Ruijgrok et al., 1997; Zhang et al., 2001) have introduced the role of ambient humidity but lack sufficient emphasis on the role of vegetation itself in modifying humidity near the surface. This may be significant, as the size of a dry, 0.5-μm particle of ammonium sulfate may increase to about 3.5 μm at saturated humidity (Ruijgrok et al., 1997). Kinetic analyses have suggested that full (95% to 100%) equilibration to the new diameter will occur during the deposition process.

Wind tunnel studies also demonstrated equivalent deposition properties of 3.36-μm particles of dense lead chloride and 6.77-μm particles of less dense uranine dye. These particles were shown to be aerodynamically equivalent, substantiating the use of aerodynamic diameter as a classification parameter for particle deposition.

Canopy Surface Effects on V_d. In general, surface roughness contributes to greater particulate deposition. As a result, V_d is typically greater for a forest than for a field or nonwoody wetland and greater for a field than for a water surface. The contrasting transport properties and deposition velocities of different size particles lead to predictable patterns of deposition. For coarse particles, the upwind leading edges of forests, hedge rows, and individual plants, as well as of individual leaves, are primary sites of deposition. Impaction at high wind speed and the sedimentation that follows the reduction in wind speed and carrying capacity of the air in these areas lead to preferential deposition of larger particles.

Air movement is slowed in proximity to vegetated surfaces. Resulting log profiles of wind and pollutant concentrations in the near-surface turbulent boundary layer above canopies reflect surface characteristics of roughness length, friction velocity, and displacement height. Plasticity, streamlining, and oscillations of foliar elements also alter the aerodynamic roughness and the level of within-canopy turbulence. Canopies of uneven age or with a diversity of species are typically aerodynamically rougher and receive larger inputs of pollutants than do smooth, low, or monoculture vegetation (Garner et al., 1989; Wiman and Ågren, 1985). Canopies on slopes facing the prevailing winds and individual plants on the windward edges of discontinuities in vegetative cover over which roughness increases receive larger inputs of pollutants than more sheltered, interior canopy regions. For example, some 80% of coarse particulate sea salt was deposited on the upwind edge of a hedgerow (Edwards and Claxton, 1964), and the concentration of ragweed (*Ambrosia spp.*) pollen was reduced by 80% within 100 m of the leading edge of a forest (Neuberger et al., 1967).

Beier et al. (1992) and Beier (1991) discussed two methods for estimating the dry deposition of base cations to forest edges: (1) a difference method between measured precipitation and throughfall concentrations of base cations, and (2) a calculation method based on known ratios of Na^+ deposition in wet and dry forms (Ulrich, 1983). A combination of these two approaches produced the best estimates of SO_4^{-2}, Ca^{+2}, Mg^{+2}, and K^+ particle deposition. Using these methods, particulate SO_4^{-2} (Beier, 1991) and particulate Ca^{+2}, Mg^{+2}, and K^+ (Beier et al., 1992) were found to decrease by an order of magnitude from the forest edge to the forest interior. A number of authors also have shown that particle deposition is elevated at forest edges when compared to a uniform forest canopy (Draaijers et al., 1988; Grennfelt, 1987; Lindberg and Owens, 1993), and Draaijers et al. (1992) reported that differences are likely to exist between forest types because of variable canopy structure. Draaijers et al. (1988) further emphasized that enhanced particle deposition at or near forest edges is strongly dependent on the velocity and wind direction during observations.

The factors leading to horizontal gradients are confounded by time- and distance-related sedimentation. For example, geologic dust (mostly around 7 µm aerodynamic diameter) collects on stems of wild oats (*Avena spp.*; Davidson and Friedlander, 1978) and on eastern white pine (*Pinus strobus*; Heichel and Hankin, 1972; Smith 1973) downwind of roadways. Rapid sedimentation of coarse crustal particles suggests that potential direct effects may be restricted to roadway margins, forest edges, and, because of the density of unpaved roads in agricultural areas, crop plants.

Simulated deposition to an ecologically complex, mixed canopy was considerably higher than to a pure spruce stand in which most of the leaf area was concentrated in regions of low wind speed. Limitations to the application of these models to predict deposition over large regions include a limited understanding both of the nature of microscopic particle-surface interactions and of the effects of complex terrain and species composition on macroscopic transport processes.

Macroscopic turbulent transport processes, related to r_a at successive layers through the canopy can be separated from microscopic processes, related to r_b and r_c (or r_{cp}) at each deposition surface (e.g., Peters and Eiden, 1992; Wiman and Lannefors, 1985). The macroscopic approach deals with deposition as the product of a turbulent diffusion coefficient and a concentration (C_z) at each canopy layer, both of which vary with particle size and with height (Z) in the canopy. The microscale parameters involve those factors that determine absorption of a particle at each surface as captured imperfectly by r_c. Shelter effects caused by the crowding of foliar elements within the canopy can be ignored if the wind speed within each canopy layer is specified. This approach requires knowledge of the vertical distribution of particle concentration and foliage density in the canopy airspace along with profiles of wind speed or turbulence.

Once introduced into a forest canopy, elements associated with course particles tend to decrease markedly with canopy depth; whereas elements associated with fine particles do not (Lovett and Lindberg, 1992). Trace elements and alkaline-earth elements are enriched below the canopies of both southern (Lindberg et al., 1986) and northern (Eaton et al., 1973) hardwood forests. Vertical gradients in concentration of coarse particles and of elements associated with coarse particles were observed in a mixed conifer/birch forest canopy (Wiman and Lannefors, 1985; Wiman et al., 1985) and in a mixed oak forest (e.g., Ca^{+2}, Figure 4-6A; Lovett and Lindberg, 1992). The highly reactive gas HNO_3 also exhibited a vertical gradient but with a steep decline at the top of the canopy (Figure 4-6B). Lovett and Lindberg (1992) studied concentration profiles of various gases and particles within an closed canopy forest and concluded that coarse particle concentrations associated with elements like Ca^{+2} would decrease markedly with depth in the canopy, but they found only minor reductions with depth in the concentrations of fine aerosols containing SO_4^{-2}, NH_4^+, and H^+. These data suggest that all foliar surfaces within a forest canopy are not exposed equally to particle deposition: upper canopy foliage would receive maximum exposure to coarse and fine particles, but foliage within the canopy would receive primarily fine aerosol exposures. Fine-mode particles (e.g., sulfate, Figure 4-6C) and unreactive gases typically do not exhibit such vertical profiles, suggesting that uptake is smaller in magnitude and more evenly distributed throughout the canopy. In multilayer

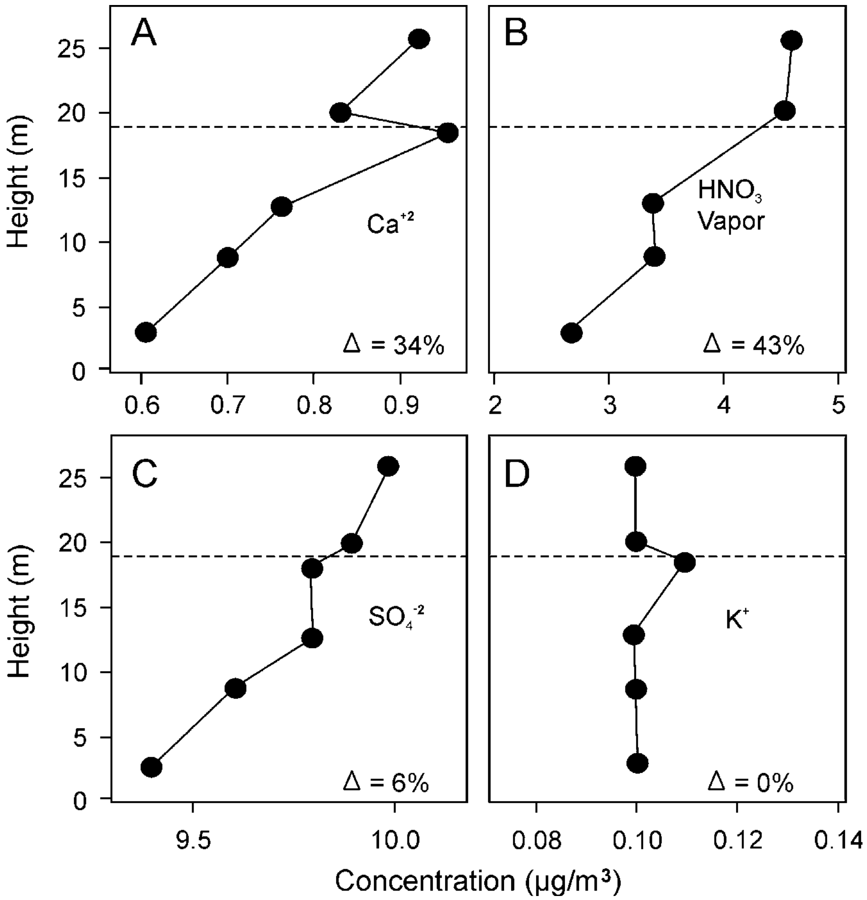


Figure 4-6. Vertical stratification of diverse, chemically speciated particles in a mixed oak forest. Nitric acid vapor, as a highly reactive, nonparticulate species, is shown for comparison. The horizontal dotted line indicates canopy height, and Δ indicates the percent depletion from above to below the canopy. Data from Table 2-4 of Lovett and Lindberg (1992).

canopies, simultaneous reentrainment and deposition may effectively uncouple deposition from local concentration. Polydisperse size distributions of many chemical species effectively prevent the use of a single estimate of V_d for any element if highly accurate results are required.

Although gradients (Figures 4-6 and 4-7) may be related to local V_d within the canopy (Bennett and Hill, 1975), the absence of a gradient may reflect either low rates of deposition or very high rates relative to turbulent replenishment from above the canopy (Tanner, 1981). Below- or within-canopy emissions may confound interpretation of vertical gradients. Linear gradients of the gaseous pollutants hydrogen fluoride (HF) and ozone (O_3) reflected large uptake

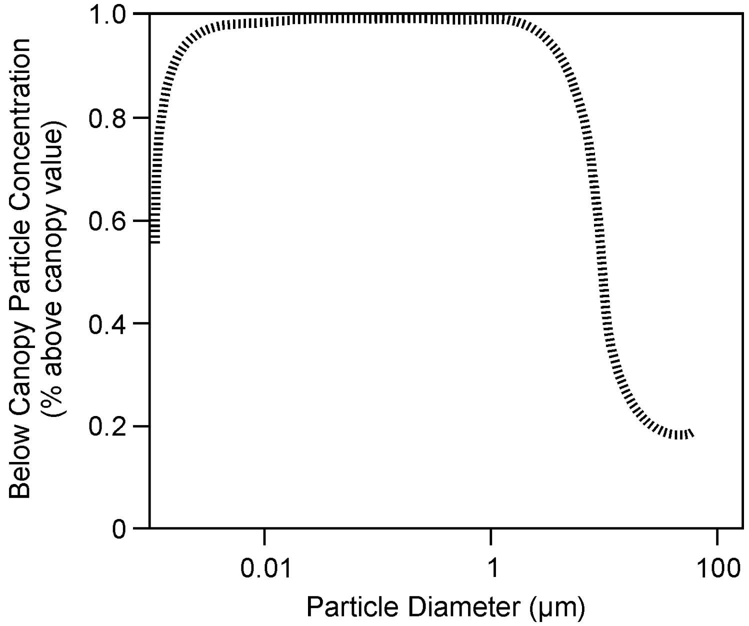


Figure 4-7. The relationship between particle size and concentration below a spruce canopy with wind velocity at a height of 16.8 m equaling 5 m s^{-1}. Modified from Peters and Eiden (1992).

rates; whereas small gradients in NO suggested little uptake by foliage (Bennett and Hill, 1973, 1975). However, soil efflux of NO could have complicated the latter interpretation. The lack of a vertical gradient and a peak near the top of the active canopy in particulate K^+ (Figure 4-6D) was interpreted as evidence for a biogenic source within the deciduous forest canopy with moderate rates of deposition (Lindberg et al., 1986; Lovett and Lindberg, 1992).

The size dependence of this vertical stratification of particulate concentration (see Figure 4-7) is reflected in current simulation models (Wiman et al., 1985; Peters and Eiden, 1992). The model of Wiman and Ågren (1985) predicts a uniform vertical distribution of fine-mode particles and a pronounced vertical gradient of coarse-mode particles which is in agreement with observations (Lovett and Lindberg, 1992).

Simulation of the horizontal deposition patterns at the windward edge of a spruce forest downwind of an open field with the canopy between 1 and 25 m above the ground indicated that deposition was maximal at the forest edge where wind speed and impaction were greatest. Simulation of the vertical deposition pattern was more complex. Deposition was not greatest at the top of the canopy where wind speed was highest, but at z = 0.75 h where the balance between leaf area (obstacles for impaction) and wind speed (momentum for impaction) was optimal, although neither parameter alone was maximal. Simulated deposition in this spruce forest increased considerably with increasing LAI at the forest edge, where wind speed was insensitive to LAI but the number of obstacles increased. Inside the forest, where both wind speed and impaction increasingly were attenuated by increasing LAI, deposition increased only marginally in spite of the increase in obstacle frequency.

To scale surface-specific measurements of particle deposition to forest or crop canopies, conversions of the following type have been suggested:

$$V_{d.canopy} = V_{d.surface} * \text{scaling factor}, \tag{4-5}$$

with empirical scaling factors proposed by Lindberg et al. (1988).

To appropriately scale surface-specific measurements of particle deposition to landscapes, one must consider the complexity of grassland, crop, and forest canopies in order to avoid serious over- or under-estimates of particle deposition. Individual species exposed to similar ambient concentrations may receive a range of particulate loading that is more closely related to foliar damage than the ambient concentration (Vora and Bhatnagar, 1987).

Both uptake and release of specific constituents of PM may occur within a single canopy (e.g., K^+; Lovett and Lindberg, 1992). The leaf cuticular surface is a region of dynamic exchange processes through leaching and uptake. Exchange occurs with epiphytic microorganisms and bark and through solubilization and erosion of previously deposited PM. Vegetation emits a variety of particulate and particulate precursor materials. Terpenes and isoprenoids predominate and, on oxidation, become condensation nuclei for heterogeneous particle formation. Salts and exudates on leaves and other plant parts continually are abraded and suspended as particles, as are plant constituents from living and dead foliage (Rogge et al., 1993a). Soil minerals, including radioactive strontium, nutrient cations and anions, and trace metals are transferred to the active upper foliage and then to the atmosphere in this way. Although not representing a net addition to an ecosystem, particle release from vegetation is a mechanism for redistributing chemical pollutants derived from the soil or prior deposition within a canopy, potentially enhancing direct effects and confounding estimates of V_d.

Range of Deposition Velocity

As noted in an earlier criteria document (U.S. Environmental Protection Agency, 1982) and in McMahon and Denison (1979), estimates of V_d for PM_{10} particles to vegetation are variable and suggest a minimum between 0.1 and 1.0 µm as predicted from first principles (Monteith and Unsworth, 1990; Sehmel, 1980). Determinations in wind tunnels with passive collectors and micrometeorological methods tend to converge in this range. The range of V_d for sulfate from passive collectors was found to be from 0.147 to 0.356 cm s^{-1}; and, from eddy covariance techniques, a mean V_d of 0.27 cm s^{-1} was observed (Dolske and Gatz, 1984). Micrometeorological techniques over grass (Wesely et al., 1985); indirect, inert collector techniques within an oak forest (Lindberg and Lovett, 1985); and many other empirical determinations (e.g., McMahon and Denison, 1979; Table 4-4) generally support this range. Over aerodynamically smooth snow (Duan et al., 1988; Table 4-5), measurements of V_d were an order of magnitude smaller. Very coarse particles, often non-size-specified primary geologic material, frequently exhibit V_d greater than 1.0 cm s^{-1} (e.g., Clough, 1975). The increase in V_d with decreasing size below 0.1 µm is probably hidden in most empirical determinations of V_d because the total mass in this fraction is very small despite the large number of individual particles. Table 4-6 shows published estimates of V_d with variability estimates for fine particles of specified aerodynamic diameters dominated by a range of chemical species.

Ibrahim et al. (1983) evaluated the deposition of ammonium sulfate particles to a range of surfaces and found that particles having a mean diameter of 0.7 µm had deposition velocities ranging from 0.039 to 0.096 cm s^{-1}. Larger particles (having mean diameters of 7 µm) had greater deposition velocities (between 0.096 and 0.16 cm s^{-1}). The authors further concluded that the hygroscopic nature of the sulfate particle could increase its size and enhance deposition near sources of water (e.g., snow). Using eddy correlation approaches, Hicks et al. (1989) found a mean daily V_d for sulfur-containing PM to be 0.6 cm s^{-1}. However, they suggested that the V_d value could be as high as 1 cm s^{-1} during the day and near zero at night.

Lindberg et al. 1990 found a wide discrepancy between deposition velocities for NO_3^- between study sites in Oak Ridge, TN ($\approx$ 2 cm s^{-1}) and Göttingen, Germany ($\approx$ 0.4 cm s^{-1}). They suggest that the increased V_d at Oak Ridge could be explained by the primary occurrence of NO_3^- in coarse particles that exhibit greater V_d than fine particles (Davidson et al., 1982). Large

TABLE 4-4. REPORTED MEAN DEPOSITION VELOCITIES (V_d) FOR SULFATE, CHLORINE, NITRATE, AND AMMONIUM AND ION-CONTAINING PARTICLES

Chemical Species/ Surface	V_d (cm s^{-1})[a]	Method	Reference
SO_4^{-2}			
Inert plates	0.13	Extraction	Lindberg and Lovett (1985)
Inert plates	≈0.14	Extraction	Lindberg et al. (1990)
Inert plates	0.14	Extraction	Davidson and Wu (1990)[a]
Inert bucket	0.51	Extraction	Davidson and Wu (1990)[a]
Foliage	0.29	Extraction	Davidson and Wu (1990)[a]
Chaparral	0.15	Extraction	Bytnerowicz et al. (1987a)
Grass canopy	0.10	Gradient	Allen et al. (1991)
Grass canopy	0.07	Gradient	Nicholson and Davies (1987)
Pine foliage	0.07	Extraction	Wiman (1981)
Plant canopies	0.50	Gradient	Davidson and Wu (1990)[a]
Grass canopy	0.22	Eddy covariance	Weseley et al. (1985)
Cl^-			
Inert bucket	3.1	Extraction	Dasch and Cadle (1985)
Inert bucket	5	Extraction	Dasch and Cadle (1986)
Beech canopy	1	Throughfall	Höfken et al. (1983)
Spruce canopy	1.9	Throughfall	Höfken et al. (1983)
NO_3^-			
Inert plates	0.4 - 2	Extraction	Lindberg et al. (1990)
Ceanothus	0.4	Extraction	Bytnerowicz et al. (1987a)
Glycine max	0.24	Extraction	Dolske (1988)
Ligustrum	0.1 - 0.5	Extraction	John et al. (1985)
Quercus	0.7 - 1.1	Extraction	Dasch (1987)
Quercus			
summer	0.55	Throughfall	Lovett and Lindberg (1984)
winter	0.7	Throughfall	Lovett and Lindberg (1984)
Quercus			
summer	0.3	—	Lovett and Lindberg (1986)
winter	0.1	—	Lovett and Lindberg (1986)
Pinus	0.5 - 1.3	Extraction	Dasch (1987)
Pasture	0.7 - 0.8	Gradient	Huebert et al. (1988)
Ulmus	1.1	Extraction	Dasch (1987)
NH_4^+			
Calluna/Molina	0.18	Gradient	Duyzer et al. (1987)
Ceanothus	0.4	Extraction	Bytnerowicz et al. (1987a)
Kalmia	0.03 - 0.14	Extraction	Tjepkema et al. (1981)
Pinus	0.01 - 0.06	Extraction	Dasch (1987)

[a] These data represent the mean of data by measurement technique as reported in the cited reference. The reader is referred to the referenced articles for information on the specific cations contributing to the means.

TABLE 4-5. REPRESENTATIVE EMPIRICAL MEASUREMENTS OF DEPOSITION VELOCITY (V_d) FOR PARTICULATE DEPOSITION

V_d x ± SE (cm s^{-1})	Particle Size (µm)	Method	Reference
0.034 ± 0.014 0.021 ± 0.005	0.15 - 0.30 0.5 - 1.0	Eddy covariance with optical counter, flat snow surface	Duan et al. (1988)
0.1 ± 0.03	0 - 2	Profile, fine SO_4^{-2}, short grass	Allen et al. (1991)
0.22 ± 0.06	0.1 - 2.0	Eddy covariance with flame photometer plus denuder, 40-cm grass, fine SO_4^{-2}	Wesely et al. (1985)
0.13 ± 0.02 0.75 ± 0.24 1.1 ± 0.1	(SO_4^{-2}) (K^+) (Ca^{+2})	Inert surface collectors (petri dish) in oak forest	Lindberg and Lovett (1985)
0.9 2.5 9.4	2.75 5.0 8.5	Wind tunnel to pine shoots; polystyrene beads; within-canopy wind speed, 2.5 m s^{-1}	Chamberlain and Little (1981)

TABLE 4-6. REPORTED MEAN DEPOSITION VELOCITIES FOR POTASSIUM, SODIUM, CALCIUM, AND MAGNESIUM BASE CATION CONTAINING PARTICLES

Chemical Species/Surface	V_d (cm s^{-1})	Method	Reference
K^+			
Inert plates	0.75	Extraction	Lindberg and Lovett (1985)
Inert bucket	0.51 - 2.4	Extraction	Dasch and Cadle (1985)
Na^+			
Inert bucket	1.7 - 2.9	Extraction	Dasch and Cadle (1985)
Inert plate	0.8 - 8.2	Extraction	
Ca^{+2}			
Inert plates	1.1	Extraction	Lindberg and Lovett (1985)
Inert plates	≈2	Extraction	Lindberg et al. (1990)
Inert bucket	1.7 - 3.2	Extraction	McDonald et al. (1982)
Mg^{+2}			
Inert bucket	1.1 - 2.7	Extraction	Dasch and Cadle (1985)

values of V_d for base-cation-containing particles (> 1 cm s^{-1}) suggest their occurrence in coarse particles (Lindberg and Lovett, 1985).

The several attempts to estimate V_d for SO_4^{-2}, NO_3^-, and NH_4^+ with the throughfall mass balance approach (Davidson and Wu, 1990; Gravenhorst et al., 1983; Höfken and Gravenhorst, 1982) have produced higher V_d values that are considered suspect. They have not been included in Tables 4-4 and 4-6. Overestimates of V_d for SO_4^{-2} and NO_3^- particles derived from throughfall mass balance approaches may be the result of gaseous SO_2 and HNO_3 gaseous deposition to foliar surfaces (Lindberg and Lovett, 1985). A similar contribution of NH_3 deposition may lead to erroneously high V_d values for NH_4^+ when the throughfall method is attempted in areas of high NH_3 concentrations. Dolske's (1988) reported V_d values for NO_3^- deposition to soybean ranged from 0.4 to 31 with a mean of 0.24 cm s^{-1}. However, because Dolske's leaf extraction measurements included a component of HNO_3 vapor, the V_d values may represent more than deposition caused by aerosol nitrate alone.

The quantitative importance of dry particulate deposition depends upon the chemical species, topography, precipitation regime, and surface characteristics, including vegetation properties. Across the diverse landscapes of the Integrated Forest Study (Johnson and Lindberg, 1992a), the relative contribution of dry deposition for Ca^{+2} ranged from about 0% to nearly 90% (Figure 4-8). In contrast, for S the total range was from just over 0% to about 30%. An average for these forest systems demonstrates that deposition of (usually coarse) base cations was nearly 50% by dry particulate deposition (Figure 4-9). Both N and S were around 15%. While the relative significance of dry particle deposition varies from site to site, it cannot be excluded from the analysis at any site.

In a recent review, Wesely and Hicks (2000) concluded that a comprehensive understanding of particulate deposition remains a distant goal. In general, there is only modest confidence in available particulate deposition parameterizations at this time, although recent experimental and theoretical efforts to improve this situation have been made (e.g., Erisman et al., 1997, and companion articles; Zhang et al., 2001; Kim et al., 2000).

The successful treatment of dry deposition of gaseous pollutants (e.g., SO_2 and O_3) linking turbulent deposition to surface physiological properties has allowed incorporation of these models into landscape and regional scale models. This has allowed gaseous deposition to be scaled up for purposes of atmospheric chemistry and vegetation damage assessment. These

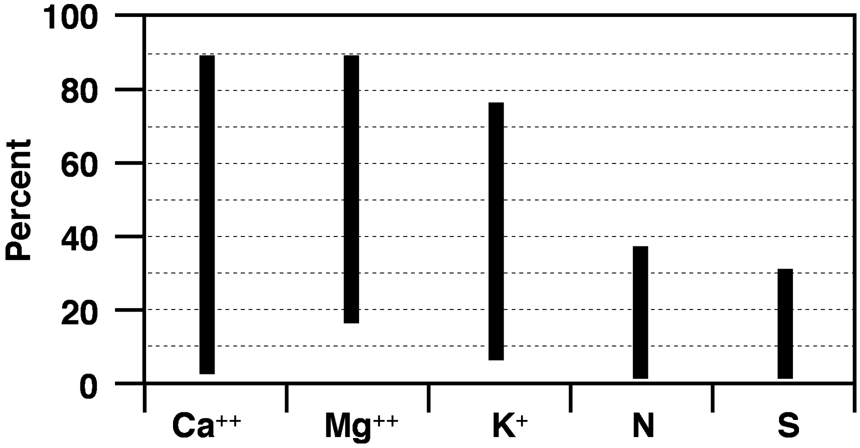


Figure 4-8. Range of percent of total deposition delivered in the dry particulate fraction, across the sites of the Integrated Forest Study (after Johnson and Lindberg, 1992a).

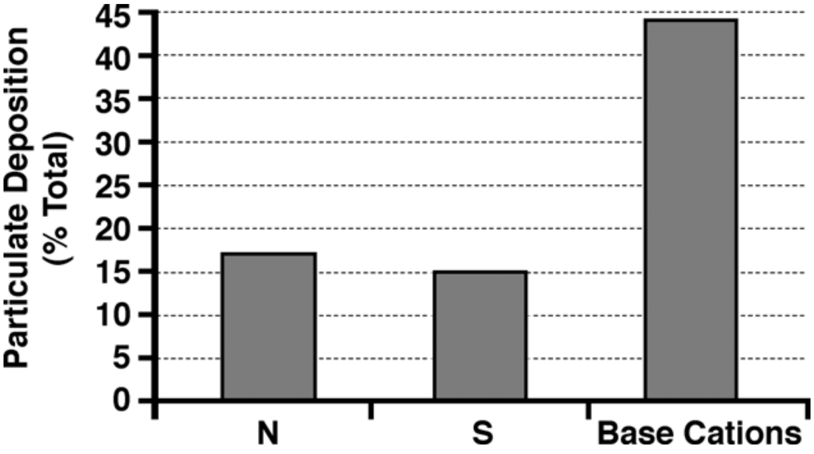


Figure 4-9. Contribution of particulate deposition to total deposition of nitrogen, sulfur, and base cations (after Johnson and Lindberg, 1992a; Lovett, 1992; Lovett and Lindberg, 1993; Lindberg et al., 1990; Kelly and Meagher, 1986).

advances have not been matched by progress in deposition of PM. A serious remaining impediment is the lack of suitable techniques for measuring deposition of heterogeneous and polydisperse particles, such as the gradient and eddy covariance techniques that are used for gaseous pollutant species. As with gaseous pollutants, parameterization of particle deposition in hilly terrain, to patchy surfaces (small agricultural fields, forest edges), and under extremely windy conditions, remains to be fully developed. These limitations must be addressed before a full accounting of regional PM effects on vegetation in natural and managed ecosystems can be achieved.

Occult Deposition

Gaseous pollutant species may dissolve in the suspended water droplets of fog and clouds. The stability of the atmosphere and persistence of the droplets often allow a gas/liquid phase equilibrium to develop. This permits the use of air mass history or ambient concentrations of specific pollutants to estimate fog or cloud water concentrations. Further estimates of the deposition velocity of the polluted droplets allows calculation of depositional fluxes. Unfortunately, interception of fog or cloud droplets by plant parts or other receptor surfaces remains difficult to predict and to measure. Fog formation influences the total atmospheric burden and deposition of particulate matter (Pandis and Seinfeld, 1989) by accreting and removing particles from the air, by facilitating particle growth through aqueous oxidation reactions, and by enhancing deposition as noted. Aqueous condensation may occur onto preexisting fine particles, and such particles may coalesce or dissolve in fog or cloud droplets. Material transported in fog and cloud water and intercepted by vegetation escapes detection by measurement techniques designed to quantify either dry or wet deposition; hence it is hidden (i.e., “occult”) from the traditional measurements.

Occult deposition of fog and cloud droplets is by impaction and gravitational settling in concert with the instantaneous particle (droplet) size. This mode of deposition may be significant at high elevation sites, particularly near the base of orographic clouds. While coastal fog may be generally more pristine than high-elevation continental fogs, this is not true in areas subject to inland radiation fog (e.g., the increasingly polluted San Joaquin Valley of Central California) and in areas where the marine layer is advected through a highly polluted urban area (e.g., the Los Angeles basin of Southern California). Fog water in these areas may be at least as contaminated as that occurring at higher elevations.

Low elevation radiation fog has different formation and deposition characteristics than high elevation cloud or coastal fog water droplets. A one-dimensional deposition model has recently been described for a radiation fog episode (Von Glasow and Bott, 1999). A substantially greater concentration of key polluting species (e.g., NO_3^-, SO_4^{-2}, organics) may be observed in smaller than in larger droplets in fog (Collett et al., 1999). Acidity differences exceeding 1 pH unit were also observed in the San Joaquin Valley winter radiation fog, with smaller particles being more acidic. This has implications for aqueous phase oxidation of sulfur and nitrogen compounds, in particular, while sulfur oxidation by ozone (the dominant reaction in this environment even during winter) is well known in typically acidic fog droplets. However, the alkaline larger droplets in the San Joaquin Valley could lead to greater nitrate production through aqueous ozonation reactions (Collett et al., 1999). The size class distinctions have substantial implications for deposition of particulate pollutant species in the fog droplets due to the larger V_d for impaction and occult deposition of the larger fog particles.

Acidic cloud water deposition has been associated with forest decline in industrialized areas of the world (Anderson et al., 1999). Clouds can contain high concentrations of acids and other ions. The four most prevalent ions found in cloud water samples, in decreasing order of concentration, were usually sulfate (SO_4^{-2}), hydrogen (H^+), ammonium (NH_4^+), and nitrate (NO_3^-). The concentrations of these major ions tend to co-vary within cloud events, and typically there was an inverse relationship between liquid water content (LWC) of the cloud and ionic concentration of the cloud water. Cloud water typically is 5 to 20 times more acid than rain water. This can increase pollutant deposition and exposure of vegetation and soils at high-elevation sites by more than 50% when compared with rainfall and dry deposition.

The widespread injury to mountain forests documented in West Germany since the 1970s and other parts of Europe and more recently in the Appalachian Mountains has been attributed to exposure to the cloud water reducing cold tolerance of red spruce. Forest injury also has been attributed to increased leaching of cations and amino acids and increased deposition of nitrogen and aluminum toxicity resulting from acidic deposition and the combined effect of acidic precipitation, acid fog, oxidants, and heavy metals (Anderson et al., 1999). The Mountain Acid Deposition Program (MADPro) was initiated in 1993 as part of the Clean Air Status and Trends Network (CASTnet). MADPro monitoring efforts focused on the design and implementation of an automated cloud water collection system in combination with continuous measurement of cloud liquid water content (LWC) and meteorological parameters relevant to the cloud deposition process.

Results from the MADPro automated cloud-water collectors at three selected mountain sites (Whiteface Mt., NY; Whitetop Mt., Va; and Clingman's Dome, TN) taken hourly from nonprecipitating clouds during non-freezing seasons of the year from 1994 to 1997 were promptly analyzed for pH, conductivity, and concentration of dissolved ions give an indication of exposures at the three sites. Cloud LWC was measured at each site. The mean cloud water frequencies and LWC were higher at Whiteface Mountain, NY, that in the southern Appalachians. The four most prevalent ions found in cloud water samples, in order of decreasing concentrations, usually were sulfate (SO_4^{-2}), hydrogen (H^+), ammonium (NH_4^+), and nitrate (NO_3^-). The concentrations of these ions tended to co-vary within cloud events and typically there was an inverse relationship between LWC of the cloud and ionic concentration of the cloud water. Highest ionic concentrations were seen in mid-summer. Ionic concentrations of samples from southern sites were significantly higher than samples from Whiteface Mountain, but further analysis indicated that this was due at least in part to North to South differences in the LWC of clouds (Anderson et al., 1999).

Several factors make occult deposition particularly effective for delivery of dissolved and suspended materials to vegetation. Concentrations of particulate-derived materials are often many-fold higher in cloud or fog water than in precipitation or ambient air in the same area due to orographic effects and from gas-liquid partitioning coefficients of specific chemical species. Fog and cloud water deliver PM in a hydrated and, therefore, bioavailable form to foliar surfaces. Previously dry-deposited PM may also become hydrated through delinquence or by dissolution in the film of liquid water from fog deposition. The presence of fog itself maintains conditions of high relative humidity and low radiation, thus reducing evaporation and contributing to the persistence of these hydrated particles on leaf surfaces. Deposition of fog water is very efficient (Fowler et al., 1991) with a V_d (fog 10-24 µm; Gallagher et al., 1988) essentially equal to the aerodynamic conductance for momentum transfer $(r_a)^{-1}$. This greatly enhances deposition by sedimentation and impaction of submicron aerosol particles that exhibit very low V_d prior to fog droplet formation (Fowler et al., 1989). The near equivalence of V_d and $(r_a)^{-1}$ simplifies calculation of fog water deposition and reflects the absence of vegetative physiological control over surface resistance. Fog particles outside this size range may exhibit V_d below $(r_a)^{-1}$. For smaller particles, this decline reflects the increasing influence of still air and boundary layer effects on impaction as particle size and momentum decline. For larger particles, momentum is sufficient to overcome these near surface limitations, but V_d may decline as turbulent eddy transport to the surface becomes inefficient with increasing inertia (Gallagher et al., 1988). The deposition to vegetation for PM in fog droplets is directly proportional to wind speed, droplet size, concentration, and fog density (liquid water content per volume air) although the latter two may be inversely related. In some areas, typically along foggy coastlines or at high elevations, occult deposition represents a substantial fraction of total deposition to foliar surfaces (Fowler et al., 1991, Figure 4-2).

4.2.2.3 Magnitude of Deposition

Dry deposition of PM is most effective for coarse particles including primary geologic material and for elements such as iron and manganese. Wet deposition is most effective for fine particles of atmospheric (secondary) origin (e.g., nitrogen and sulfur, Table 4-6) and elements such as cadmium, chromium, lead, nickel, and vanadium (Reisinger, 1990; Smith, 1990a,b,c; Wiman and Lannefors, 1985). The occurrence of occult deposition is more restricted. The relative magnitudes of the different deposition modes varies with ecosystem type, location, elevation, and chemical burden of the atmosphere. For the Walker Branch Watershed, a deciduous forest in rural eastern Tennessee, dry deposition constituted a major fraction of the total annual atmospheric input of cadmium and zinc (≈20%), lead (≈55%), and manganese (≈90%). Whereas wet deposition fluxes during precipitation events exceeded dry deposition fluxes by one to four orders of magnitude (Lindberg and Harriss, 1981), dry deposition was nearly continuous. Immersion of high-elevation forests in cloud water may occur for 10% or more of the year, significantly enhancing transfer of PM and dissolved gases to the canopy. Occult deposition in the Hawaiian Islands dominated total inputs of inorganic N (Heath and Huebert, 1999). Much of this N was volcanically derived during the generation of volcanic fog in part through reactions with seawater. In this humid climate, the dominance of occult rather than wet deposition is notable.

High-elevation forests receive larger particulate deposition loadings than equivalent low elevation sites. Higher wind speeds enhance the rate of aerosol impaction. Orographic effects enhance rainfall intensity and composition and increase the duration of occult deposition. Coniferous species in these areas with needle-shaped leaves also enhance impaction and retention of PM delivered by all three deposition modes (Lovett, 1984).

In more arid regions, such as the western United States, the importance of dry deposition may be larger. In the San Gabriel Mountains of southern California, for example, while annual deposition of SO_4^{-2} (partly of marine origin) was dominated by wet deposition (Fenn and Kiefer, 1999), deposition of NO_3^- was dominated by dry deposition, as was that of NH_4^+ at two of three sites. Similarly, at a series of low elevation sites in southern California (Padgett et al., 1999), dry deposition of NO_3^- was dominated by dry deposition. In both cases, however, the contribution of gaseous HNO_3 was probably substantial.

Nitrates, Sulfates and Cations

Much particulate sulfate and nitrate is found on particles in the 0.1- to 1.0-μm size range (U.S. Environmental Protection Agency, 1982). However, most sulfate and nitrate, base cation and heavy metal inputs to forested ecosystems results from the deposition of larger particles (Chapter 2; Lindberg and Lovett, 1985; Lindberg et al., 1982). The influence of aerodynamic diameter is particularly critical for nitrogen species, because they exist as a wide range of particle sizes in the atmosphere (Milford and Davidson, 1987). For example, at many sites in North America, NO_3^- is characterized by a bimodal size distribution with modes above and below 1 μm. The supermicron particles are often the result of reactions between HNO_3 and coarse alkaline aerosols (Wolff, 1984) as, for example, in the San Joaquin Valley of California (Lindberg et al., 1990). Although the annual deposition of NH_4^+ is distributed similarly among the fine and coarse particles, particulate NO_3^- is found predominantly in the coarse-particle fraction (Table 4-7). Similar to the pattern for NH_4^+, the estimated annual deposition of SO_4^{-2} particles occurs in both the fine- and coarse-particulate fractions (Table 4-8), while base cation deposition is virtually restricted to contributions from coarse particles (Table 4-9).

Although the annual chemical inputs to ecosystems from particle deposition is significant by itself, it is important to compare it with the total chemical inputs from all sources of atmospheric deposition (i.e., precipitation, particles, and gaseous dry deposition). Figure 4-10 shows the mean percentage contribution of NO_3^- and NH_4^+, SO_4^{-2}, and base cation-containing particles to the total nitrogen, sulfur, and base cation deposition load to forest ecosystems (derived from Tables 4-7 through 4-9). Although the mean contribution of particulate deposition to cumulative nitrogen and sulfur deposition is typically less than 20% of annual inputs from all

TABLE 4-7. MEAN ANNUAL NITROGEN DEPOSITION (equivalents/ha/yr) FROM FINE AND COARSE PARTICLES COMPARED TO TOTAL NITROGEN DEPOSITION FROM ALL SOURCES TO A VARIETY OF FOREST ECOSYSTEMS

		Dry Particle Deposition						
		Fine		Coarse				
Region/Forest Type	Location	NO_3^-	NH_4^+	NO_3^-	NH_4^+	Total	Annual Total Nitrogen[a]	References[b]
North America								
Douglas fir	Washington	2	9	58	27	96	345	1,2
Loblolly pine	Georgia	2	27	36	37	102	647	1,2
Loblolly pine	North Carolina	3	35	89	66	193	997	1,2
Loblolly pine	Tennessee	0.8	18	27	7	53	699	1,2
Loblolly pine	Tennessee	0.2	14	8	1	23	410[c]	3
Slash pine	Florida	6	16	105	4	131	431	1,2
White pine	North Carolina	1	22	23	23	69	510	1,2
Red spruce	Maine	2	14	64	102	182	545	1,2
Red spruce	North Carolina	3	74	133	43	253	1,939	1,2
Red spruce	New York	1	9	5	2	17	1,136	1,2
Alder	Washington	1	5	58	27	91	339	1,2
Maple/beech	New York	0.3	5	37	13	55	567	1,2
Oak	Tennessee					307	857	4
Oak	Tennessee	1	36	83	8	128	720	5
Europe								
Norway spruce	Norway	8	21	52	29	110	775	1,2
Norway spruce	Germany	21	62	56	4	143	1,250[c]	3

TABLE 4-8. MEAN ANNUAL SULFATE DEPOSITION (equivalents/ha/yr) FROM FINE AND COARSE PARTICLES COMPARED TO TOTAL SULFUR DEPOSITION FROM ALL SOURCES TO A VARIETY OF FOREST ECOSYSTEMS

		Dry Particle Deposition				
Region/Forest Type	**Location**	**Fine**	**Coarse**	**Total**	**Annual Sulfur Deposition**[a]	**References**[b]
North America						
Douglas fir	Washington	12	62	74	320	1,2
Loblolly pine	Georgia	47	74	121	776	1,2
Loblolly pine	North Carolina	57	59	116	1,050	1,2
Loblolly pine	Tennessee	27	69	96	941	1,2
Loblolly pine	Tennessee	22	44	66	570[c]	3
Slash pine	Florida	25	129	154	514	1,2
White pine	North Carolina	33	55	88	552	1,2
Red spruce	Maine	34	115	149	585	1,2
Red spruce	North Carolina	135	161	296	2,214	1,2
Red spruce	New York	10	4	14	1,096	1,2
Alder	Washington	6	62	68	325	1,2
Maple/beech	New York	7	32	39	488	1,2
Oak forest	Tennessee	70	190	260	1,600	4
Europe						
Norway spruce	Germany	58	97	155	1,100[c]	3
Norway spruce	Norway	19	79	98	663	1,2

[a] Includes deposition from precipitation, gases, and particles.

[b] 1 = Johnson and Lindberg (1992a), 2 = Lindberg (1992) and Lindberg and Lovett (1992), 3 = Lindberg et al. (1990); 4 = Lindberg et al. (1986).

[c] Includes only the growing season from April to October 1987.

TABLE 4-9. MEAN ANNUAL BASE CATION DEPOSITION (equivalents/ha/yr) FROM FINE AND COARSE PARTICLES COMPARED TO TOTAL BASE CATION DEPOSITION FROM ALL SOURCES TO A VARIETY OF FOREST ECOSYSTEMS

		Dry Base Cation Particles Deposition[a]				
Region/Forest Type	**Location**	**Fine**	**Coarse**	**Total**	**Total Annual Deposition[b]**	**References[c]**
North America						
Douglas fir	Washington	9	180	189	670	1,2
Loblolly pine	Georgia	17	130	147	300	1,2
Loblolly pine	North Carolina	30	340	370	780	1,2
Loblolly pine	Tennessee	6.1	220	226	410	1,2
Mixed Hardwood	Tennessee	9.5[d]	121[d]	131[d]	899[d]	3
Slash pine	Florida	17	600	617	1,200	1,2
White pine	North Carolina	4	150	154	280	1,2
Red spruce	Maine	5	150	155	240	1,2
Red spruce	North Carolina	25	440	465	1,500	1,2
Red spruce	New York	2	36	38	230	1,2
Alder	Washington	4	180	184	660	1,2
Maple/beech	New York	1	84	85	200	1,2
Oak forest	Tennessee	11[e]	312[e]	323[e]	452[e]	3
Europe						
Spruce	Germany[d]					3
Spruce	Norway	6	180	186	390	1,2

[a] Includes K^+, Na^+, Ca^{+2}, and Mg^{+2}.

[b] Includes deposition from precipitation, gases, and particles.

[c] 1 = Ragsdale et al. (1992), 2 = Johnson and Lindberg (1992a), 3 = Lindberg et al. (1986).

[d] Includes H^+, K^+, Na^+, Ca^{+2}, Mg^{+2} for the growing season from April to October 1987.

[e] Includes only Ca^{+2} and K^+.

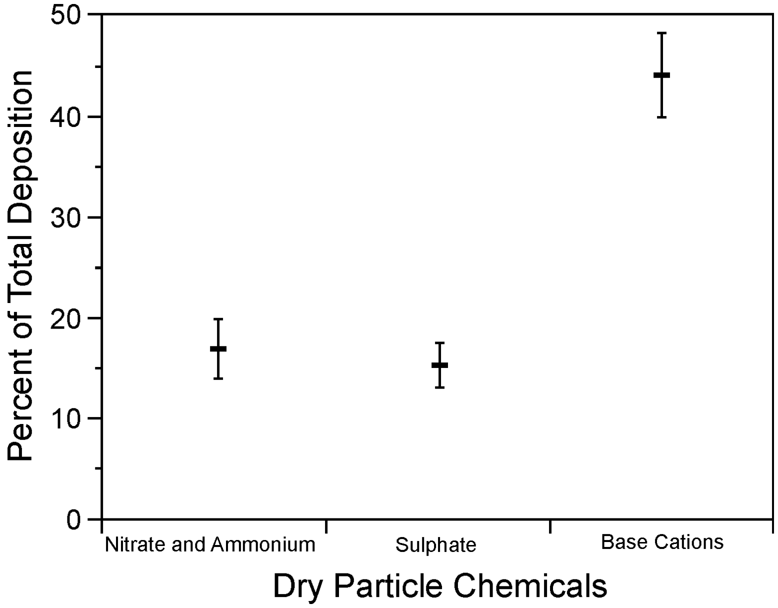


Figure 4-10. Mean (±SE) percent of total nitrogen, sulfur, or base cation deposition contributed by fine plus coarse particles. Data are means from Tables 4-7 through 4-9.

atmospheric sources, particulate inputs of base cations average half the total base cations entering forest ecosystems from the atmosphere.

An extensive comparison of particle to total chemical deposition is provided by the Integrated Forest Study (IFS; Johnson and Lindberg, 1992a; Lovett, 1994; Lovett and Lindberg, 1993; Lindberg and Lovett, 1992; Ragsdale et al., 1992). Other similar data sets are available (Kelly and Meagher, 1986; Miller et al., 1993; Lindberg et al., 1986, 1990). These data in (Tables 4-7 through 4-9) clearly indicate that the contribution of coarse and fine aerosols to deposition to forest ecosystems is strongly dependent on the chemical species.

Dry deposition is an important flux of sulfur and nitrogen compounds at all of the IFS sites and ranges from 9 to 59% of total (wet + dry + cloud) deposition for sulfur, 25% to 70% for NO_3^- and 2% to 33% for NH_4^+. For only NH_4^+ is wet deposition consistently greater than dry deposition (Lovett, 1994).

After emission from their sources, air pollutants are transformed and transported by atmospheric processes (i.e, atmospheric meteorology) until deposited from the atmosphere to an aquatic or terrestrial ecosystem. As a result, ground-level concentrations of an air pollutant depend on the proximity to the sources, prevailing meteorology, and nature and extent of atmospherical reactions between the source and the receptor (Holland et al., 1999). A more direct relationship exists between source strength and downwind ambient concentrations for primary air pollutants (e.g., SO_2) than for secondary pollutants (e.g., sulfate, SO_4^{-2}). Interaction of the chemical and physical atmospheric processes and source locations for all of the pollutants have a tendency to produce data patterns that show large spatial and temporal variability.

Holland et al. (1999) analyzed CASTnet monitoring data and using generative additive models (GAM) estimated the form and magnitude of trends of airborne concentrations of $SO_{2,}$ SO_4^{2-}, and nitrogen from 1989 to 1995 at 34 rural long-term CASTnet monitoring sites in the eastern United States. These models provide a highly flexible method for describing potential nonlinear relationships between concentrations, meteorology, seasonality, and time (e.g., how weekly SO_2 varies as a function of temperature). For most of the 34 sites in the eastern United State, estimates of change in SO_2 concentrations showed a decreasing functional form in 1989-1990, followed by a relatively stable period during 1991-1993), then a sharper decline beginning in 1994 (Holland et al., 1999).

Regional trends of seasonal and annual wet deposition and precipitation-weighted concentrations (PWCs) of sulfate in the United States over the period 1980-1995 were developed by Shannon (1999) from monitoring data and scaled to a mean of unity. In order to reduce some effects of year to year climatological variability, the unitless regional deposition and PWC trends were averaged (hereafter referred to a CONCDEP). During the 16 year period examined in the study, estimated aggregate emissions of SO_2 in the United States and Canada fell approximately 12% from about 1980 to 1982, it remained roughly level for a decade and then fell approximately another 15% from 1992 to 1995 — for an overall decrease of about 18%. Eastern regional trends of sulfate concentrations and deposition and their average CONCDEP, also exhibited patterns of initial decrease, near steady state, and final decrease with year to-to-year variability. The overall relative changed in CONCDEPs are greater than the changes in SO_2 emissions.

Concentrations and calculated deposition (concentration times amount of water) of SO_4^{-2} at the Hubbard Brook Experiment Forest (HBEF) in the White Mountains of central New Hampshire have been measured since June of 1964 (Likens et al., 2001). These measurements represent the longest continuous record of precipitation chemistry in North America. The long-term measurements generally concur with those of Shannon (1999) discussed above. Major declines in emissions of SO_2 have been observed during recent decades in the eastern United States and have been correlated with significant decreases in SO_4^{-2} concentrations in precipitation (Shannon, 1999).

Deposition of sulfates and nitrates are very clearly linked to emissions. Reduction in emissions must occur before concentrations can be reduced below current levels (Likens et al., 2001). Deposition is the key variable as sensitive ecosystems in the eastern North America have not yet shown improvement in response to decreased emissions of SO_2 (Driscoll et al., 1989; Likens et al., 1996). Clearly, additions of other chemicals, such as nitric acid and base cations, must be considered in addition to sulfur when attempting to resolve the acid rain problem (Likens et al., 1996, 1998). The effects of sulfur and nitrogen deposition on ecosystems are discussed in Section 4.2.2.2.

The long-term record indicates that a reduction in the deposition of basic cations (Ca^{+2}, Mg^{2+}, K^+, Na^+) in bulk precipitation was associated with significant declines in sulfate deposition cited above for the HBEF region (Driscoll et al., 1989). Decreases in streamwater concentrations of basic cations have decreased simultaneously, suggesting that streamwater concentrations of basic cations are relatively responsive to changes in atmospheric inputs. Regardless of the cause, the decline in atmospheric influx of basic cations could have important effects on nutrient availability as well as on the acid/base status of soil and drainage water (Driscoll et al., 1989).

Trace Elements

Deposition velocities for fine particles to forest surfaces have been reported in the range of 1 to 15 cm s^{-1} (Smith, 1990a). For example, total, annual heavy metal deposition amounts are highly variable depending on specific forest location and upwind source strength (Table 4-10). Lindberg et al. (1982) quantified the dry deposition of heavy metals to inert surfaces and to leaves of an upland oak forest. As noted for other chemical species, V_d was highly dependent on particle size and chemical species (Table 4-11) with the larger particles depositing more efficiently.

TABLE 4-10. MEAN (±SE) PARTICLE SIZE, DEPOSITION RATES, AND DERIVED DEPOSITION VELOCITIES (V_d) FOR HEAVY METAL DEPOSITION TO THE UPPER CANOPY (INERT PLATES OR LEAVES) OF AN UPLAND OAK FOREST

Metal	Particle Size (µm)	Deposition Rate (pg cm^{-2} h^{-1})	V_d (cm s^{-1})
Manganese	3.4 ± 0.7	91 ± 23	6.4 ± 3.6
Cadmium	1.5 ± 0.7	0.3 ± 0.1	0.37 ± 0.18
Zinc	0.9 ± 0.2	6 ± 1	0.38 ± 0.1
Lead	0.5	23 ± 8	0.06 ± 0.01

Source: Lindberg et al. (1982).

TABLE 4-11. TOTAL HEAVY METAL DEPOSITION TO TEMPERATE LATITUDE FORESTS

Heavy Metal	Forest Deposition kg ha^{-1} year^{-1} (Range)
Cadmium	0.002 - 0.02
Copper	0.016 - 0.24
Lead	0.099 - 1000
Nickel	0.014 - 0.15
Zinc	0.012 - 0.178

Source: Smith (1990c).

Preferential association of heavy metals with fine particles results in reduced control in emission control systems. Metal removal efficiencies for baghouse filters are typically 95 to 99% for all but mercury, but fine particle capture is much less efficient. Wet scrubber efficiency varies with design and pressure drop, typically 50 to 90% (McGowan et al., 1993). Fine particles also have the longest atmospheric residence times and, therefore, can be carried long distances. Depending on climate conditions and topography, fine particles may remain airborne for days to months and may be transported 1,000 to 10,000 km or more from their source. This long-distance transport and subsequent deposition qualify heavy metals as regional- and global-scale air pollutants. Ecosystems immediately downwind of major emissions sources (such as power generating, industrial, or urban complexes) may receive locally heavy inputs. Mass balance budgets (inputs and outputs) of seven heavy metals (cadmium, copper, iron, lead, manganese, nickel, and zinc) have been determined at the Hubbard Brook Experimental Forest (White Mountain National Forest) in New Hampshire. This forest is about 120 km northwest of Boston and relatively distant from major sources of heavy metal emissions. However, continental air masses that have passed over centers of industrial and urban activity also frequently follow storm tracks over northern New England. Resulting annual inputs for the seven heavy metals at Hubbard Brook for 1975 to 1991 are presented in Figure 4-11. Note that the 44-fold decrease in lead deposition is correlated with removal of lead from motor vehicle fuels.

Trace element investigations conducted in roadside, industrial, and urban environments have shown that impressive burdens of particulate heavy metals accumulate on vegetative surfaces. Lead deposition to roadside vegetation (prior to its removal from fuel) was 5 to 20, 50 to 200, and 100 to 200 times lead deposition to agricultural crops, grasses, and trees, respectively, in non-roadside environments. In an urban setting, it has been estimated that the leaves and twigs of a 30-cm (12-in.) diameter sugar maple remove 60, 140, 5800, and 820 mg of cadmium, chromium, lead, and nickel, respectively, during the course of a single growing season (Smith, 1973).

Semivolatile Organics

Organic compounds partition between gas and particle phases, and particulate deposition depends largely on the particle sizes available for adsorption (Pankow, 1987; Smith and Jones, 2000). Dry deposition of organic materials (e.g., dioxins, dibenzofurans, polycyclic aromatics) is often dominated by the coarse fraction, even though mass loading in this size fraction may be small (Lin et al., 1993) relative to the fine PM fraction. For example, measurements in Bavaria in both summer and winter revealed that > 80% of organics were in the fine (< 1.35 μm) fraction (Kaupp and McLachlan, 1999). Nevertheless, in most cases, calculated values of dry deposition were dominated by the material adsorbed to coarse particles. Wet deposition, in contrast, was dominated by the much larger amount of material associated with fine particles. In this environment (where monthly precipitation is about 50 mm in winter and summer), wet

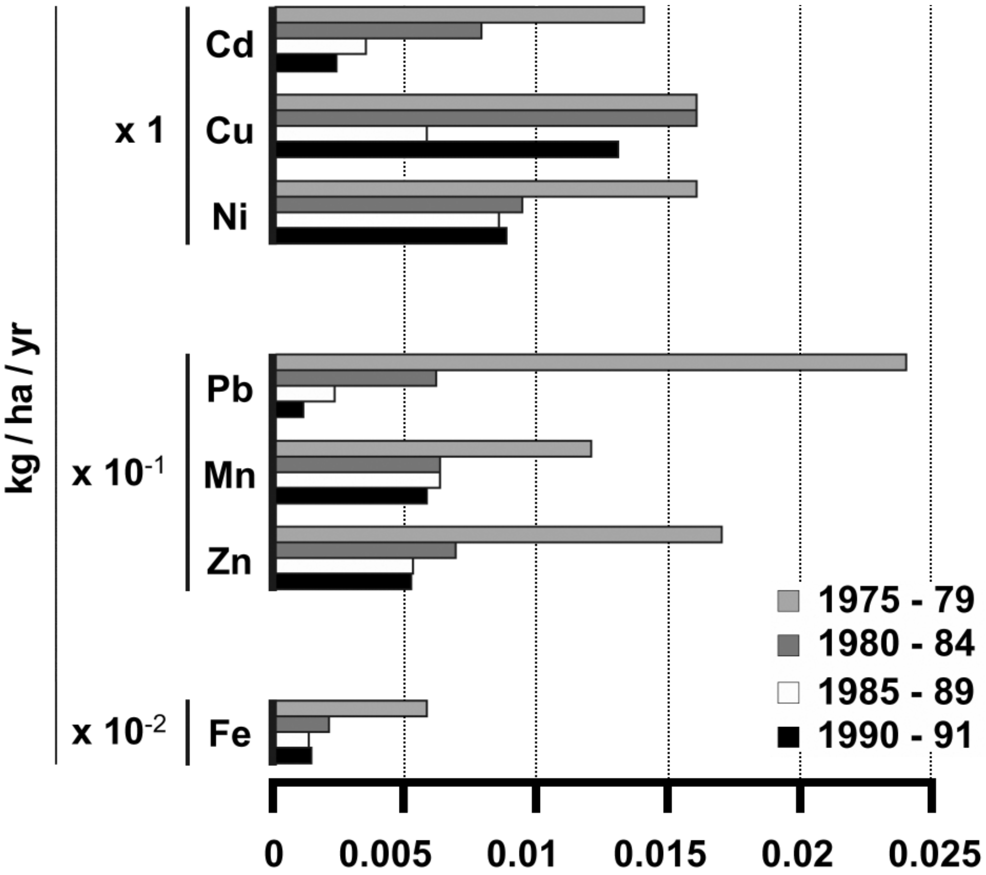


Figure 4-11. **Annual total deposition of heavy metals to Hubbard Brook Experimental Forest, NH (Smith, 1990a).**

deposition dominated, with dry deposition accounting for only 14 to 25% of total deposition (Kaupp and McLachlan, 1999). Lower relative contents of more volatile species in summer than winter (Kaupp and McLachlan, 1999) indicate the critical importance of gas-particle phase interconversions in determining deposition.

Effective deposition of PM is required before biological effects on plants or ecosystems can occur. It is clear that substantially improved techniques for monitoring and predicting deposition will be required to characterize with certainty quantitative relationships between rates and quantities of PM deposition associated with such effects.

4.2.3 Assessment of Atmospheric PM Deposition Effects

Introduction

The discussion in the pages that follow assesses and characterizes the overall ecological condition or integrity of the ecosystems within the United States affected by the deposition of the anthropogenic stressors associated with PM and indicates their status. The six Essential Ecological Attributes (EEAs) – the Landscape Condition, Biotic Condition, and Chemical/ Physical Characteristics, Ecological Processes, Hydrology/Geomorphology, and Natural Disturbance Regimes (Table 4-1) provide a hierarchical framework for determining ecosystem status. Measurable characteristics related to structure, composition, or functioning of ecological systems may be determined by the use of endpoints or ecological indicators of condition that are significant either ecologically or to society (Harwell et al., 1999).

The relationships among the EEAs are complex because all are interrelated (i.e., changes in one EEA may affect, directly or indirectly, every other EEA). The ecological processes create and maintain patterns, which consist of elements in the system and the way they are arranged; whereas the patterns in turn affect how the processes are expressed (Science Advisory Board, 2002). Changes in patterns or processes result in changes in the status and functioning of an ecosystem. The information in the sections that follow discusses changes in Landscape and Biotic patterns and in Ecological and Chemical/Physical Processes resulting from the stressors in PM deposition (Figure 4-12).

The elements of Biotic Condition are organized as nested hierarchy with several levels. These include the structural and composition aspects (patterns) of the biota within landscape, ecosystem or ecological community, species/population, organism and genetic/molecular level (Science Advisory Board, 2002). Within these biological levels of organization, changes in the biodiversity, composition, and structural elements relate directly to functional integrity (such as trophic status or structural integrity within habitats). Changes in biodiversity are of particular significance in altering the functioning of ecosystems.

As previously stated, ecosystems are dynamic, self-adjusting, self-maintaining, complex, adaptive systems, in which patterns at the higher levels of biotic organization emerge from interactions and selection processes at localized levels (Levin, 1998). Ecosystems components must have an adequate supply of energy, mineral nutrients, and water to maintain themselves and function properly. During the ecological processes of energy and material flow, the energy

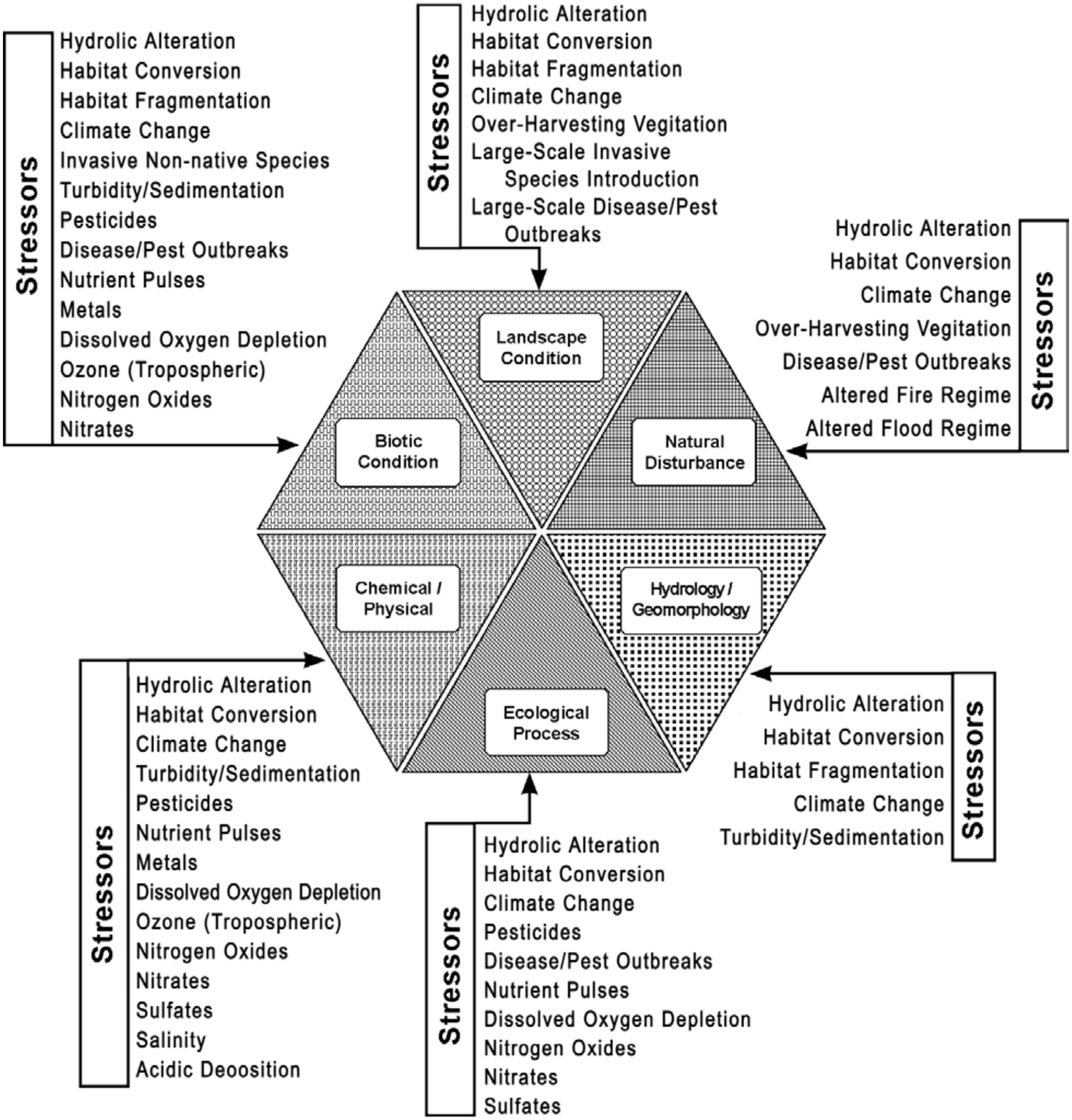


Figure 4-12. Sample stressors and the essential ecological attributes they affect (after Science Advisory Board, 2002).

obtained by plants (the producers) from sunlight during photosynthesis (primary production) and chemical nutrients (e.g., nitrogen, phosphorus, sulfur cycling) taken up from the soil are transferred to other species (the consumers) within the ecosystem through food webs. The movement of chemical nutrients (materials) through an ecosystem is cyclic, as the nutrients are used or stored and eventually returned to the soil by decomposer organisms. Energy, on the other hand, is transferred from organism to organism through an ecosystem in food webs and, finally, is dissipated into the environment as heat (Odum, 1993).

Ecosystem and community patterns are characterized by the interaction of their component species, the ecosystems processes of energy flow, nutrient flux, water and material flow and by the effect their activities have on the physical and chemical environment. The flows of energy and nutrient cycling provide the interconnectedness among the elements of the biotic hierarchy and transform the community from random collection of species into an integrated whole, an ecosystem. Elucidating these interactions across scales is fundamental to understanding the relationships between biodiversity and ecosystem functioning (Levin, 1998).

Human existence on this planet depends on the life-support services provided by the interaction of the different EEAs. Both ecosystem structure (biotic condition) and functions (ecological processes) play an essential role in providing ecosystem goods (products) and services (Table 4-12; Daily, 1997). Ecosystem processes maintain clean water, clean air, a vegetated Earth, and a balance of organisms, the functions that enable humans to survive. The benefits they impart include absorption and breakdown of pollutants, cycling of nutrients, binding of soil, degradation of organic waste, maintenance of a balance of gases in the air, regulation of radiation balance and climate, and the fixation of solar energy (World Resources, 2000-2001; Westman, 1977; Daily, 1997). Economic benefits and values associated with ecosystem functions, goods and services, and the need to preserve them because of their value to human life are discussed by Costanza et al. (1997) and (Pimentel et al., 1997). Goods have market value; whereas services usually are not considered to have market value.

Attempts have been made to calculate the value of biodiversity and the world’s ecosystem services and natural capital (Goulder and Kennedy,1997; Pimentel et al., 1997; Costanza et al., 1997). The majority of these have been controversial because of a lack of agreement on the philosophical basis for placing a value on ecosystem services. Costanza et al. (1997) state that it may never be possible to make a precise estimate of the services provided by ecosystems; however, their estimates indicate the relative importance of ecosystem services, not their true value considering that the loss of ecosystem services can affect human existence. One problem with traditional economic analysis is that following consumption, the material and energy

TABLE 4-12. PRIMARY GOODS AND SERVICES PROVIDED BY ECOSYSTEMS

Ecosystem	Goods	Services
Agroecosystems	Food crops Fiber corps Crop genetic resources	Maintain limited watershed functions (infiltration, flow control, and partial soil protection) Provide habitat for birds, pollinators, and soil organisms important to agriculture Sequester atmospheric carbon Provide employment
Coastal ecosystems	Fish and shellfish Fishmeal (animal feed) Seaweeds (for food and industrial use) Salt Genetic resources	Moderate storm impacts (mangroves, barrier islands) Provide wildlife (marine and terrestrial) habitat and breeding areas/hatcheries/nurseries Maintain biodiversity Dilute and treat wastes Provide harbors and transportation routes Provide human and wildlife habitat Provide employment Contribute aesthetic beauty and provide recreation
Forest ecosystems	Timber Fuelwood Drinking and irrigation water Fodder Nontimber products (vines, bamboos, leaves, etc.) Food (honey, mushrooms fruit, and other edible plants; game) Genetic resources	Remove air pollutants, emit oxygen Cycle nutrients Maintain array of watershed functions (infiltration, purification, flow control, soil stabilization) Maintain biodiversity Sequester atmospheric carbon Moderate weather extremes and impacts Generate soil Provide employment Provide human and wildlife habitat Contribute aesthetic beauty and provide recreation
Freshwater	Drinking and irrigation water Fish Hydroelectricity Genetic resources	Buffer water flow (control timing and volume) Dilute and carry away wastes Cycle nutrients Maintain biodiversity Provide aquatic habitat Provide transportation corridor Provide employment Contribute aethetic beauty and provide recreation
Grassland ecosystems	Livestock (food, game, hides, and fiber) Drinking and irrigation water Genetic resources	Maintain array of watershed functions (infiltration, purification, flow control, and soil stabilization) Cycle nutrients Remove air pollutants and emit oxygen Maintain biodiversity Generate soil Sequester atmospheric carbon Provide human and wildlife habitat Provide employment Contribute aesthetic beauty and provide recreation

Source: World Resources (2000-2001).

embedded in economic goods disappear from the universe of economic analysis although the laws of thermodynamics conservation guarantee their persistence (Moomaw, 2002). An industrial ecology approach considers the full life cycle of materials and energy and recognizes that economic wastes still need to be accounted for following consumption of goods. For example, nitrogen incorporated in fertilizer does not disappear after fuel is burned to produce smog; it continues to cascade through the biosphere. The degraded ecosystem continues to provide fewer ecosystem services for the indefinite future. Some nitrogen in the form of nitric acid may rain down on crops and forests, providing nutrients in degraded form. This diluted nitrogen has the economic equivalent of "scrap value," even if humans do not find it expedient to recover it, given present techniques (Moomaw, 2002).

Heal (2000), on the other hand, feels that attempts to value ecosystems and their services are misplaced: "Economics cannot estimate the importance of natural environments to society: only biology can do that" (Heal, 2000). The role of economics is to help design institutions that will provide incentives to the public and policy makers for the conservation of important natural systems and for mediating human impacts on the biologically diverse ecosystems and the biosphere so that they are sustainable. The approach of Harwell et al. (1999) and the report by the Ecological Processes and Effects Committee of the SAB (Science Advisory Board, 2002) also deals with the need to understand human effects on ecosystems so that ecosystem management can define what ecological conditions are desired. Further, they state that the establishment of ecological goals involves a close linkage between scientists and decision makers in which science informs decision makers and the public by characterizing the ecological conditions that are achievable under particular management regimes. Decision makers then can make choices that reflect societal values including issues of economics, politics, and culture. For management to achieve their goals, the general public, scientific community, resource managers, and decision makers need to be routinely apprised of the condition or integrity of ecosystems so that ecological goals may be established (Harwell et al., 1999).

Biodiversity, the variety of life, encompasses all levels of biological organization, including species individuals, populations, and ecosystems (Figure 4-1; Wilson, 1997). Human-induced changes in biotic diversity and alterations in the structure and functioning of ecosystems are the two most dramatic ecological trends in the past century (Vitousek et al., 1997). There are few ecosystems on Earth today that are not influenced by humans

(Freudenburg and Alario, 1999; Vitousek et al., 1997; Matson et al., 1997; Noble and Dirzo, 1997). The scientific literature is filled with publications discussing the importance of ecosystem structure (patterns) and function (processes). The deposition of particulate matter from the atmosphere has the potential to alter ecosystem structure and function by altering nutrient cycling and changing biodiversity. There is a need, therefore, to understand how ecosystems respond to both natural and anthropogenic stresses in order to determine whether or not anthropogenic stresses are affecting ecosystem services and products (Table 4-12).

Concern has risen in recent years regarding the consequences of changing the biological diversity of ecosystems (Tilman, 2000; Ayensu et al., 1999; Wall, 1999; Hooper and Vitousek, 1997; Chapin et al., 1998). The concerns arise because human activities are creating disturbances that are decreasing biodiversity; altering the complexity and stability of ecosystems; and producing changes in ecological processes and the structure, composition and function of ecosystems (Figure 4-13; Pimm, 1984; Levin, 1998; Chapin et al., 1998; Peterson et al., 1998; Tilman, 1996; Tilman and Downing, 1994; Wall, 1999; Daily and Ehrlich, 1999). The above changes can affect the ecosystem services vital to human life.

4.2.3.1 Effects on Vegetation and Ecosystems

Exposure to a given mass concentration of airborne PM may lead to widely differing phytotoxic responses, depending on the particular mix of deposited particles. Effects of particulate deposition on individual plants or ecosystems are difficult to characterize because of the complex interactions among biological, physicochemical, and climatic factors. Most direct effects, other than regional effects associated with global changes, occur in the severely polluted areas surrounding industrial point sources, such as limestone quarries, cement kilns, and metal smelting facilities. Fine particles are more widely distributed from their source. Experimental applications of PM constituents to foliage typically elicit little response at the more common ambient concentrations. The diverse chemistry and size characteristics of ambient PM and the lack of clear distinction between effects attributed to phytotoxic particles and to other air pollutants further confound understanding of the direct effects on foliar surfaces. The majority of documented toxic effect of particles on vegetation reflect their chemical content (acid/base, trace metal, nutrient), surface properties, or salinity. Studies of direct effects of particles on vegetation have not yet advanced to the stage of reproducible exposure experiments. Difficulties

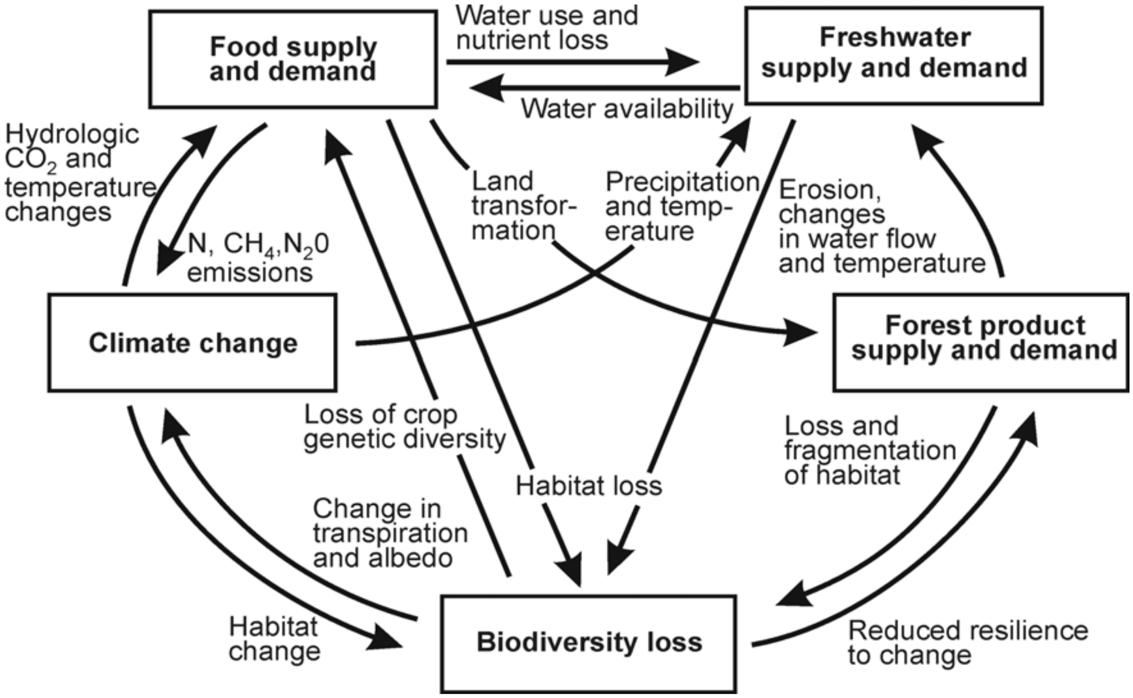


Figure 4-13. Linkages among various ecosystem goods and services (food, water, biodiversity, forest products) and other driving forces (climate change) (modified from Ayensu et al., 1999).

in experimental application of ambient particles to vegetation have been discussed by Olszyk et al. (1989). It is now clear that many phytotoxic gases are deposited more readily, assimilated more rapidly, and lead to greater direct injury to vegetation than do most common particulate materials (Guderian, 1986). The dose-specific responses (dose-response curves) obtained in early experiments following the exposure of plants to phytotoxic gases generally have not been observed following the application of particles.

Unlike gaseous dry deposition, neither the solubility of the particles nor the physiological activity of the surface is likely to be of first order of importance in determining deposition velocity (V_d). Factors that contribute to surface wetness and stickiness may be critical determinants of sticking efficiency. Available tabulation of deposition velocities are highly variable and suspect. High-elevation forests receive larger particle deposition loadings than equivalent lower elevations sites because of higher wind speeds and enhanced rates of aerosol impaction; orographic effects on rainfall intensity and composition; increased duration of occult deposition; and, in many areas, the dominance of coniferous species with needle-shaped leaves (Section 4.2.2.3; Lovett, 1984). Recent evidence indicates that all three modes of deposition (wet, occult, and dry) must be considered in determining inputs to ecosystems or watersheds, because each may dominate over specific intervals of space.

Atmospheric PM may affect vegetation directly following deposition on foliar surfaces or indirectly by changing the soil chemistry or through changes in the amount of radiation reaching the Earth's surface through PM-induced climate change processes. Indirect effects, however, are usually the most significant because they can alter nutrient cycling and inhibit plant nutrient uptake.

Direct Effects of PM Deposition

Coarse and fine PM deposition affects both (a) patterns in the elements of EEA categories subsumed under Biotic Condition and (b) processes subsumed under Chemical/Physical and Ecological Processes in the EPEC framework described earlier. Measurable responses have been observed as reductions in photosynthesis and in salinity of the soil and foliar effects of nitrate, sulfate, and acidic and heavy metal deposition.

Particles transferred from the atmosphere to foliar surfaces may reside on the leaf, twig, or bark surface for extended periods; be taken up through the leaf surface; or be removed from the plant via resuspension to the atmosphere, washing by rainfall, or litter-fall with subsequent transfer to the soil. Any PM deposited on above-ground plant parts may exert physical or chemical effects. The effects of "inert" PM are mainly physical; whereas those of toxic particles are both chemical and physical. The effects of dust deposited on plant surfaces or soil are more likely to be associated with their chemistry than simply with the mass of deposited particles and may be more important than any physical effects (Farmer, 1993). Nevertheless, vegetative surfaces represent filtration and reaction/exchange sites (Tong, 1991; Youngs et al., 1993).

Direct Effects of Coarse Particles

Coarse particles, ranging in size from 2.5 to 100 µm, are chemically diverse, dominated by local sources, and typically deposited near their source because of their sedimentation velocities. Airborne coarse particles are derived from the following sources: road, cement kiln, and foundry dust; fly ash; tire particles and brake linings; soot and cooking oil droplets; biogenic materials (e.g, plant pollen, fungal spores, bacteria and viruses); abraded plant fragments; sea salt; and hydrated deliquescent particles of otherwise fine aerosol. In many rural areas and some urban areas, the majority of mass in the coarse particle mode is in the elements silicon, aluminum, calcium, and iron, suggesting a crustal origin as fugitive dust from disturbed land, roadways, agriculture tillage, or construction activities. Rapid sedimentation of coarse particles tends to restrict their direct effects on vegetation largely to roadsides and forest edges.

Physical Effects — Radiation. Dust can cause physical and chemical effects. Deposition of inert PM on above-ground plant organs sufficient to coat them with a layer of dust may result in changes in radiation received, a rise in leaf temperature, and the blockage of stomata. Increased leaf temperature and heat stress; reduced net photosynthesis; and leaf chlorosis, necrosis, and abscission were reported by Guderian (1986). Road dust decreased the leaf temperature on *Rhododendron catawbiense* by ca., 4 °C (Eller, 1977); whereas foundry dust caused an 8.7 °C increase in leaf temperature of black poplar (*Populus nigra*) under the conditions of the experiment (Guderian, 1986). Deciduous (broad) leaves exhibited larger temperature increases because of particle loading than did conifer (needle) leaves, a function of poorer coupling to the atmosphere. Inert road dust caused a three- to four-fold increase in the absorption coefficient of leaves of English ivy (Eller, 1977; Guderian, 1986) for near infrared radiation (NIR; 750 to 1350 nm). Little change in absorption occurred for photosynthetically active radiation (PAR; 400 to 700 nm). The increase in NIR absorption was equally at the expense of reflectance and transmission in these wavelengths. The amount of energy entering the leaf increased by ca., 30% in the dust-affected leaves. Deposition of coarse particles increased leaf temperature and contributed to heat stress; reduced net photosynthesis; and caused leaf chlorosis, necrosis, and abscission (Dässler et al., 1972; Parish, 1910; Guderian, 1986; Spinka, 1971).

Starch storage in dust-affected leaves increased with dust loading under high (possibly excessive) radiation, but decreased following dust deposition when radiation was limiting. These modifications of the radiation environment had a large effect on single-leaf utilization of light. The boundary layer properties, determined by leaf morphology and environmental conditions, strongly influenced the direct effects of particle deposition on radiation heating

(Eller, 1977; Guderian, 1986) and on gas exchange. Brandt and Rhoades (1973) attributed the reduction in growth of trees to crust formation from limestone dust on the leaves. Crust formation reduced photosynthesis and the formation of carbohydrates needed for normal growth, induced premature leaf-fall, damaged leaf tissues, inhibited growth of new tissue, and reduced starch storage. Dust may decrease photosynthesis, respiration, and transpiration; and it may allow penetration of phytotoxic gaseous pollutants, thereby causing visible injury symptoms and decreased productivity. Permeability of leaves to ammonia increased with increasing dust concentrations and decreasing particle size (Farmer, 1993).

Dust also has been reported to physically block stomata (Krajíčková and Mejstřík, 1984). Stomatal clogging by particulate matter from automobiles, stone quarries, and cement plants was also studied by Abdullah and Iqbal (1991). The percentage of clogging was low in young leaves when compared with old and mature leaves and the amount of clogging varied with species and locality. The maximum clogging of stomata observed was about 25%. The authors cited no evidence that stomatal clogging inhibited plant functioning. The heaviest deposit of dust is usually on the upper surface of broad-leaved plants; whereas the majority of the stomata are on the lower surface where stomatal clogging would be less likely.

Chemical Effects. The chemical composition of PM is usually the key phytotoxic factor leading to plant injury. Cement-kiln dust on hydration liberates calcium hydroxide that can penetrate the epidermis and enter the mesophyll; and, in some cases, this has caused the leaf surface alkalinity to reach a pH of 12. Lipid hydrolysis, coagulation of the protein compounds, and ultimately plasmolysis of the leaf tissue result in reduction in the growth and quality of plants (Guderian, 1986). In experimental studies, application of cement kiln dust of known composition for 2 to 3 days yielded dose-response curves between net photosynthetic inhibition or foliar injury and dust application rate (Darley, 1966). Lerman and Darley (1975) determined that leaves must be misted regularly to produce large effects. Alkalinity was probably the essential phytotoxic property of the applied dusts.

Salinity. Particulate matter enters the atmosphere from oceans following the mixing of air into the water column and the subsequent bursting of bubbles at the surface. The effervescence of bubbles on the surface of the ocean forcefully ejects droplets of sea water into the air. These droplets, concentrated by evaporation, are carried inland by wind and deposited on the seaward side of coastal plants (Boyce, 1954). This occurs largely in the surf line (i.e., near land and potentially sensitive terrestrial receptors). This process can be a significant source of sulfate, sodium, chloride, and trace elements (as well as living material) in the atmospheric aerosol impacting coastal vegetation. Sea-spray particles (Taback et al., 1979) are approximately 24% greater in size than 10 µm, and 54% are between 3 and 10 µm. Thus, only about 20% are fine (0 to 2.5 µm) particles; and deposition by sedimentation and impaction is concentrated near the coast, whereas particle size distribution shifts toward the fine fraction over longer inland transport distances. Airborne concentrations of this marine PM decrease quickly with distance inland from the surfline both by deposition and dilution within atmospheric mixed layer (McKay et al., 1994; Nelis et al., 1994). Near-shore sediments with associated pollutants present in coastal runoff may be suspended in the surf and reentrained into the air. This can be a substantial source of microorganisms and of radionuclides to coastal vegetation (Nelis et al, 1994; McKay et al., 1994).

Sea-salt particles can serve as nuclei for the absorption and subsequent reaction of other gaseous and particulate air pollutants. Both nitrate and sulfate from the atmosphere have been found to associate with coarse and fine sea-salt particles (Wu and Okada, 1994). Direct effects on vegetation reflect these inputs, as well as classical salt injury caused by the sodium and chloride that constitute the bulk of these particles. Foliar accumulation of airborne salt particles may lead to foliar injury, thusly affecting the species composition in coastal environments (Smith, 1984).

The effects of winds and sea spray on coastal vegetation has been reported in the literature since the early 1800s (Boyce, 1954). However, there has been a difference of opinion as to whether the injury to coastal vegetation resulted from windblown aerial salts or from mechanical injury (i.e., sand blasting) due to wind alone. Though the significance of sea water dashed on fore dunes and rocky coasts had been recognized by several authors, Wells and Shunk (1937, 1938) and Wells (1939) were the first to recognize the importance of salt spray in coastal ecology. Wells and Shunk (1937) reported that salt spray carried over dunes was the most important factor influencing growth form, zonation, and succession in coastal dunes. Salt spay injury was recorded 1.25 miles inland on the North Carolina coast. On the basis of observations in the Cape Fear area, they determined that the shape of coastal "wind form" shrubs were the result of sea spray carried by high winds. They found injury on shrubs only near the coast while those at a greater distances inland showed no injury whatsoever after a strong southeast wind that persisted for a period of nineteen hours during cloudy weather and abundant soil moisture.

To determine the cause of injury, injured and uninjured shoots were titrated for chlorides. A marked difference was observed between the injured and uninjured shoots (Wells and Shunk, 1937, 1938). Experimental spraying of shoots of woody plants with seawater resulted in a pattern of injury similar to the injury observed on seaside shrubs. The absence of the more inland species, such as persimmon (*Diosporos virginiana* L.), turkey oak (*Quercus laevis* Walt.), longleaf pine (*Pinus palustris* Mill., *P. australis* Michx.), and wire grass (*Aristida stricta* Michx.), was explained on the basis of intolerance of these species to salt spray. The dominance of live oak (*Quercus virginiana* Mill.), as a practically pure stand on Smith Island (also known as Bald Head Island), NC, and along the eastern and southern NC coast, was determined by Wells (1939) to be due to the tree's tolerance to salt spray. He termed the long term stabilization of the live oak stand as a new type of climax, the "salt spray climax." The later work of Oosting and Billings (1942) near Beaufort, NC, corroborated the findings of Wells and Shunk, 1937, 1938).

The report by Boyce (1954) is probably the most extensive on salt-spray communities. Dune sands in many coastal areas have been shown to have extremely low concentrations of dissolved salts. Studies have indicated that the salt content of the coastal dunes of Virginia, Massachusetts, and California did not exceed the maximum occurring in ordinary cultivated soils. Oosting and Billings (1942) found no correlation between soil salinity and plant distribution on the North Carolina coast. Surface crusts of sand dunes have been shown to have high concentrations of chlorides which could be attributed to sea spray, while concentrations of chlorides in underlying layers was low. The surface layer, however, varied with exposure of the dunes to oceanic winds (Boyce, 1954).

Boyce (1954), Wells (1939), and Wells and Shunk (1938) concluded on the basis of their studies that necrosis and death of plant tissues results from the high deposition of salt spray and high accumulation of the chloride ion in the plant tissues. Very little salt is taken up by plant roots; most enters through the aerial organs. Leaves of plants exposed to salt spray show a distinct pattern of injury (Wells and Shunk, 1938). Necrotic areas first appear at the leaf tips and upper margins and then progress slowly in an inverted "V" toward the petiole. This leaf injury pattern was verified experimentally. Mechanical injury resulting from leaves and twigs beating against each another in the wind causes the formation of small lesions through which salt can enter. After entry into the plant, the chloride ion is rapidly translocated to the apices of the leaves and twigs where it accumulates to injurious concentrations and results in the death of only a portion of the plant. The differential deposition and translocation of the chloride ion results in the death of the seaward leaves and twigs. The result is the continued growth of the uninjured branches in an inland direction. As a result, the canopy angle varies with the intensity of the spray (Boyce, 1954).

Little or no mineral ions are available in the silicate sands of the of coastal dunes. Consequently, plants obtain mineral ions needed for growth from the salt spray. Seawater contains all of the mineral ions required for growth except nitrogen and phosphorus. The amount of nitrogen and phosphorus in seawater varies over a wide range (Boyce, 1954). Experiments indicated that available nitrogen in sea spray was a conditioning factor. Low nitrogen availability increased the tolerance of dune species to salt spray. Increasing the availability of nitrogen resulted in a different pattern of plant zonation and distribution. Dicotyledonous species were restricted to areas of lower spray intensity. The severity of chloride injury was associated more with the amount of available potassium than with the concentration of chlorides within the limits of 280-360 mg Cl/liter (Boyce, 1954).

Other sources of phytotoxic saline PM include aerosols from cooling towers and roadway deicing salt. Cooling towers used to dissipate waste heat from steam-electric power generating facilities may emit salt if brackish water or saltwater is used as a coolant (McCune et al., 1977; Talbot, 1979). Foliar injury is related to salt droplets deposited by sedimentation or impaction from cooling tower drift. The distance of the salt drift determines the amount of deposition and location of injury. Environmental conditions most conducive to injury were absence of precipitation, which can wash salt off leaves, and high relative humidity (RH; Talbot, 1979). Increased injury is associated with wind speed and salt concentrations. Typical toxicity symptoms from acute exposures include marginal foliar necrosis and lesions; shoot-tip dieback; leaf curl; and interveinal necrosis (McCune et al., 1977). Based on experimental data, Grattan et al. (1981) observed that, to cause injury, salt deposited on leaf surfaces must dissolve and be absorbed into leaf tissue. Their work also indicated the importance of RH in foliar uptake.

If RH remained below 70%, even heavy deposition of salt did not induce injury in peppers, soybeans, and tomatoes.

Injury to vegetation from the application of deicing salt was related to salt spray blown or drifting from the highways by Hofstra and Hall (1971) and Viskari and Kärenlampi (2000). The most severe injury was observed nearest to the highways. The results presented in these studies agrees with that of Wyttenbach et al. (1989), who observed that conifers planted near roadway margins in the eastern United States often exhibit foliar injury due to toxic levels of saline aerosols deposited from deicing solutions. Piatt and Krause (1974) demonstrated that road and site factors influence the spread of deicing salt into forested areas. The slope away from the road influenced the distance from the road where injury was observed and the percent slope was correlated with distance.

Effects of Fine Particles

Fine PM in rural areas is generally secondary in nature, having condensed from the vapor phase or been formed by chemical reaction from gaseous precursors in the atmosphere, and is generally smaller than 1 to 2.5 µm. Nitrogen and sulfur oxides, volatile organic gases, condensates of volatilized metals, and products of incomplete combustion are common precursors for fine PM. Reactions of many of these materials with an oxidizing atmosphere contribute to high secondary PM concentrations during summer months in many U.S. areas or during late fall and winter in areas with high nitrate concentrations. The conclusion that sufficient data were not available for adequate quantification of dose-response functions for direct effects of fine aerosols on vegetation, reached in the 1982 PM/SO_X AQCD (U.S. Environmental Protection Agency, 1982), continues to be true today. Only a few studies on the direct effects of acid aerosols have been completed (U.S. Environmental Protection Agency, 1982). The major effects are indirect and occur through the soil (Section 4.2.3.2).

Nitrogen. Nitrate is observed in both fine and coarse particles. Nitrates from atmospheric deposition represent a substantial fraction of total nitrogen inputs to southeastern forests (Lovett and Lindberg, 1986). However, much of this is contributed by gaseous nitric acid vapor; and a considerable amount of the particulate nitrate is taken up indirectly through the soil. Garner et al. (1989) estimated deposition of nitrogen to forested landscapes in eastern North America at

10 to 55 kg/ha/year for nitrate and 2 to 10 kg/ha/year for ammonium. About half of these values were ascribed to dry deposition.

Driscoll et al. (2003) estimated anthropogenic nitrogen inputs to eight large watersheds in the Northeastern United States for the year 1997. Inputs of total nitrogen deposition ranged from 14 kg/ha/year in the Casco Bay watershed, ME, to 68 kg/ha/year in the Massachusetts Bay watershed. Atmospheric deposition of nitrogen was the second largest source ranging in amounts from 5 to 10 kg/ha/year (11-36% of the total; Driscoll et al., 2003). Nitrogen deposition in the western United States ranges from 1 to 4 kg/ha/year over much of the region to as high as 30 kg/year downwind of major urban and agricultural areas. An unknown amount of nitrogen deposited to the West Coast originates in Asia (Fenn et al., 2003a).

Atmospheric additions of particulate nitrogen in excess of vegetation needs are lost from the system, mostly as leachate from the soil as nitrate. Managed agricultural ecosystems may be able to utilize deposited particulate nitrogen more efficiently than native ecosystems although many cultivated systems also lose considerable nitrogen as nitrate in runoff, deep drainage, or soil water. It has proven difficult to quantify direct foliar fertilization by uptake of nitrogen from ambient particles.

There is no doubt that foliar uptake of nitrate can occur, as clearly shown by the efficacy of foliar fertilization in horticultural systems. Potassium nitrate was taken up by leaves of deciduous fruit trees (Weinbaum and Neumann, 1977) and resulted in increased foliar nitrogen concentrations. Not all forms of nitrogen are absorbed equally, nor are all equally benign. Following foliar application of 2600 ppm of nitrogen as $Ca(NO_3)_2$, $(NH_4)_2SO_4$, or $(NH_2)_2CO$ to apple canopies (Rodney, 1952; Norton and Childers, 1954), leaf nitrogen levels were observed to increase to similar levels; but calcium nitrate and ammonium sulfate caused visible foliar injury; whereas urea did not. Urea is generally the recommended horticultural foliar fertilizer.

The mechanism of uptake of foliarly deposited nitrate is not well established. Nitrate reductase is generally a root-localized enzyme: it is generally not present in leaves, but is inducible there. Induction typically occurs when the soil is heavily enriched in NO_3^-. As the root complement of nitrate reductase becomes overloaded, unreduced nitrate reaches the leaves through the transpiration stream. Nitrate metabolism has been demonstrated in leaf tissue (Weinbaum and Neumann, 1977) following foliar fertilization. Residual nitrate reductase activity in leaves may be adequate to assimilate typical rates of particulate nitrate deposition.

Uptake of nitrate may be facilitated by codeposited sulfur (Karmoker et al., 1991; Turner and Lambert, 1980).

Nitrate reductase is feedback-inhibited by its reaction product NH_4^+. The common atmospheric aerosol, NH_4NO_3, therefore may be metabolized in two distinct biochemical steps: first the ammonium (probably leaving nitric acid) and then the nitrate. Losses of nitric acid by volatization during this process, if they occur, have not been quantified.

Direct foliar effects of particulate nitrogen have not been documented. Application of a variety of fine nitrogenous aerosol particles (0.25 μm) ranging from 109 to 244 $\mu g/m^3$ nitrogen with or without 637 $\mu g/m^3$ sulfur caused no consistent short-term (2- to 5-h) effect on gas exchange in oak, maize, or soybean leaves (Martin et al., 1992).

Although no evidence exists for the direct transfer of nutrient particulate aerosols into foliage, a few studies give insights into the potential for ammonium and nitrate transfer into leaves. Fluxes of both NO_3^- and NH_4^+, measured in wet deposition and in throughfall plus stemflow in forests, commonly indicate higher fluxes of nitrogen above the canopy (Parker, 1983; Lindberg et al., 1987; Sievering et al., 1996), and imply net foliar uptake. Lovett and Lindberg (1993) reported a linear relationship between inorganic nitrogen fluxes in deposition and throughfall, suggesting that uptake may be considered passive to some extent.

Garten and Hanson (1990) studied the movement of ^{15}N-labeled nitrate and ammonium across the cuticles of red maple (*Acer rubrum*) and white oak (*Quercus alba*) leaves when applied as an artificial rain mixture. Brumme et al. (1992), Bowden et al. (1989), and Vose and Swank (1990) have published similar data for conifers. These studies show the potential for nitrate and ammonium to move into leaves, where it may contribute to normal physiological processes (e.g., amino acid production; Wellburn, 1990). Garten (1988) showed that internally translocated ^{35}S was not leached readily from tree leaves of yellow poplar (*Liriodendron tulipifera*) and red maple (*Acer rubrum*), suggesting that SO_4^{-2} would not be as mobile as the nitrogen-containing ions discussed by Garten and Hanson (1990). Further, when the foliar extraction method is used, it is not possible to distinguish sources of chemicals deposited as gases or particles (e.g., nitric acid [HNO_3], nitrogen dioxides [NO_2], nitrate [NO_3^-]), or sources of ammonium (deposited as ammonia [NH_3] or ammonium ion [NH_4^+]; Garten and Hanson, 1990).

Particle deposition contributes only a portion of the total atmospheric nitrogen deposition reaching vegetation; but, when combined with gaseous and precipitation-derived sources, total nitrogen deposition to ecosystems has been identified as a possible causal factor leading to changes in natural ecosystems (See Section 4.2.2).

Sulfur. Anthropogenic sulfur emissions are > 90% SO_2. Most of the remaining emission of sulfur is directly as sulfate (U.S. Environmental Protection Agency, 1996a). Sulfur dioxide is hydrophilic and is rapidly hydrated and oxidized to sulfite and bisulfite and then to sulfate, which is approximately 30-fold less phytotoxic. The ratio of SO_4^{-2}/SO_2 increases with aging of the air mass and, therefore, with distance from the source. Sulfate is sufficiently hygroscopic in humid air that it may exist significantly in the coarse particulate fraction. Because dilution of both SO_2 and particulate SO_4^{-2} occurs with distance from the source, it is unusual for damaging levels of particulate sulfate to be deposited. Gas to particle conversion in this case is of benefit to vegetation.

Sulfur is an essential plant nutrient. Low dosages of sulfur serve as a fertilizer, particularly for plants growing in sulfur-deficient soil (Hogan et al., 1998). However, current levels of sulfate deposition reportedly exceed the capacity of most vegetative canopies to immobilize the sulfur (Johnson, 1984). Nitrogen uptake in forests may be regulated loosely by sulfur availability, but sulfate additions in excess of needs do not typically lead to injury unless deposited in acidic precipitation (Turner and Lambert, 1980).

There are few field demonstrations of foliar sulfate uptake (Krupa and Legge, 1986, 1998). Sulfate in throughfall is often enriched above levels in precipitation. The relative importance of foliar leachate and prior dry-deposited sulfate particles remains difficult to quantify (Cape et al., 1992). Leaching rates are not constant and may respond to levels of other pollutants, including acids. Uptake and foliar retention of gaseous and particulate sulfur are confounded by variable rates of translocation and accessibility of deposited materials to removal and quantification by leaf washing. Following soil enrichment with $^{35}SO_4^{-2}$ in a Scots pine forest, the apparent contribution of leachate to throughfall was only a few percent following an initial burst of over 90% because of extreme disequilibrium in labeling of tissue sulfate pools (Cape et al., 1992).

Olszyk et al. (1989) provide information on the effects of multiple pollutant exposures including particles (NO_3^-, 142 μg/m^3; NH_4^+, 101 μg/m^3; SO_4^{-2}, 107 μg/m^3). They found that only gaseous pollutants produced direct (harmful) effects on vegetation for the concentrations documented, but the authors hypothesized that long-term accumulation of the nitrogen and sulfur compounds contributed from particle deposition might have effects on plant nutrition over long periods of time. Martin et al. (1992) exposed oak (*Quercus macrocarpa*), soybean (*Glycine max*), and maize (*Zea mays*) plants to acute exposures (2 to 5 h) of aerosols (0.25 µm) containing only nitrate (109 µg/m^3), ammonium and nitrate (244 and 199 µg/m^3), or ammonium and sulfate (179 and 637 µg/m^3). They found that these exposures, which exceeded the range of naturally occurring aerosol concentrations, had little effect on foliar photosynthesis and conductance. Martin et al. (1992) concluded that future investigations should focus on the effects of particles on physiological characteristics of plants following chronic exposures.

Acidic Deposition. The effects of acidic deposition have been accorded wide attention in the media and elsewhere (Altshuller and Linthurst, 1984; Hogan et al., 1998). Probably the most extensive assessment of acidic deposition processes and effects is the NAPAP Biennial Report to Congress: An Integrated Assessment (National Science and Technology Council, 1998). Concern regarding the effects of acidic deposition on crops and forest trees has resulted in extensive monitoring and research. Exposures to acidic rain or clouds can be divided into "acute" exposures to higher ionic concentrations (several µmol/L) and "chronic" long-term repeated exposures to lower concentrations (Cape, 1993). Pollutant concentrations in rainfall have been shown to have little capacity for producing direct effects on vegetation (Altshuller and Linthurst, 1984; Hogan et al., 1998); however, fog and clouds, which may contain solute concentrations up to 10 times those found in rain, have the potential to cause direct effects. More than 80% of the ionic composition of most cloud water is made up of four major pollutant ions: H^+, NH_4^+, NO_3^-, and SO_4^{-2}. Ratios of hydrogen to ammonium and sulfate to nitrate vary from site to site with all four ions usually present in approximately equal concentrations. Available data from plant effect studies suggest that hydrogen and sulfate ions are more likely to cause injury than ions containing nitrogen (Cape, 1993).

The possible direct effects of acidic precipitation on forest trees have been evaluated by experiments on seedlings and young trees. The size of mature trees makes experimental exposure difficult, therefore necessitating extrapolations from experiments on seedlings and saplings; however, such extrapolations must be used with caution (Cape, 1993). Both conifers and deciduous species have shown significant effects on leaf surface structures after exposure to simulated acid rain or acid mist at pH 3.5. Some species have shown subtle effects at pH 4 and above. Visible lesions have been observed on many species at pH 3 and on sensitive species at pH 3.5 (Cape, 1993). The relative sensitivities of forest vegetation to acidic precipitation based on macroscopic injury have been ranked as follows: herbaceous dicots > woody dicots > monocots > conifers (Percy, 1991).

Huttunen (1994) described the direct effects of acid rain or acidic mist on epicuticular waxes whose ultrastructure is affected by plant genotype and phenotype. The effects of air pollutants on epicuticular waxes of conifers have received greater study than the waxes of other species. Leaf age and the shorter life span of broad-leaved trees make them less indicative of the effects of acid precipitation. Many experimental studies indicate that epicuticular waxes that function to prevent water loss from plant leaves can be destroyed by acid rain in a few weeks (Huttunen, 1994). This function is crucial in conifers because of their longevity and evergreen foliage. Microscopic observations of epicuticular wax structures have, for a long time, suggested links between acidic deposition and aging. In Norway spruce (*Picea abies*), acid rain causes not only the aging of needles (which in northern conditions normally last from 11 to 14 years) to be shortened, but also accelerates the erosion rate of the waxes as the needles age.

The effects of acidic precipitation and fog on red spruce (*Picea rubens*) have been studied extensively (Schier and Jensen, 1992). Visible foliar injury of the needles in the form of a reddish-brown discoloration has been observed on red spruce seedlings experimentally exposed to acidic mist, but this visible symptom has not been observed in the field. Ultrastructural changes in the epicuticular wax were observed both experimentally and on spruce growing at high elevations. Laboratory studies indicate that visible injury usually does not occur unless the pH is 3 or less (Schier and Jensen, 1992). Cape (1993) reported that, when compared with other species, red spruce seedlings appeared to be more sensitive to acid mist. From studies of conifers and a review of the literature, Huttunen (1994) concluded that acidic precipitation causes direct injury to tree foliage and indirect effects through the soil. The indirect effects of acidic precipitation are discussed in Section 4.2.3.2.

Based on a review of the many studies in the literature involving field and controlled laboratory experiments on crops, Cape (1993) drew a number of conclusions concerning the direct effects of acidic precipitation on crops:

- foliar injury and growth reduction occur below pH 3;
- allocation of photosynthate is altered, with increased shoot to root ratios;

- expanded and recently expanded leaves are most susceptible, and injury occurs first to epidermal cells;
- leaf surface characteristics such as wettability, buffering capacity, and transport of material across the leaf surface contribute to susceptibility and differ among species;
- data obtained from experiments in greenhouses or controlled environmental chambers cannot be used to predict effects on plants grown in the field;
- quantitative data from experimental exposures cannot be extrapolated to field exposures because of differences and fluctuations in concentrations, durations, and frequency of exposure;
- there are large differences in response within species;
- timing of exposure in relation to phenology is of utmost importance;
- plants may be able to recover from or adapt to injurious exposures; and
- sequential exposure to acidic precipitation and gaseous pollutants is unlikely to be more injurious than exposure to individual pollutants.

Studies by Chevone et al. (1986), Krupa and Legge (1986), and Blaschke (1990) differ with the last conclusion of Cape listed above. Their studies indicate that interactions between acidic deposition and gaseous pollutants do occur. Acidity affects plant responses to both O_3 and SO_2. Chevone et al. (1986) observed increased visible injury on soybean and pinto bean when acid aerosol exposure preceded O_3 exposure; whereas linear decreases in dry root weight of yellow poplar occurred as acidity increased with simultaneous exposures to O_3 and simulated acid rain. Krupa and Legge (1986) also noted increased visible injury to pinto bean plants when aerosol exposure preceded O_3 exposure. In none of the studies cited above did acid rain per se produce significant growth changes. In contrast, Blaschke (1990) observed a decrease in ectomycorrhizal frequency and short root distribution caused by acid rain exposure in combination with either SO_2 or O_3.

Trace Elements. All but 10 of the 90 elements that comprise the inorganic fraction of the soil occur at concentrations of less than 0.1% (1000 μg/g) and are termed “trace” elements. Trace elements with a density greater than 6 g cm^{-3}, referred to as “heavy metals,” are of particular interest because of their potential toxicity for plant and animals. Although some trace metals are essential for vegetative growth or animal health, they are all toxic in large quantities. Combustion processes produce metal chlorides that tend to be volatile and metal oxides that tend to be nonvolatile in the vapor phase (McGowan et al., 1993). Most trace elements exist in the atmosphere in particulate form as metal oxides (Ormrod, 1984). Aerosols containing trace elements derive predominantly from industrial activities (Ormrod, 1984). Generally, only the heavy metals cadmium, chromium, nickel, and mercury are released from stacks in the vapor phase (McGowan et al., 1993). Concentrations of heavy metals in incinerator fly ash increase with decreasing particle size.

Vegetational surfaces, especially the foliage, present a major reaction and filtration surface to the atmosphere and act to accumulate particles deposited via wet and dry processes described in Section 4.2.2 (Tong, 1991; Youngs et al., 1993). The chemical constituents of particles deposited on foliar surfaces may be taken up through the leaf surface. The greatest particle loading is usually on the adaxial (upper) leaf surface where particles accumulate in the mid-vein, center portion of the leaves. Additionally, the mycelium of fungi becomes particularly abundant on leaf surfaces as the growing season progresses and is in intimate association with deposited particles (Smith, 1990c).

Investigations of trace elements present along roadsides and in industrial and urban environments indicate that impressive burdens of particulate heavy metals can accumulate on vegetative surfaces. Foliar uptake of available metals could result in metabolic effects in above-ground tissues. Only a few metals, however, have been documented to cause direct phytotoxicity in field conditions. Copper, zinc, and nickel toxicities have been observed most frequently. Low solubility, however, limits foliar uptake and direct heavy metal toxicity because trace metals must be brought into solution before they can enter into leaves or bark of vascular plants. In those instances when trace metals are absorbed, they are frequently bound in leaf tissue and are lost when the leaf drops off (Hughes, 1981). Trace metals in mixtures may interact to cause a different plant response when compared with a single element; however, there has been little research on this aspect (Ormrod, 1984). In experiments using chambers, Marchwinska and Kucharski (1987) studied the effects of SO_2 alone and in combination with PM components (Pb, Cd, Zn, Fe, Cu, and Mn) obtained from a zinc smelter bag filter. The combined effects of SO_2 and PM further increased the reduction in yield of beans caused by SO_2;

whereas the combination, though severely injuring the foliage, produced little effect on carrots and parsley roots except after long-term exposures (when there was a decrease in root weight).

Trace metal toxicity of lichens has been demonstrated in relatively few cases. Nash (1975) documented zinc toxicity in the vicinity of a zinc smelter near Palmerton, PA. Lichen species richness and abundance were reduced by approximately 90% in lichen communities at Lehigh Water Gap near the zinc smelter when compared with those at Delaware Water Gap. Zinc, cadmium, and SO_2 were present in concentrations toxic to some species near the smelter; however, toxic zinc concentrations were detected farther away than the detectable limits of SO_2 (Nash, 1975). Experimental data suggest that lichen tolerance to Zn and Cd falls between 200 and 600 ppm (Nash, 1975).

Though there has been no direct evidence of a physiological association between tree injury and exposure to metals, heavy metals have been implicated because their deposition pattern is correlated with forest decline. The role of heavy metals has been indicated by phytochelatin measurements. Phytochelatins are intracellular metal-binding peptides that act as specific indicators of metal stress. Because they are produced by plants as a response to sublethal concentrations of heavy metals, they can indicate that heavy metals play a role in forest decline (Gawel et al., 1996). Concentrations of heavy metals increased with altitude, as did forest decline, and increased concentrations across the study region that show increased levels of forest injury, as well.

Phytochelatin concentrations were measured in red spruce and balsam fir (*Abies balsamea*) needles throughout the 1993 growing season at 1000 m on Whiteface Mountain in New York. Mean foliar concentrations in red spruce were consistently higher than in balsam fir from June until August, with the greatest and most significant difference occurring at the peak of the growing season in mid-July. In July, the phytochelatin concentrations were significantly higher than at any other time measured. Balsam fir did exhibit this peak, but maintained a consistently low level throughout the season. Both the number of dead red spruce trees and phytochelatin concentrations increased sharply with elevation (Gawel et al., 1996). The relationship between heavy metals and the decline of forests in northeastern United States was further tested by sampling red spruce stands showing varying degrees of decline at 1000 m on nine mountains spanning New Hampshire, Vermont, and New York. The collected samples indicated a systematic and significant increase in phytochelatin concentrations associated with the extent of tree injury. The highest phytochelatin concentrations were measured during 1994 from sites most severely affected by forest decline in the Green Mountains, VT, and the Adirondack Mountains, NY. These data strongly imply that metal stress causes tree injury and contributes to forest decline in the northeastern United States (Gawel et al., 1996).

One potential direct effect of heavy metals is on the activity of microorganisms and arthropods resident on and in the leaf surface ecosystem. The fungi and bacteria living on and in the surfaces of leaves play an important role in the microbial succession that prepares leaves for decay and litter decomposition after their fall (U.S. Environmental Protection Agency, 1996b). Numerous fungi were consistently isolated from foliar surfaces at various crown positions from London plane trees growing in roadside environments in New Haven, CT. Those existing primarily as saprophytes included *Aureobasidium pullulans, Chaetomium sp.*, *Cladosporium sp.*, *Epicoccum sp.*, and *Philaphora verrucosa*. Those existing primarily as parasites included *Gnomonia platani*, *Pestalotioposis sp.*, and *Pleurophomella sp*. The following cations were tested in vitro for their ability to influence the growth of these fungi: cadmium, copper, manganese, aluminum, chromium, nickel, iron, lead, sodium, and zinc. Results indicated variable fungal response with no correlation between saprophytic or parasitic activity and sensitivity to heavy metals. Both linear extension and dry weight data indicated that the saprophytic *Chaetomum sp.* was very sensitive to numerous metals. *Aureobasidium pullulans*, *Epicoccum sp.*, and especially *P.verrucosa*, on the other hand, appeared to be much more tolerant. Of the parasites, *G. platani* appeared to be more tolerant than *Pestalotiopsis sp.* and *Pleurophomella sp*. Metals exhibiting the broadest spectrum growth suppression were iron, aluminum, nickel, zinc, manganese, and lead (Smith and Staskawicz, 1977; Smith, 1990c). These in vitro studies employed soluble compounds containing heavy metals. Trace metals probably occur naturally on leaf surfaces as low-solubility oxides, halides, sulfates, sulfides, or phosphates (Clevenger et al., 1991; Koslow et al., 1977). In the event of sufficient solubility and dose, however, changes in microbial community structure on leaf surfaces because of heavy metal accumulation are possible.

Organic Compounds. Volatile organic compounds in the atmosphere are partitioned between the gas and particle phases, depending on the liquid phase vapor pressure at the ambient atmospheric temperature, the surface area of the particles per unit volume of air, the nature of the particles and of the chemical being adsorbed; and they can be removed by wet and dry deposition (McLachlan, 1996a). Materials as diverse as DDT, polychlorinated biphenyls (PCBs), and polynuclear aromatic hydrocarbons (PAHs) are being deposited from the atmosphere on rural as well as urban landscapes (Kylin et al., 1994). Motor vehicles emit particles to the atmosphere from several sources in addition to the tailpipe. Rogge et al. (1993b) inventoried the organic contaminants associated with fine particles (diameter ≤2.0 µm) in road dust, brake-lining-wear particles, and tire tread debris. More than 100 organic compounds were identified in these samples, including n-alkanols, benzoic acids, benzaldehydes, polyalkylene glycol ethers, PAHs, oxy-PAH, steranes, hopanes, natural resins, and other compound classes. A large number of PAHs, ranging from naphthalene ($C_{10}H_8$) to 5- and 6-ring and higher PAHs, their alkyl-substituted analogues, and their oxygen- and nitrogen-containing derivatives are emitted from motor vehicle sources (Seinfeld, 1989).

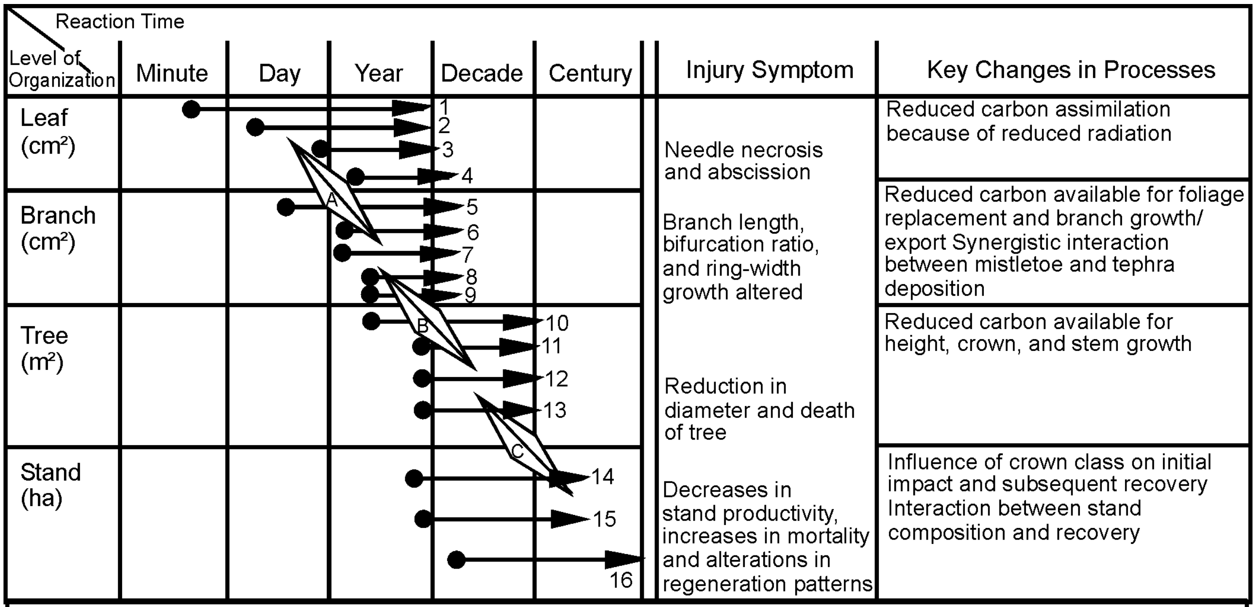
Plants may be used as environmental monitors to compare the deposition of PAH, persistent organic pollutants (POPs), or semivolatile organic components (SOCs) between sites (e.g., urban versus rural; Wagrowski and Hites, 1997; Ockenden et al., 1998; McLachlan, 1999). Vegetation can be used qualitatively to indicate organic pollutant levels as long as the mechanism of accumulation is considered. The substance may enter the plant via the roots or, as mentioned above, be deposited as a particle onto the waxy cuticle of leaves or be taken up through the stomata. The pathways are a function of the chemical and physical properties of the pollutant such as its lipophilicity, water solubility, vapor pressure (which controls the vapro-particle partitioning) and Henry's law constant; environmental conditions such as ambient temperature and the organic content of the soil; and the plant species, which controls the surface area and lipids available for accumulation (Simonich and Hites, 1995). Ockenden et al. (1998) have observed that, for lipophilic POPs, atmospheric transfer to plant has been the main avenue of accumulation. Plants can differentially accumulate POPs. Results have shown differences between species with higher concentrations in the lichen (*Hypogymnia physiodes*) than in Scots pine needles (*Pinus sylvestris*). Even plants of the same species, because they have different growth rates and different lipid contents (depending on the habitat in which they are growing), have different rates of sequestering pollutants. These facts confound data interpretations and must be taken into account when considering their use as passive samplers.

Vegetation itself is an important source of hydrocarbon aerosols. Terpenes, particularly α-pinene, β-pinene, and limonene, released from tree foliage may react in the atmosphere to form submicron particles. These naturally generated organic particles contribute significantly to the blue haze aerosols formed naturally over forested areas (Geron et al., 2000).

The low water solubility with high lipoaffinity of many of these organic xenobiotics strongly control their interaction with the vegetative components of natural ecosystems. The cuticles of foliar surfaces are covered with a wax layer that helps protect plants from moisture and short-wave radiation stress. This epicuticular wax, consisting mainly of long-chain esters, polyesters, and paraffins, has been demonstrated to accumulate lipophilic compounds. Organic air contaminants in the particulate or vapor phase are absorbed to and accumulate in the epicuticular wax of vegetative surfaces (Gaggi et al., 1985; Kylin et al., 1994). Direct uptake of organic contaminants through the cuticle or the vapor-phase uptake through the stomates are characterized poorly for most trace organics. The phytotoxicity and toxicity of organic contaminants to soil microorganisms is not well studied (Foster, 1991).

4.2.3.2 Ecosystem Response to Stresses

Ecosystem response to stress begins within the Biotic Condition Attribute at the population level with changes in patterns resulting from the response of sensitive individual plants or animals. Ecosystem response to pollutant deposition is a direct function of the ecosystem's ability to ameliorate resulting change (Strickland et al., 1993). Plant responses, changes in both structural and compositional patterns, and functional ecological processes must be scaled in both time and space and be propagated from the individual to the more complex levels of community interaction to produce observable changes in an ecosystem (see Figure 4-14). Among ecosystem biota, at least three levels of biological interaction are involved: (1) the individual plant and its environment; (2) the population and its environment; and (3) the biological community composed of many species and its environment (Billings, 1978). Individual organisms within a population vary in their ability to withstand the stress of environmental change. The response of individual organisms within a population is based on their genetic constitution (genotype), stage of growth at time of exposure to stress, and the microhabitat in which they are growing (Levin, 1998). The range within which these organisms can exist and function determines the ability of the population to survive. Those able to cope with the stresses survive and reproduce.

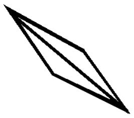


For a given level, the dot associated with a line begins with a process (e.g.photosynthesis for #1 under leaf) and ends with the associated structure (e.g., the needle).

Evaluating Impacts Within a Level of Organization

Leaf Level	Carbon exchange-1 Carbon pools-2 Needle number and size-3 Needle retention/abscission-4	Tree Level	Height and diameter growth-10 Crown shape and size-11 Tree vigor-12 Mortality-13
Branch Level	Carbon allocation-5 Branch growth-6 Branch morphology-7 Branch vigor-8 Branch retention-9	Stand Level	Productivity-14 Mortality-15 Species composition-16

Evaluating Interactions Between Different Levels of Organization



The diagonal arrow indicates the interaction between any two levels of organization. The types of interaction are due to the properties of variability and compensation.

A - Refers to the interaction between the leaf and branch levels, where, for example, variability at the branch level determines leaf quantity, and compensation at the leaf level in photosynthesis may compensate for the reduction in foliage amount.

B - Refers to the interaction between the branch and the tree, where variability in branches determines initial interception, branch vigor, and branch location in the crown; compensation may be related to increased radiation reaching lower branches.

C - Refers to the interaction between the tree and the stand. Both genetic and environmental variability, inter- and intraspecific compensations, and tree historical and competitive synergisms are involved.

Figure 4-14. Effects of environmental stress on forest trees are presented on a hierarchial scale for the leaf, branch, tree, and stand levels of organization. The evaluation of effects within a level of organization are indicated by horizontal arrows. The evaluation of interactions between different levels of organization are indicated by diagonal arrows.

Source: Hinckley et al. (1992).

Competition among the different species results in succession (community change over time) and, ultimately, produces ecosystems composed of populations of plant species that have the capability to tolerate the stresses (Rapport and Whitford, 1999; Guderian, 1985).

The number of species in a community usually increases during succession in unpolluted atmospheres. Productivity, biomass, community height, and structural complexity increase. Severe stresses, on the other hand, divert energy from growth and reproduction to maintenance and return succession to an earlier stage (Waring and Schlesinger, 1985). Ecosystems are subject to natural periodic stresses, such as drought, flooding, fire, and attacks by biotic pathogens (e.g., fungi, insects). Extremely severe natural perturbations return succession to an earlier stage; reduce ecosystem structure and functions (i.e., produce a scarcity of life forms and extinguish symbiotic interactions); disrupt the plant processes of photosynthesis and nutrient uptake, carbon allocation, and transformation that are directly related to energy flow and nutrient cycling; shorten food chains; and reduce the total nutrient inventory (Odum, 1993). This transformation, however, sets the stage for recovery that permits the perturbed ecosystem to adapt to changing environments (Holling, 1986). Therefore, these perturbations are seldom more than a temporary setback, and recovery can be rapid (Odum, 1969).

In contrast, anthropogenic stresses usually are severe, debilitating stresses. Severely stressed ecosystems do not recover readily, but may be further degraded (Odum, 1969; Rapport and Whitford, 1999). Anthropogenic stresses can be classified into four main groups: (1) physical restructuring (e.g., changes resulting from land use); (2) introduction of exotic species; (3) over harvesting; and (4) discharge of toxic substances into the atmosphere, onto land, and into water. Ecosystems usually lack the capacity to adapt to the above stresses and maintain their normal structure and functions unless the stress is removed (Rapport and Whitford, 1999). These stresses result in a process of degradation marked by a decrease in biodiversity, reduced primary and secondary production, and a lower capacity to recover and return to its original state. In addition, there is an increased prevalence of disease, reduced nutrient cycling, increased dominance of exotic species, and increased dominance by smaller, short-lived opportunistic species (Odum, 1985; Rapport and Whitford, 1999). Discharge of toxic substances into the atmosphere, onto land, and into water can cause acute and chronic stresses; and, once the stress is removed, a process of succession begins that can ultimately return the ecosystem to a semblance of its former structure. Air pollution stresses, if acute, are usually short-term and the effects soon visible. Chronic stresses, on the other hand, are long-term stresses whose effects occur at different levels of ecosystem organization and appear only after long-term exposures, as in the case of acidic deposition in the northeast or ozone in California (Shortle and Bondietti, 1992; U.S. Environmental Protection Agency, 1996b).

The possible effects of air pollutants on ecosystems have been categorized by Guderian (1977) as follows:

(1) accumulation of pollutants in the plant and other ecosystem components (such as soil and surface- and groundwater),
(2) damage to consumers as a result of pollutant accumulation,
(3) changes in species diversity because of shifts in competition,
(4) disruption of biogeochemical cycles,
(5) disruption of stability and reduction in the ability of self-regulation,
(6) breakdown of stands and associations, and
(7) expansion of denuded zones.

How changes in these functions can result from PM deposition and influence ecosystems is discussed in the following text. It should be remembered that, although the effects of PM are being emphasized, the vegetational components of ecosystems also are responding to multiple stresses from multiple sources.

Response to Direct Effects of PM

In the previous section, it was noted that PM affects patterns in the EEA Biotic Condition and processes in the Chemical/Physical and Ecological Processes categories. The presence of PM in the atmosphere may affect vegetation directly, following physical contact with the foliar surface (Section 4.2), but in most cases, the more significant effects are indirect. These effects may be mediated by suspended PM (i.e., through effects on radiation and climate) and by particles that pass through the vegetative canopies to the soil.

The majority of studies dealing with direct effects of particulate dust and trace metals on vegetation have focused on responses of individual plant species and were conducted in the laboratory or in controlled environments (Saunders and Godzik, 1986). A few have considered the effects of particles on populations, communities, and ecosystems. Most of these focused on ecosystems in industrialized areas heavily polluted by deposits of both chemically inert and active dusts. Effects can result from direct deposition or indirectly by deposition onto the soil. Reductions in growth, yield, flowering, and reproductive processes of plants from particulate deposition have been reported (Saunders and Godzik, 1986). Sensitivities of individual species have been associated with changes in composition and structural patterns of natural ecosystems.

Evidence from studies of effects of PM deposition, specifically chemically inert and active dusts indicates that, within a population, plants exhibit a wide range of sensitivity, which is the basis for the natural selection of tolerant individuals. Rapid evolution of certain populations of tolerant species at sites with heavy trace element and nitrate deposition has been observed (Saunders and Godzik, 1986). Tolerant individuals present in low frequencies in populations when growing in unpolluted areas have been selected for tolerance at both the seedling and adult stages when exposed to trace metal or nitrate deposition (Ormrod, 1984; U.S. Environmental Protection Agency, 1993). Chronic pollutant injury to a forest community may result in the loss of sensitive species, loss of tree canopy, and maintenance of a residual cover of pollutant-tolerant herbs or shrubs that are recognized as successional species (Table 4-13; Smith, 1974). These changes in forest patterns result from altered ecological processes.

Responses of ecosystems to stresses (unless severe or catastrophic) are difficult to determine because the changes are subtle (Garner, 1991). This is particularly true of responses to particles. Changes in the soil may not be observed until accumulation of the pollutant has occurred for 10 or more years, except in the severely polluted areas around heavily industrialized point sources (Saunders and Godzik, 1986). In addition, the presence of other co-occurring pollutants makes it difficult to attribute the effects to PM alone. In other words, the potential for alteration of ecosystem function and structure exists but is difficult to quantify, especially when there are other pollutants present in the ambient air that may produce additive or synergistic responses even though PM concentrations may not be elevated.

Physical Effects

The direct effects of limestone dust on plants and ecosystems has been known for many years. Changes have been observed in both ecosystem patterns and processes. Long-term changes in the structure and composition of the seedling-shrub and sapling strata of an experimental site near limestone quarries and processing plants in Giles County in southwestern

TABLE 4-13. ECOSYSTEM FUNCTIONS IMPACTED BY AIR POLLUTION EFFECTS ON TEMPERATE FOREST ECOSYSTEMS

Forest Soil and Vegetation: Activity and Response	Ecosystem Consequence and Impact
(1) Forest tree reproduction, alteration, or inhibition	(1) Altered species composition
(2) Forest nutrient cycling, alteration a. Reduced litter decomposition b. Increased plant and soil leaching and soil weathering c. Disturbance of microbial symbioses	(2) Reduced growth, less biomass
(3) Forest metabolism a. Decreased photosynthesis b. Increased respiration c. Altered carbon allocation	(3) Reduced growth, less biomass
(4) Forest stress, alteration a. Phytophagous insects, increased or decreased activity b. Microbial pathogens, increased or decreased activity c. Foliar damage increased by direct air pollution influence	(4) Altered ecosystem stress: increased or decreased insect infestations; increased or decreased disease epidemics; and reduced growth, less biomass, and altered species composition

Source: Smith (1974).

Virginia were reported by Brandt and Rhoades (1972, 1973). Dominant trees in the control area, a part of the oak-chestnut association of the eastern deciduous forests of eastern North America, were chestnut oak *(Quercus prinus)*, red oak *(Q. rubra)*, and red maple *(Acer rubrum)*. An abundance of uniformly distributed saplings and seedlings were visible under the tree canopy, and herbs appeared in localized areas in canopy openings. Chestnut oak dominated the area, and the larger trees were 60 to 80 years old. The dusty site was dominated by white oak *(Q. alba)*; whereas red oak and tulip poplar *(Liriodendron tulipifera)* were subcodominants. The largest trees were 100 years old and had necrotic leaves, peeling bark, and appeared to be in generally poor condition except for tulip poplar (which thrived in localized areas). The site contained a tangled growth of seedlings and shrubs, a few saplings, and a prevalence of green briar *(Smilax spp.)* and grape *(Vitis spp)*. The sapling strata in the area was represented by red maple, hickory *(Carya spp.)*, dogwood *(Cornus florida)*, and hop-hornbeam *(Ostrya virginiana)*. Saplings of none of the leading dominant trees were of importance in this stratum. The most obvious form of vegetation in the seedling-shrub stratum, because of their tangled appearance, were dogwood, hop-hornbeam, redbud *(Cercis canadensis)*, and sugar maple *(Acer saccarum)*.

Crust formation reduced photosynthesis, induced premature leaf fall and destruction of leaf tissues, inhibited growth of new tissue, and reduced the formation of carbohydrate needed for normal growth and storage (Brandt and Rhoades, 1973). The authors (Brandt and Rhoades, 1972), citing Odum (1969), also stated that one result of the accumulation of toxic pollutants in the biosphere (as the result of human activities) is the simplification of both plant and animal communities. In plant communities, structure is determined by sampling various strata within the community. Each stratum comprises a particular life form (e.g., herbs, seedlings, saplings, trees). Dust accumulation favored growth of some species and limited others. For example, sugar maple was more abundant in all strata of the dusty site when compared with the control site where it was present only as a seedling. The growth of tulip poplar, dogwood, hop-hornbeam, black haw *(Viburnum prunifolium),* and redbud (*C. canadensis*) appeared to be favored by the dust. Growth of conifers and acidophiles such as rhododendron (*Rhododendron maximum*), however, was limited. Although dust accumulation began in 1945, the heaviest accumulation occurred between 1967 and 1972 during the time of the study.

Changes in community composition were associated closely with changes in the growth of the dominant trees. Decrease in density of seedlings and saplings and in mean basal area, as well as lateral growth of red maple, chestnut oak, and red oak, occurred in all strata. On the other hand, all of these characteristics increased in tulip poplar, which was a subordinate species before dust accumulation began but had assumed dominance at the time of the study. Reduction in growth of the dominant trees had apparently given tulip poplar competitive advantage because of its ability to tolerate dust. Changes in soil alkalinity occurred because of the heavy deposition of limestone dust; however, the facilities necessary for critical analysis of the soils were not available. From the foregoing, it is obvious that PM physical effects in the vicinity of limestone quarries and processing plants can affect ecosystems.

Changes in ecosystem structure resulting from exposures to sea salt were cited previously (Section 4.3.1.1). The dominance of live oak (*Quercus virginiana*) as a practically pure stand on Smith Island (Bald Head), NC and along the eastern and southern coast of North Carolina has been explained as due to its tolerance to salt spray. The absence of more inland species is attributed to their intolerance to salt spray. Wells (1939) termed the long-term stabilization of live oak as “salt spray climax,” a new type of climax.

Acidic Deposition

The effects of acidic deposition have been discussed in several previous reports. The 1982 EPA document, *Air Quality Criteria for Particulate Matter and Sulfur Oxides*, devoted a chapter to the effects of acidic deposition (U.S. Environmental Protection Agency, 1982). In 1984, EPA published *The Acidic Deposition Phenomenon and Its Effects* (Altshuller and Linthurst, 1984), and, in 1991, NAPAP published the result of its extensive study, *Acidic Deposition: State of Science and Technology* (Irving, 1991). The major effects of acidic deposition occur through the soil and are discussed under indirect effects. However, included among the direct responses of forest trees to acidic deposition are increased leaching of nutrients from foliage; accelerated weathering of leaf cuticular surfaces; increased permeability of leaf surfaces to toxic materials, water, and disease agents; and altered reproductive processes (Altshuller and Linthurst, 1984).

Trace Elements

Possible direct responses of trace elements on vegetation result from their deposition and residence on the phyllosphere (i.e., leaf surfaces). Fungi and other microorganisms living on the leaves of trees and other vegetation play an important role in leaf decomposition after litterfall (Miller and McBride, 1999; Jensen, 1974; Millar, 1974). Possible effects of heavy metals on nutrient cycling and their effects on leaf microflora appear not to have been studied.

A trace metal must be brought into solution before it can enter into the leaves or bark of vascular plants. Low solubility limits entry. In those instances when trace metals are absorbed, they frequently are bound in the leaf tissue and then are lost from the plant when the leaf drops off (Hughes, 1981) are transferred to the litter layer where they can affect litter decomposition, an important source of soil nutrients. Changes in litter decomposition processes influence nutrient cycling in the soil and limit the supply of essential nutrients. Both Cotrufo et al. (1995) and Niklińska et al. (1998) point out that heavy metals affect forest litter decomposition. Cotrufo et al. (1995) observed that decomposition of oak leaves containing Fe, Zn, Cu, Cr, Ni, and Pb was influenced strongly during the early stages by metal contamination. Fungal mycelium was significantly less abundant in litter and soil in contaminated sites when compared with control sites. Niklińska et al. (1998) stated that toxic effects of heavy metals on soil respiration rate have been reported by many scientists, and that, in polluted environments, this results in accumulation of undecomposed organic matter. However, they state that results of experiments should identify the most important "natural" factors affecting soil/litter sensitivity because the effects of heavy metals on respiration rates depend on the dose of heavy metals, the type of litter, types of metals deposited, and the storage time before respiration tests are made.

Trace metals, particularly heavy metals (e.g., cadmium, copper, lead, chromium, mercury, nickel, zinc) have the greatest potential for influencing forest growth (Smith, 1991). Experimental data indicate that the broadest spectrum of growth suppression of foliar microflora resulted from iron, aluminum, and zinc. These three metals also inhibited spore formation, as did cadmium, chromium, manganese, and nickel (see Smith, 1990c). In the field, the greatest injury occurs from pollution near mining, smelting, and other industrial sources (Ormrod, 1984). Direct metal phytotoxicity can occur only if the metal can move from the surface into the leaf or directly from the soil into the root.

Organic Compounds

Primary and secondary organic compounds formed in the atmosphere, the effects of some of which are discussed below, have been referred to under the following terms: toxic substances, pesticides, hazardous air pollutants (HAPS), air toxics, semivolatile organic compounds (SOCs), and persistent organic pollutants (POPS). Again, it should be remembered that chemical substances denoted by such headings are not criteria air pollutants controlled by the National Ambient Air Quality Standards under Section 109 of the Clean Air Act (CAA), but rather are controlled under Sect.112, Hazardous Air Pollutants (U.S. Code, 1991). Their possible effects on humans and ecosystems are discussed in a number of government documents and in many other publications. They are mentioned here because many of the chemical compounds are partitioned between gas and particle phases in the atmosphere. As particles, they can become airborne, be distributed over a wide area, and affect remote ecosystems. Some of the chemical compounds are of concern because they may reach toxic levels in food chains of both animals and humans; whereas others tend to decrease or maintain the same toxicity as they move through the food chain. Some examples of movement through food chains are provided below.

Many chemical compounds from a variety of anthropogenic sources are released into the ambient air (see Section 4.2.1). In the atmosphere, the emitted compounds initially go through a mixing process, and the airborne particles then are distributed over a wide area and ultimately deposited on ecosystem components. Atmospheric deposition of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs), as an example, can be divided into three different forms: (1) dry gaseous, (2) dry particle-bound, and (3) wet deposition. Dry particle-bound deposition occurs when the PM containing the pollutant is deposited on the plant surface; whereas wet deposition ranges from hail to rain to fog and dew fall (McLachlan, 1996b).

Human exposure to PCDD/Fs has been demonstrated to be caused almost exclusively by the ingestion of animal fat from fish, meat, and dairy products. Almost half of human exposure to PCDD/Fs is caused by consumption of beef and dairy products (McLachlan,1996b). Cattle obtain most of their PCCD/Fs though grass. Therefore, the grass → cattle → milk/beef pathway is critical for human exposure. It has been shown that root uptake/translocation is an insignificant pathway of PCDD/Fs to aerial plant parts. Wet and dry particle deposition are the most important for the accumulation of the higher chlorinated cogeners in vegetation. The persistence of PCDD/Fs in plants has not been investigated extensively; however, biodegradation probably does not occur in that these compounds are found primarily in the lipophilic cuticle and are very resistant to microbial degradation (McLachlan, 1996b). Feed contaminated with soil containing the pollutant can be another source of exposure of beef and dairy cattle, as well as chickens. The PCDD/Fs are near a steady state in milk cows and laying hens; however, animals raised for meat production (such as beef cattle and pigs) may accumulate them. The beef cattle and pigs cannot excrete the contaminants in a lipid-rich matrix such as milk or eggs. Thus, all of the PCDD/Fs, ingested are stored in the body. In agricultural food chains, there is a biodilution of PCDD/Fs, with the fugacity decreasing by up to three orders of magnitude between the air and cows milk (McLachlan, 1996b). Fürst et al. (1993), based on surveys to determine the factors that influence the presence of PCDD/PCDF in cows milk, earlier concluded that regardless of which pathway, soil → grass → cow or air → grass → cow, it was the congener of the chemical that was most important.

Chlorinated persistent organic pollutants (POPS), such as PCBs, PCDFs, and PCDDs, can be transported as particles through the atmosphere from industrial and agricultural sources; be brought down via wet and dry deposition in remote regions, such as the Arctic; and have been detected in all levels of the Arctic food chain (Oehme et al., 1995). High concentrations of PCB (1 to 10 ppm) were found in seals, but the concentrations increased to 10 to 100 ppm in polar bears. The polar bear is the top predator in the Arctic and feeds preferentially on ringed seals and, to a lesser extent, on other seal species. Bioconcentration factors of organochlorines in the Arctic food web, reaching 10^7 for fish and seals, are biomagnified in polar bears (Oehme et al., 1995). Polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans have also been found in seals (Oehme et al., 1995). Milk taken from anaesthetized polar bears was also found to contain PCDD/PCDF. Very little is known regarding the intake of milk by polar bear cubs. However, estimates of the intake of milk containing detectable levels of PCDD/PCDF and PCB and the additional consumption of seal blubber confirm that these pollutants are passed on to the next generation (Oehme et al., 1995).

Section 112 of the CAA provides the legislative basis for U.S. hazardous air pollutant (HAP) programs. In response to mounting evidence that air pollution contributes to water pollution, Congress included Section 112m (*Atmospheric Deposition to Great Lakes and Coastal Waters*) in the 1990 CAA Amendments that direct the EPA to establish a research program on atmospheric deposition of HAPS to the "Great Waters."

Actions taken by EPA and others to evaluate and control sources of Great Waters pollutants of concern appear to have positively affected trends in pollutant concentrations measured in air, sediment, and biota. Details concerning these effects may be found in "Deposition of Air Pollutants to the Great Waters," Third Report to Congress (U.S. Environmental Protection Agency, 2000a). The Third Report (EPA-453/R-00-005, June 2000), like the First and Second Reports to Congress, focuses on 15 pollutants of concern, including pesticides, metal compounds, chlorinated organic compounds, and nitrogen compounds. The new scientific information in the Third Report supports and builds on three broad conclusions presented in the previous two EPA Reports to Congress:

(1) Atmospheric deposition from human activities can be a significant contributor of toxic chemicals and nitrogen compounds to the Great Waters. The relative importance of atmospheric loading for a particular chemical in a water body depends on many factors (e.g., characteristics of the water body, properties of the chemical, and the kind and amount of atmospheric deposition versus water discharges).

(2) A plausible link exists between emissions of toxic pollutants of concern into the air above the Great Waters; the deposition of these pollutants (and their transformation products); and the concentrations of these pollutants found in the water, sediments, and biota, especially fish and shellfish. For mercury, fate and transport modeling and exposure assessments predict that the anthropogenic contribution to the total amount of methylmercury in fish is, in part, the result of anthropogenic mercury releases from industrial and combustion sources increasing mercury body burdens (i.e., concentrations) in fish. Also, the consumption of fish is the dominant pathway of exposure to methylmercury for fish-consuming humans and wildlife. However, what is known about each stage of this process varies with each pollutant (for instance, the chemical species of the emissions and its transformation in the atmosphere).

(3) Airborne emissions from local as well as distant sources, from both within and outside the United States, contribute pollutant loadings to waters through atmospheric deposition. Determining the relative roles of particular sources — local, regional, national, and possibly global, as well as anthropogenic, natural, and reemission of pollutants — contributing to specific water bodies is complex, requiring careful monitoring, atmospheric modeling, and other analytical techniques.

Response to Indirect Effects of PM

The presence of PM in the atmosphere directly affects vegetation following physical contact with foliar surfaces (as discussed above), but in many cases the more significant effects are indirect. These effects may be mediated by suspended PM (i.e., through effects on radiation and climate) and by particles that pass through vegetative canopies to reach the soil. Effects mediated through the atmosphere are considered briefly below and in greater detail later, under Section 4.5.

The major indirect plant responses are chiefly soil-mediated and depend primarily on the chemical composition of the individual stressors deposited in PM. The chemical stressors must be bioavailable in order to produce an effect. The effects of exposures may result in changes in biota patterns and in chemical/physical soil conditions that affect ecological processes, such as nutrient cycling and uptake by plants.

The soil environment, composed of mineral and organic matter, water, air, and a vast array of bacteria, fungi, algae, actinomycetes, protozoa, nematodes, and arthropods, is one of the most dynamic sites of biological interactions in nature (Wall and Moore, 1999; Alexander, 1977). The quantity of organisms in soils varies by locality. Bacteria and fungi are usually most abundant in the rhizosphere, the soil around plant roots that all mineral nutrients must pass through. Bacteria and fungi benefit from the nutrients in the root exudates (chiefly sugars) in the soil and, in turn, they play an essential role by making mineral nutrients available for plant uptake (Wall and Moore, 1999; Rovira and Davey, 1974). Their activities create chemical and biological changes in the rhizosphere by decomposing organic matter and making inorganic minerals available for plant uptake. Bacteria are essential in the nitrogen and sulfur cycles and make these elements available for plant uptake and growth (see Section 4.3.3). Fungi are directly essential to plant growth. Attracted to the roots by the exudates, they develop mycorrhizae, a mutualistic, symbiotic relationship, that is integral in the uptake of the mineral nutrients (Allen, 1991). The impact in ecosystems of PM, particularly nitrates, sulfates, and metals, is determined by their effects on the growth of the bacteria involved in nutrient cycling and the mycorrhizal fungi involved in plant nutrient uptake.

Atmospheric Turbidity: Effects on Direct Beam and Photosynthetically Active Radiation. Photosynthetic processes underlie the contribution of vegetative surfaces to nutrient and energy cycling. The characteristics and net receipts of environmental radiation determine the rates of both photosynthesis and the heat-driven process of water cycling. Atmospheric turbidity due to particulate loading can substantially alter the characteristics and net receipts of solar radiation. One measure of atmospheric turbidity, Linke's turbidity factor, T, can be derived as a direct function of light extinction by solid particles. It is defined as the ratio of the total extinction coefficient and the extinction due exclusively to gases:

$$T = \sigma/\sigma g = 1 + w\sigma_w/\sigma_g + s\sigma_s/\sigma_g \qquad (4\text{-}6)$$

where s and w are the relative concentrations of dust and water vapor in the atmosphere, and σ_s and σ_w are the wavelength-dependent scattering coefficients for solid, dry particles and water vapor. The scattering coefficients are in units of inverse distance, such as km^{-1} (Rosenberg, 1974). According to this expression, a clean atmosphere would have a turbidity value of 1. Given that turbidity and visibility are both functions of light scattering, the trends in and physical processes underlying reduced visibility discussed in Section 4.3 are directly relevant to the discussion of radiative effects on vegetation due to particulate matter.

Turbidity, as defined above, describes the degree of scattering occurring in the atmosphere due to particles and gases. Total, particle-based extinction, however, is the sum of both scattering and absorption. Absorption of short-wavelength solar radiation reduces the amount of radiation reaching the Earth's surface and leads to atmospheric heating. If the absorbing particles re-radiate in the infrared range, some of this energy is lost as long-wave re-radiation to space. The balance of this energy is captured at the surface as down-welling infrared radiation. Canopy temperature and transpirational water use by vegetation are particularly sensitive to long-wave, infrared radiation. Atmospheric heating by particles reduces vertical temperature gradients, potentially reducing the intensity of atmospheric turbulent mixing. The magnitude of such potential effects on turbulent transport within canopies remains unknown although the damping of eddy transport might inhibit canopy gas exchange. Suppressed tropospheric mixing could also intensify local temperature inversions and increase the severity of pollution episodes (Pueschel, 1993) with direct inhibitory effects on photosynthetic processes.

Atmospheric turbidity increases the intensity of diffuse (sky) radiation (Hoyt, 1978). In a clear atmosphere, diffuse radiation may be on the order of 10% of total solar radiation (Choudhury, 1987). However, in highly turbid, humid conditions, this fraction may increase, to as much as 100% of the incident solar intensity in extreme cases. The direct-to-diffuse-radiation ratio is highest at solar noon and lowest near dawn or dusk when the path length through the atmosphere is longest. The wavelength dependence of particle scattering induces an enrichment of PAR with respect to total or direct beam radiation.

Aerosols produced by incomplete combustion, from forest fires to specifically anthropogenic processes such as diesel fuel combustion, contain significant fractions of black carbon which absorbs across the solar and terrestrial radiation spectra. The presence of absorbing aerosols reduces the ratio of photosynthetically active radiation to total radiation received at the surface, potentially reducing photosynthetic water uptake efficiency. The net effect of aerosol absorption on the surface depends on the relative magnitudes of the particulate absorption coefficients in the visible and infrared area and on the albedo of the Earth's surface.

The greater effect of particulate loading on visibility and turbidity is due to scattering. Non-absorbing, scattering aerosols raise the overall albedo of the atmosphere and reduce the amount of radiation reaching the surface by the amount reflected or scattered back into space. Analysis of data collected by a global network of thermopile pyranometers operated by the World Meteorological Organization show a 50-year global trend of a 2.7% per decade reduction in the amount of solar radiation reaching the Earth's surface. This has been associated with an increasing global albedo caused by an increasing abundance of atmospheric particles. By evaluating the WMO data set with four different approaches to the statistical analyses, Stanhill and Cohen (2001) have estimated that average global solar radiation receipts have declined by 20 Wm^{-2} since 1958. Examples of individual measurement sites include Barrow, Alaska (71 °N), where the average solar irradiance from 1963 – 1993 was 100.9 W m^{-2} and the estimated linear trend was -0.23% per year; and Jerusalem, Israel (32 °N), where the average solar irradiance from 1954 – 1994 was 244.2 W m^{-2} and the estimated linear trend was -0.37% per year.

Increased Turbidity and Altered Radiative Flux: Effects on Vegetative Processes. In a detailed canopy-response model (e.g., Choudhury, 1987), radiation is considered in its direct and diffuse components. Foliar interception by canopy elements is considered for both up- and down-welling radiation (a two-stream approximation). In this case, the effect of atmospheric PM on turbidity influences canopy processes both by radiation attenuation and by influencing the efficiency of radiation interception throughout the canopy through conversion of direct to diffuse radiation (Hoyt, 1978). Diffuse radiation is more uniformly distributed throughout the canopy and increases canopy photosynthetic productivity by distributing radiation to lower leaves. The treatment of downwelling direct-beam radiation in the two-stream approach remains an elaboration of the simplified Beer's Law analogy with solar angle, leaf area distribution, and orientation individually parameterized (Choudhury, 1987). Diffuse downwelling radiation is a function of diffuse and direct radiation at the top of the canopy and penetration within the canopy according to cumulative leaf area density and foliage orientation. Diffuse upwelling radiation results from scattering and reflectance of both direct and diffuse downwelling radiation within the canopy and by the soil.

Rochette et al. (1996) conducted simultaneous measurements of radiation and water use efficiencies by maize and found that, in the absence of water stress and with adequate fertilization, 90% of all variation in crop net photosynthesis (P-n) could be explained by variations in PAR. Alternatively, an evaluation of the available experimental literature and statistics on crop yields by Stanhill and Cohen (2001) indicate that plant productivity is more affected by changes in evapo-transpiration induced by changes in the amount of solar radiation plants receive than by changes in the amount of PAR plants receive.

The enrichment in PAR present in diffuse radiation appears, however, to offset a portion of the effect of an increased atmospheric albedo due to atmospheric particles. An observational and theoretical study by Bange et al. (1997) of the level of radiation use efficiency (RUE) of sunflowers indicated a degree of compensation for reduced incident radiation by a proportional increase in diffuse radiation. Variables measured by Bange et al. (1997) included biomass, phenology, leaf area, canopy light extinction, grain size, and harvest index. Crops subject to reduced direct beam/increased diffuse radiation produced biomass, phenology, leaf area and canopy light extinction at leaves similar to unshaded crops, but yielded smaller grains and a lower harvest index. RUE was also seen to improve for soybeans and maize with a proportional increase in diffuse radiation with respect to direct beam (Sinclair et al., 1992; Healey et al., 1998) although the effect on harvest index was not indicated. Following a comparison of the relative efficiencies of canopy photosynthesis to diffuse and direct PAR for a Scots pine forest, an aspen forest, a mixed deciduous forest, a tall grass prairie and a winter wheat crop, Gu et al. (2002) concluded (1) diffuse radiation over direct radiation results in higher light use efficiencies by plant canopies; (2) diffuse radiation has much less tendency to cause canopy photosynthetic saturation; (3) the advantages of diffuse radiation over direct radiation increase with radiation level; (4) temperature as well as vapor pressure deficit can cause different responses in diffuse and direct canopy photosynthesis, indicating that their effects on terrestrial ecosystem carbon assimilation may depend upon radiation regimes, thus sky conditions.

The potentially significant effect of regional haze on the yield of crops because of reduction in solar radiation has been examined by Chameides et al. (1999). Using a case study approach, Chameides et al. (1999), studied the effects of regional haze on crop production in China where regional haze is especially severe. A rudimentary assessment of the direct effect of atmospheric aerosols on agriculture suggests that yields of approximately 70% of crops are being depressed by at least 3 to 5% by regional scale air pollution and its associated haze (Chameides et al., 1999).

Effects of Nitrogen Deposition. Nitrogen is required by all organisms. It is a major constituent of the nucleic acids that determine the genetic character of all living things and the enzyme proteins that drive the metabolic machinery of every living cell (Galloway, 1998; Galloway and Cowling, 2002). Though nitrogen composes 80% of the total mass of the Earth's atmosphere, it is not biologically available. Nitrogen fixation is accomplished in nature by certain unique organisms that have developed the capability of converting N_2 to biologically active reduced forms of nitrogen such as ammonia, amines, and amino acids which are the structural constituents of proteins and nucleic acids (Galloway and Cowling, 2002).

Nitrogen has long been recognized as the nutrient most important for plant growth. It is of overriding importance in plant metabolism and, to a large extent, governs the utilization of phosphorus, potassium, and other nutrients. Most of the nitrogen in soils is associated with organic matter. Typically, the availability of nitrogen via the nitrogen cycle controls net primary productivity, and possibly, the decomposition rate of plant litter. Photosynthesis is influenced by nitrogen uptake in that ca., 75% of the nitrogen in a plant leaf is used during the process of photosynthesis. The nitrogen-photosynthesis relationship is, therefore, critical to the growth of trees and other plants (Chapin et al., 1987). Plants usually obtain nitrogen directly from the soil through their roots by absorbing NH_4^+ or NO_3^-, or it is formed by symbiotic organisms (bacteria, blue-green algae) in the roots.

Because nitrogen is not readily available and is usually in short supply, it is the chief element in agricultural fertilizers. The realization of the importance of nitrogen in crop production resulted in a search for natural nitrogen such as guano and nitrate deposits. The invention of the Haber-Bosch process in 1913 made reactive nitrogen (Nr) available for use in food production, and more than half of the food eaten by peoples of the world today is produced using fertilizer produced by this process (Galloway and Cowling, 2002).

Nitrogen in nature may be divided into two groups: nonreactive (N_2) and reactive (Nr). Reactive Nr includes all biologically, photochemically, and radioactively active nitrogen compounds in the Earth's atmosphere and biosphere (Galloway et al., 2003). Among those included are: the inorganic reduced forms of nitrogen (e.g., ammonia [NH_3] and ammonium

[NH_4^+]), inorganic oxidized forms (e.g., nitrogen oxide [NO_x], nitric acid [HNO_3], nitrous oxide [N_2O], and nitrate [NO_3^-]) , and organic compounds (e.g., urea, amine, proteins, and nucleic acids)]).

Food production continues to account for most of the newly Nr created. However, since approximately 1965 the magnitude of Nr created by humans began to exceed natural terrestrial creation of Nr and its conversion back to N_2 by denitrification. The overall increase in global Nr is the result of three main causes: (1) widespread cultivation of legumes, rice and other crops that promote conversion of N_2 to organic nitrogen through biological nitrogen fixation; (2) combustion of fossil fuels, which converts both atmospheric N_2 and fossil nitrogen to reactive NO_x; and (3) the Haber-Bosch process, which converts nonreactive NH_3 to sustain food production and some industrial activities (Galloway and Cowling, 2002; Galloway et al., 2003).

Reactive nitrogen is now accumulating in the environment on all spatial scales – local, regional and global (2002:Galloway and Cowling, 2002; Galloway et al. 2003). As a result, Nr is accumulating in various environmental reservoirs, e.g., the atmosphere, soils and waters (Galloway and Cowling, 2002). The accumulation of Nr in the environment has effects on humans and ecosystems Rabelais, 2002; van Egmond et al., 2002; Galloway, 1998).

Large uncertainties regarding the rates of Nr accumulation in the various reservoirs limits our ability to determine the temporal and spatial distribution of environmental effects. These uncertainties are of great significance because of the sequential nature of Nr on environmental processes. (Galloway and Cowling, 2002). The sequence of transfers, transformations, and environmental effects is referred to as the nitrogen cascade (Figure 4-15; Galloway and Cowling, 2002; Galloway et al, 2003). A single atom of new NH_x or NO_x can alter a wide array of biogeochemical processes and exchanges among environmental reservoirs.

The results of the Nr cascade in the global system and the wide variety of changes in the nitrogen cycle are both beneficial and detrimental to humans and to ecosystems (Galloway and Cowling, 2002; Galloway et al., 2003). Though the synthetic fertilizers used in cultivation and the cultivation-induced bacterial nitrogen fertilization (BNF) sustain a large portion of the world's population, there are consequences: (1) the wide dispersal of Nr by hydrological and atmospheric transport; (2) the accumulation of Nr in the environment because the rates of its creation are greater than the rates of its removal through denitrification to nonreactive N_2; (3) Nr creation and accumulation is projected to continue to increase in the future as per capita use of

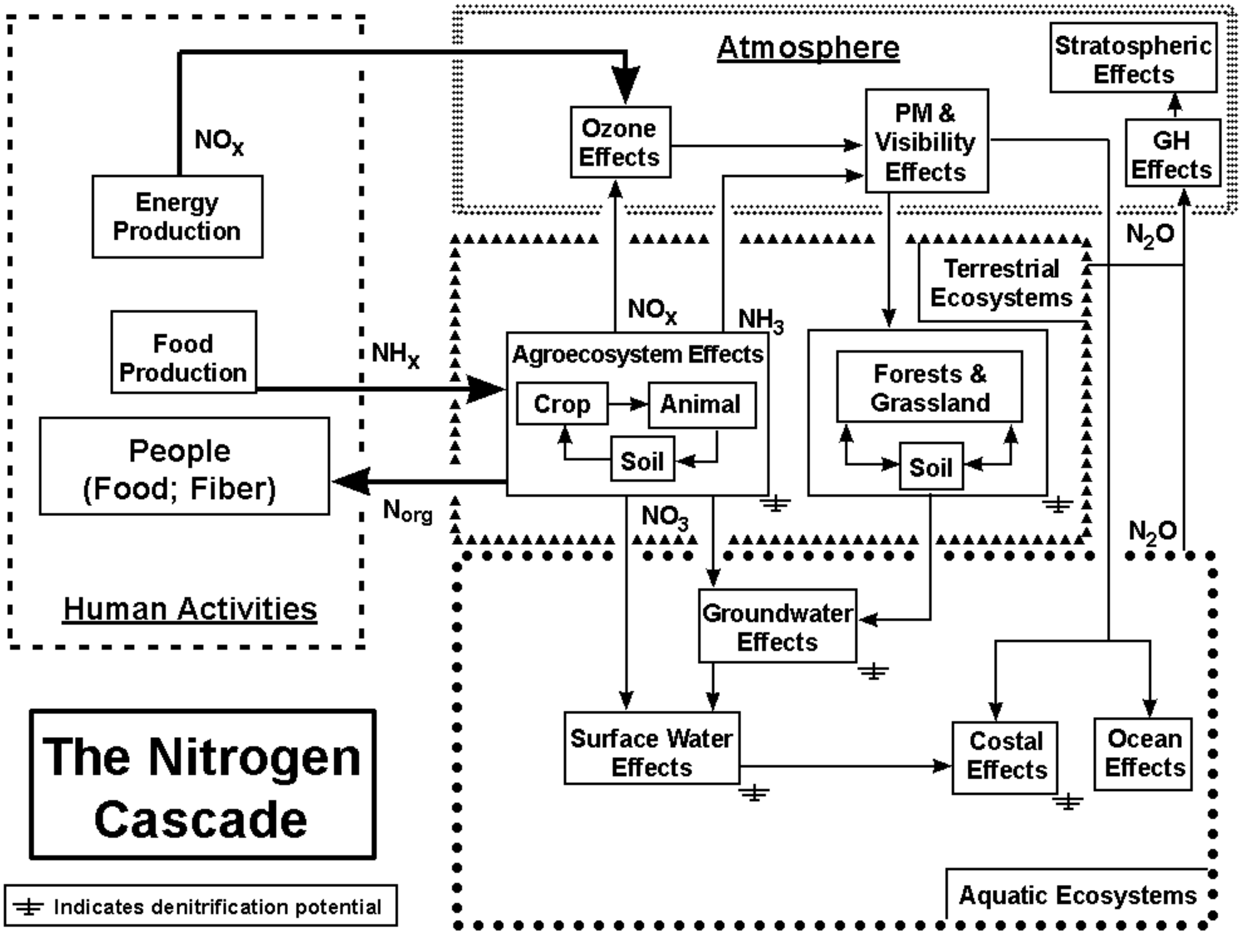


Figure 4-15. Illustration of the nitrogen cascade showing the movement of the human-produced reactive nitrogen (Nr) as it cycles through the various environmental reservoirs in the atmosphere, terrestrial ecosystems, and acquatic ecosystems.

Modified from Galloway and Cowling (2002).

resources by human populations increases; and (4) Nr accumulation contributes to many contemporary environmental problems (Galloway et al., 2003)

Among the contemporary environmental problems are the following:

- increases in Nr lead to production of tropospheric ozone and aerosols and the associated human health problems (Wolfe and Patz, 2002);

- productivity increases in forests and grasslands and then decreases wherever atmospheric Nr deposition increases significantly and critical thresholds are exceeded; Nr additions probably also decrease biodiversity in many natural habitats (Aber et al., 1995);
- reactive nitrogen in association with sulfur is responsible for acidification and loss of biodiversity in lakes and streams in many regions of the world (Vitousek et al., 1997);
- reactive nitrogen is responsible for eutrophication, hypoxia, loss of biodiversity, and habitat degradation in coastal ecosystems. It is now considered the biggest pollution problem in coastal waters (Rabelais, 2002);
- reactive nitrogen contributes to global climate change and stratospheric ozone depletion, both of which have an effect on the health of humans and ecosystems (Cowling et al., 1998).

The effect of increasing nitrogen inputs (e.g., NO_x, nitrates, nitric acid) on the nitrogen cycle in forests, wetlands, and aquatic ecosystems is discussed in detail elsewhere (U.S. Environmental Protection Agency, 1993, 1997a; Garner, 1994; World Health Organization, 1997).

The deposition of nitrogen in the United States from human activity has doubled between 1961 and 1997 due mainly to the use of inorganic nitrogen fertilizers and the emissions of nitrogen oxides (NO_x) from fossil fuel emissions with the largest increase occurring in the 1960s and 1970s (Howarth et al., 2002). Among the most important effects of chronic nitrogen deposition are changes in the composition of plant communities, disruptions in nutrient cycling, increased emissions from soil of nitrogenous greenhouse gases and accumulation of nitrogen compounds resulting in the enhanced availability of nitrate or ammonium, the soil-mediated effects of acidification, and increased susceptibility to stress factors (Fenn et al., 1998; Bobbink et al., 1998). A major concern is “nitrogen saturation,” the result of the atmospheric deposition of large amounts of particulate nitrates. Nitrogen saturation results when additions to soil background nitrogen (nitrogen loading) exceeds the capacity of plants and soil microorganisms to utilize and retain nitrogen (Aber et al., 1989, 1998; Garner, 1994; U.S. Environmental Protection Agency, 1993). Under these circumstances, disruptions of ecosystem functioning may result (Hornung and Langan, 1999).

Possible ecosystem responses to nitrate saturation, as postulated by Aber and coworkers (Aber et al., 1989), include (1) a permanent increase in foliar nitrogen and reduced foliar phosphorus and lignin caused by the lower availability of carbon, phosphorus, and water; (2) reduced productivity in conifer stands because of disruptions of physiological function; (3) decreased root biomass and increased nitrification and nitrate leaching; and (4) reduced soil fertility, resulting from increased cation leaching, increased nitrate and aluminum concentrations in streams, and decreased water quality. Saturation implies that some resource other than nitrogen is limiting biotic function.

Water and phosphorus for plants and carbon for microorganisms are the resources most likely to be the secondary limiting factors (Aber et al., 1989). The appearance of nitrogen in soil solution is an early symptom of excess nitrogen. In the final stage, disruption of forest structure becomes visible (Garner, 1994).

Changes in nitrogen supply can have a considerable effect on an ecosystem's nutrient balance (Waring, 1987). Large chronic additions of nitrogen influence normal nutrient cycling and alter many plant and soil processes involved in nitrogen cycling (Aber et al., 1989). Among the processes affected are (1) plant uptake and allocation, (2) litter production, (3) immobilization (includes ammonification [the release of ammonia] and nitrificatrion [conversion of ammonia to nitrate during decay of litter and soil organic matter]), and (4) nitrate leaching and trace gas emissions (Figure 4-16; Aber et al., 1989; Garner 1994).

Subsequent studies have shown that, although there was an increase in nitrogen mineralization initially (i.e., the conversion of soil organic matter to nitrogen in available form [see item 3 above]), nitrogen mineralization rates were reduced under nitrogen-enriched conditions. Aber et al.(1998) hypothesize that mycorrhizal assimilation and exudation, using photosynthate from the host plant as the carbons source, is the dominant process involved in immobilization of nitrogen. In addition, studies suggested that soil microbial communities change from predominantly fungal (mycorrhizal) communities to those dominated by bacteria during saturation (Aber et al., 1998).

The growth of most forests in North America is limited by the nitrogen supply. Severe symptoms of nitrogen saturation, however, have been observed in high-elevation, nonaggrading spruce-fir ecosystems in the Appalachian Mountains, as well as in the eastern hardwood watersheds at Fernow Experimental Forest near Parsons, WV. Mixed conifer forests and chaparral watersheds with high smog exposure in the Los Angeles Air Basin also are nitrogen saturated and exhibit the highest stream water NO_3^- concentrations for wildlands in North

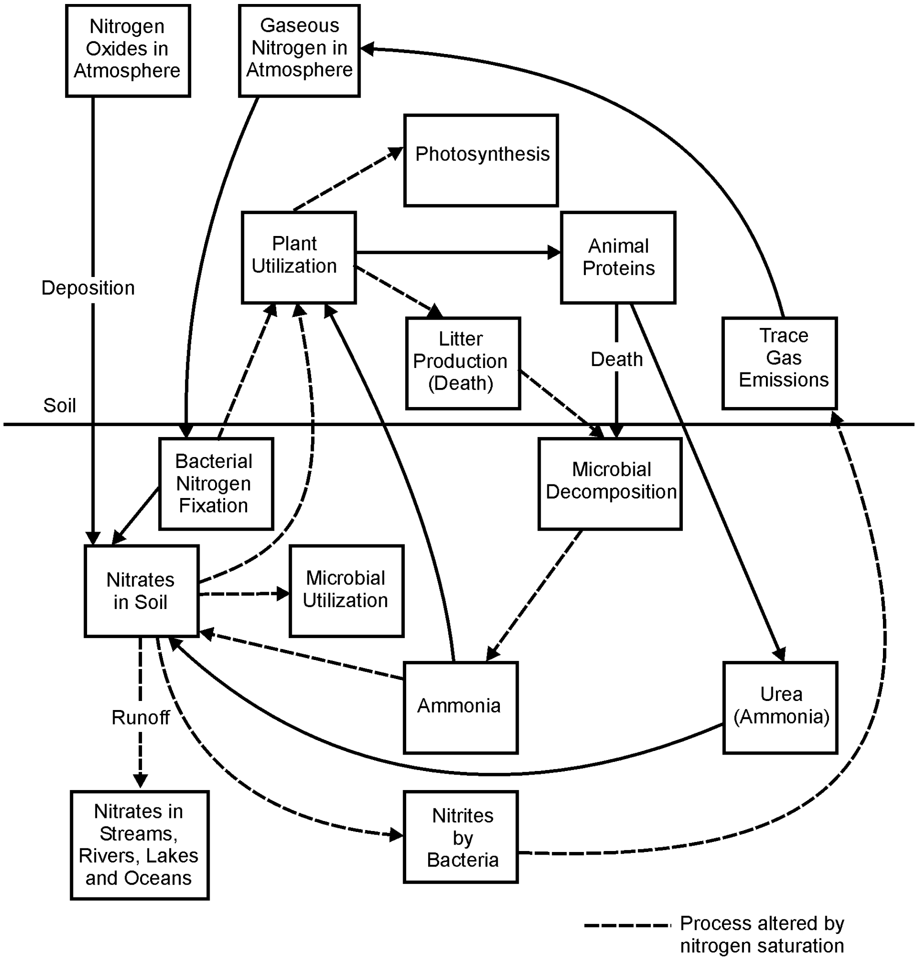


Figure 4-16. Nitrogen cycle (dotted lines indicate processes altered by nitrogen saturation).

Source: Garner (1994).

America (Bytnerowicz and Fenn, 1996; Fenn et al., 1998). Forests in southern California, the southwestern Sierra Nevada in Central California, and the Front Range in northern Colorado have all been exposed to highly elevated nitrogen deposition, and nitrogen saturated watersheds have been reported in the above mentioned areas. Annual nitrogen additions through deposition (6-11 kg ha^{-1} y^{-1}as through fall) in the southwestern Sierra Nevada are similar to nitrogen storage (4 kg ha^{-1} y^{-1}) in vegetation growth increment of western forests suggesting that current nitrogen deposition rates may be near the assimilation capacity of the overstory vegetation. Ongoing urban expansion will increase the potential for nitrogen saturation of forests from urban sources (e.g., Salt Lake City, Seattle, Tucson, Denver, central and southern California) unless there are improved emission controls (Fenn et al., 1998).

Atmospherically deposited nitrogen also can act as a fertilizer in soil low in nitrogen. Not all plants, however, are capable of utilizing extra nitrogen as plants vary in their ability to absorb ammonium and nitrate (Chapin, et al., 1987). Inputs of nitrogen to natural ecosystems that alleviate deficiencies and increase growth of some plants can alter competitive relationships and alter species composition and diversity (Ellenberg, 1987; Kenk and Fischer, 1988; U.S. Environmental Protection Agency, 1993).

Not all forest ecosystems react in the same manner to nitrogen deposition. High-elevation alpine watersheds in the Colorado Front Range (Bowman, 2000) and a deciduous forest in Ontario, Canada, also are naturally saturated even though nitrogen deposition has been moderate ($\approx$ 8 kg ha^{-1} y^{-1}). The nitrogen saturated forests in North America, including estimated inputs and outputs, are shown in Table 4-14 (Fenn et al., 1998). The Harvard Forest hardwood stand in Massachusetts, however, has absorbed > 900 kg N/ha without significant NO_3^- leaching during a nitrogen amendment study of 8 years (Table 4-14; Fenn et al.,1998). Nitrate leaching losses were high, on the other hand, in the Harvard Forest pine sites suggesting that deciduous forest may have a greater capacity for nitrogen retention. During the 8-year experimental study (1988-96), nitrate leaching was observed in the pine stand after the first year (1989) in the high nitrogen plots. Further increase was observed in 1995 and 1996, while the hardwood stand showed no significant increases in nitrate leaching until 1996. The sharp contrast in response of pine and hardwood stands indicates that the mosaic of community types across the landscape must be considered when determining regional scale response to nitrogen deposition (Magill et al., 2002). Johnson et al. (1991a) reported that measurements showing the leaching of nitrates and aluminum (Al^{+3}) from high elevation forests in the Great Smoky Mountains indicate that these forests have reached saturation.

Because the competitive equilibrium of plants in any community is finely balanced, the alteration of one of a number of environmental parameters, (e.g., continued nitrogen additions) can change the vegetation structure of an ecosystem (Bobbink, 1998; Skeffington and Wilson, 1988). Increases in soil nitrogen play a selective role. When nitrogen becomes more readily available, plants adapted to living in an environment of low nitrogen availability will be replaced by plants capable of using increased nitrogen because they have a competitive advantage.

TABLE 4-14. NITROGEN-SATURATED FORESTS IN NORTH AMERICA, INCLUDING ESTIMATED N INPUTS AND OUTPUTS

Location	Forest Type	Elevation (m)	N Input (kg ha^{-1} $year^{-1}$)	N Output (kg ha^{-1} $year^{-1}$)	Reference
Adirondack Mts. northeastern New York	Northern hardwoods or hardwood/ conifer mix	396-661	9.3[a]	Stage 1 N loss[b]	Driscoll and Van Dreason (1993)
Catskill Mts., southeastern New York	Mainly hardwood; some eastern hemlock	335-675	10.2[a]	Stage 1 and 2 N loss[b]	Stoddard (1994)
Turkey Lakes Watershed, Ontario, Canada	Sugar maple and yellow birch	350-400	7.0-7.7 (as throughfall)	17.9-23.6	Foster et al. (1989); Johnson and Lindberg (1992a)
Whitetop Mt., southwestern Virginia	Red spruce	1650	32[c]	47[c]	Joslin and Wolfe (1992); Joslin et al. (1992)
Fernow, West Virginia	Mixed hardwood	735-870	15-20	6.1	Gilliam et al. (1996); Peterjohn et al. (1996)
Great Smoky Mts. National Park, Tennessee	American beech	1600	3.1[d]	2.9	Johnson and Lindberg (1992b)
Great Smoky Mts. National Park, Becking Site, North Carolina	Red spruce	1800	10.3[d]	19.2	Johnson et al. (1991a)
Great Smokey Mts. National Park, Tower Site, North Carolina	Red spruce	1740	26.6	20.3	Johnson et al. (1991a)
Front Range, Colorado	Alpine tundra, subalpine conifer	3000-4000	7.5-8.0	7.5	Williams et al. (1996)
San Dimas, San Gabriel Mts., southern California	Chapparral and grasslands	580-1080	23.3[e]	0.04-19.4	Riggan et al. (1985)
Camp Paivika, San Bernadino Mts., southern California	Mixed conifer	1600	30	7-26[f]	Fenn et al. (1996)
Klamath Mts, northern California	Western coniferous	NA	Mainly geologic[g]	NA[g]	Dahlgren (1994)
Thompson Forest, Cascade Mts., Washington	Red alder	220	4.7 plus > 100 as N_2 fixation	38.9	Johnson and Lindberg (1992b)

[a] Estimated total N deposition from wet deposition data is from Driscoll et al. (1991) for the Adirondacks, and from Stoddard and Murdoch (1991) for the Catskills. Total deposition was estimated based on the wet deposition/total N deposition ratio (0.56) at Huntington Forest in the Adirondacks (Johnson and Lindberg, 1992b). Nitrogen deposition can be higher in some areas, especially at high-elevation sites such as Whiteface Mountain (15.9 kg ha^{-1} $year^{-1}$; Johnson and Lindberg, 1992b).

[b] Stage 1 and 2 of N loss according to the watershed conceptual model of Stoddard (1994). Nitrogen discharge (kg ha^{-1} $year^{-1}$) data are not available; only stream water NO_3^- concentration trend data were collected.

[c] Values appear high compared to other sites, especially N leaching losses. Joslin and Wolfe (1992) concede that "there is considerable uncertainty associated with the estimates of atmospheric deposition and leaching fluxes." However, elevated NO_3^- concentrations in soil solution, and lack of a growth response to N fertilization (Joslin and Wolfe, 1994) support the hypothesis that the forest at Whitetop Mountain is N saturated.

[d] Estimated total N deposition from throughfall data. Total deposition was estimated based on the throughfall/total N deposition ration (0.56) from the nearby Smokies Tower site (Johnson and Lindberg, 1992b).

[e] Annual throughfall deposition to the chaparral ecosystem.

[f] Nitrogen output is from unpublished streamwater data (Fenn and Poth, 1999). The low value represents a year of average precipitation, and the high value is for 1995, when precipitation was nearly double the long-term average. Nitrogen output includes N export in streamwater and to groundwater.

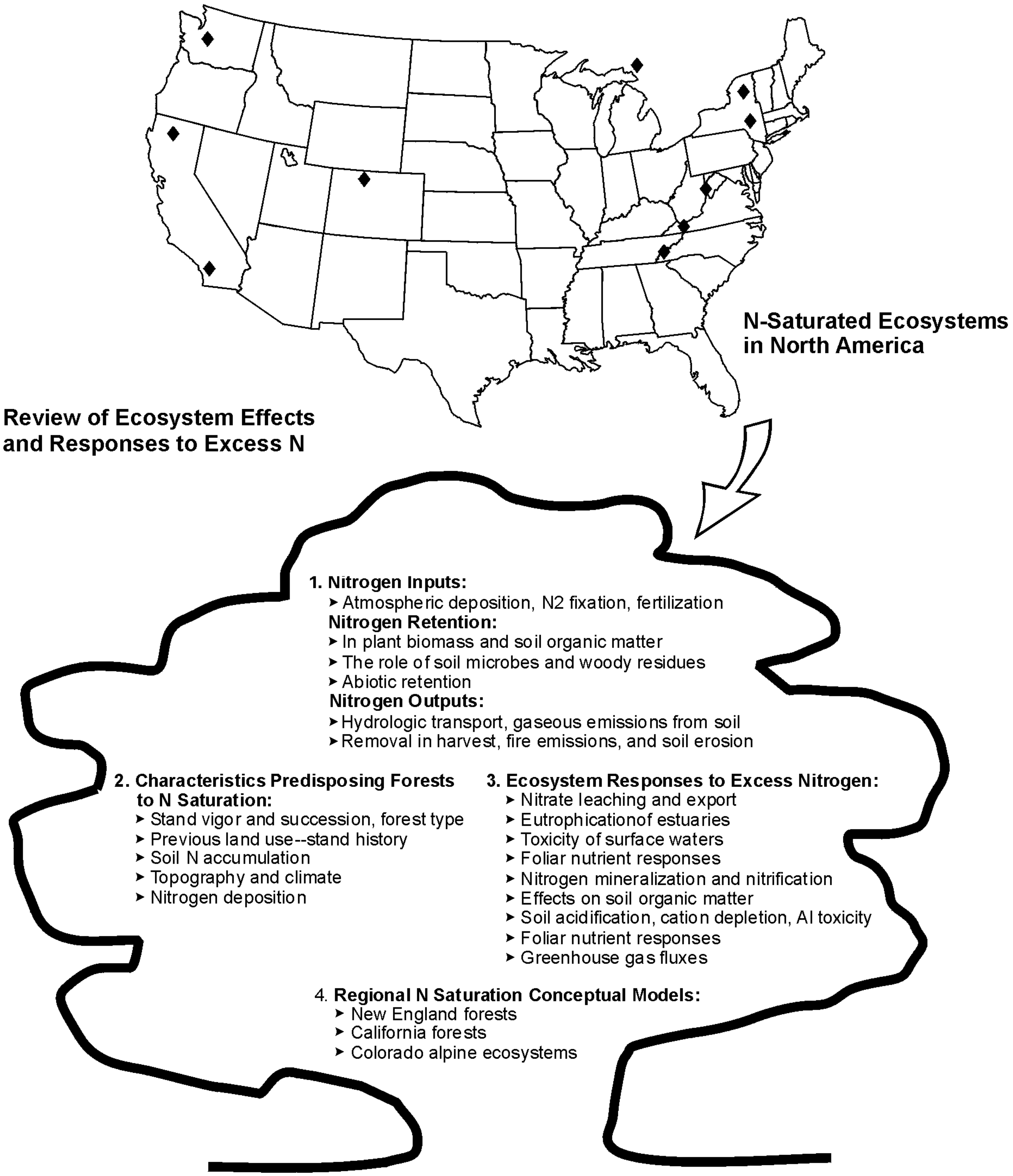
[g] Annual input and output data are not known, although N deposition in this forest is probably typical for much of the rural western United States (2-3 kg N ha^{-1} $year^{-1}$ (Young et al., 1988). Excess N is from weathering of ammonium in mica schist bedrock. The ammonium was rapidly nitrified, leading to high NO_3^- concentrations in soil solution (Dahlgren, 1994).

Plant succession patterns and biodiversity are affected significantly by chronic nitrogen additions in some North American ecosystems (Figure 4-17). The location of nitrogen saturated ecosystems in North America, and the steps leading to nitrogen saturation, are indicated on the map in Figure 4-16. Conceptual models of regional nitrogen saturation indicate saturation in New England, in the Colorado alpine ecosystems and in California forests. Fenn et al. (1998) reported that long-term nitrogen fertilization studies in both New England and Europe, as well, suggest that some forests receiving chronic inputs of nitrogen may decline in productivity and experience greater mortality. Long-term fertilization experiments at Mount Ascutney, VT, suggest that declining coniferous forest stands with slow nitrogen cycling may be replaced by deciduous fast-growing forests that cycle nitrogen rapidly (Fenn et al., 1998).

Atmospheric nitrogen deposition in the northeastern United States is largely a regional problem (Driscoll et al., 2001). In contrast, in the western United States, vast acres of land receive low levels of atmospheric nitrogen deposition that are interspersed with hot spots of elevated nitrogen deposition downwind of large expanding metropolitan centers or large agricultural operations (Fenn et al., 2003).

Fenn et al. (1998) have documented the major effects of Nr deposition in terrestrial and aquatic ecosystems in the western United States. Primarily these effects are in response to nitrogen enrichment of systems that are naturally nitrogen limited. Included in these effects are greenhouse gas emissions, higher nitrogen concentrations in plant tissues, and increased nitrification rates and nitrate (NO_3^-) levels in soils, streams, and lakes (Fenn et al., 2003b). A result of chronic Nr enrichment has resulted in important community changes in vegetation, lichens, mycorrhizae, and phytoplankton, occasionally at relatively low levels of nitrogen deposition (3 to 8 kgN/ha/year; Baron et al., 2000).

Developments in recent decades in the Colorado Front range have resulted in increased nitrogen deposition since the 1980s at high-elevation sites. Total deposition values currently range from 4-8 kgN/ha/year (Baron et al., 2000). Competition among species resulting in changes in community composition is one of the most notable responses to environmental change (Bowman, 2000). Nitrogen saturation, the result of increased deposition in the alpine tundra of Niwot Ridge in the Front Range of the Southern Rockies in Colorado, has changed nitrogen cycling and provided the potential for replacement in plant species by more competitive, faster growing species (Bowman and Steltzer, 1998; Bowman, 2000; Baron et al.,



1. **Nitrogen Inputs:**
    - Atmospheric deposition, N2 fixation, fertilization

   Nitrogen Retention:
    - In plant biomass and soil organic matter
    - The role of soil microbes and woody residues
    - Abiotic retention

   Nitrogen Outputs:
    - Hydrologic transport, gaseous emissions from soil
    - Removal in harvest, fire emissions, and soil erosion
2. **Characteristics Predisposing Forests to N Saturation:**
    - Stand vigor and succession, forest type
    - Previous land use--stand history
    - Soil N accumulation
    - Topography and climate
    - Nitrogen deposition
3. **Ecosystem Responses to Excess Nitrogen:**
    - Nitrate leaching and export
    - Eutrophicationof estuaries
    - Toxicity of surface waters
    - Foliar nutrient responses
    - Nitrogen mineralization and nitrification
    - Effects on soil organic matter
    - Soil acidification, cation depletion, Al toxicity
    - Foliar nutrient responses
    - Greenhouse gas fluxes
4. **Regional N Saturation Conceptual Models:**
    - New England forests
    - California forests
    - Colorado alpine ecosystems

Figure 4-17. Diagrammatic overview of excess nitrogen (N) in North America.

Source: Fenn et al. (1998).

2000). Plants growing in an alpine tundra, as is true of other plants growing in low resource environments (e.g., infertile soil, shaded understory, deserts), have been observed to have certain similar characteristics: a slow grow rate, low photosynthetic rate, a low capacity for nutrient uptake and low soil microbial activity (Bowman and Steltzer, 1998; Bowman, 2000). An important feature of such plants is that they continue to grow slowly and tend to respond even less when provided with an optimal supply and balance of resources (Pearcy et al., 1987; Chapin, 1991). Plants adapted to cold, moist environments grow more leaves than roots as the relative availability of nitrogen increases; however, other nutrients may soon become limiting. These patterns of vegetative development affect their capacity to respond to variation in available resources and to environmental stresses such as frost, high winds, and drought. Preformation of buds 3-4 years in advance of emergence, reduced cell numbers, and high biomass allocation to belowground organs also limits the ability of many alpine plants to respond to variations in their environment (Bowman, 2000). However, significant interspecific genetic variation influences the capacity of the alpine species to respond to changes in resource availability. The capacity of subalpine and boreal species in particular, and gymnosperms in general, to reduce nitrates in either roots or leaves appears to be limited. In addition, the ability of trees to use nitrogen varies with the age of the tree and the density of the stand (Waring, 1987).

In experimental studies of nitrogen deposition conducted by Wedin and Tilman (1996) over a 12-year period on Minnesota grasslands, plots dominated by native warm-season grasses shifted to low-diversity mixtures dominated by cool-season grasses at all but the lowest rates of nitrogen addition. Grasslands with high nitrogen retention and carbon storage rates were the most vulnerable to loss of species and major shifts in nitrogen cycling. The shift to low-diversity mixtures was associated with the decrease in biomass carbon to nitrogen (C:N) ratios, increased nitrogen mineralization, increased soil nitrate, high nitrogen losses, and low carbon storage (Wedin and Tilman, 1996). Naeem et al. (1994) experimentally demonstrated under controlled environmental conditions that the loss of biodiversity, genetic resources, productivity, ecosystem buffering against ecological perturbation, and loss of aesthetic and commercially valuable resources also may alter or impair ecosystems services.

The long-term effects of increased nitrogen deposition have been studied in several western and central European plant communities these include lowland heaths, species-rich grasslands, mesotrophic fens, ombrotrophic bogs, upland moors, forest-floor vegetation, and freshwater lakes (Bobbink, 1998). Large changes in species composition have been observed in regions with high nitrogen loadings or infield experiments after years of nitrogen addition (Bobbink et al., 1998). The increased input of nitrogen gradually increased the availability of nitrogen in the soil, and its retention because of low rates of leaching and denitrification resulted in faster litter decomposition and rate of mineralization. Faster growth and greater height of nitrophilic species enables these plants to shade out the slower growing species, particularly those in oligotrophic or mesotrophic conditions (Bobbink, 1998; Bobbink et al., 1998). Excess nitrogen inputs to unmanaged heathlands in the Netherlands has resulted in nitrophilous grass species replacing slower growing heath species (Roelofs et al., 1987; Garner, 1994). Van Breemen and Van Dijk (1988) noted that over the past several decades the composition of plants in the forest herb layers has been shifting toward species commonly found on nitrogen-rich areas. It also was observed that the fruiting bodies of mycorrhizal fungi had decreased in number.

Other studies in Europe point out the effects of excessive nitrogen deposition on mixed-oak forest vegetation along a deposition gradient largely controlled by soil acidity, nitrogen supply, canopy composition, and location of sample plots (Brunet et al., 1998; Falkengren-Grerup, 1998). Results of the study, using multivariate methods, suggest that nitrogen deposition has affected the field-layer vegetation directly by increased nitrogen availability and, indirectly, by accelerating soil acidity. Time series studies indicate that 20 of the 30 field-layer species (nonwoody plants) that were associated most closely with high nitrogen deposition increased in frequency in areas with high nitrogen deposition during the past decades. Included in the field-layer species were many generally considered nitrophilous; however, there were several acid tolerant species (Brunet et al, 1998). In an experimental study involving 15 herbs and 13 grasses, Falkengren-Grerup (1998), observed that species with a high nitrogen demand and a lesser demand for other nutrients were particularly competitive in areas with acidic soils and high nitrogen deposition. The grasses grew better than herbs with the addition of nitrogen. It was concluded that, at the highest nitrogen deposition, growth was limited for most species by the supply of other nutrients; and, at the intermediate nitrogen concentration, the grasses were more efficient than the herbs in utilizing nitrogen. Nihlgård (1985) suggested that excessive nitrogen deposition may contribute to forest decline in other specific regions of Europe.

Additionally, Schulze (1989), Heinsdorf (1993), and Lamersdorf and Meyer (1993) attribute magnesium deficiencies in German forests, in part, to excessive nitrogen deposition.

The carbon to nitrogen (C:N) ratio of the forest floor can also be changed by nitrogen deposition over time. This change appears to occur when the ecosystem becomes nitrogen saturated (Gundersen et al., 1998a). Long-term changes in C:N status have been documented in Central Europe and indicate that nitrogen deposition has changed the forest floor. In Europe, low C:N ratios coincide with high deposition regions (Gundersen et al., 1998a). A strong decrease in forest floor root biomass has been observed with increased nitrogen availability. Roots and the associated mycorrhizae appear to be an important factor in the accumulation of organic matter in the forest floor at nitrogen-limited sites. If root growth and mycorrhizal formation are impaired by nitrogen deposition, the stability of the forest floor may be affected by stimulating turnover and decreasing the root litter input to the forest floor and thus decrease the nitrogen that can be stored in the forest floor pool (Gundersen et al., 1998b). Nitrogen-limited forests have a high capacity for deposited nitrogen to be retained by plants and microorganisms competing for available nitrogen (Gundersen et al., 1998b). Nitrate leaching has been correlated significantly with nitrate status but not with nitrate depositions. Forest floor C:N ratio has been used as a rough indicator of ecosystem nitrogen status in mature coniferous forests and the risk of nitrate leaching; analyses of European databases indicated an empirical relationship between forest floor C:N ratio and nitrate leaching (Gundersen et al., 1998a). Nitrate leaching was observed when the deposition received was more than 10 kg N/ha. All of the data sets supported a threshold at which nitrate leaching seems to increase at a C:N ratio of 25. Therefore, to predict the rate of changes in nitrate leaching, it is necessary to be able to predict the rate of changes in the forest floor C:N ratio. Decreased foliar and soil nitrogen and soil C:N ratios, as well as changes in nitrogen mineralization rates, have been observed when comparing responses to nitrogen deposition in forest stands east and west of the Continental Divide in the Colorado Front Range (Baron et al., 2000; Rueth and Baron, 2002). Understanding the variability in forest ecosystem response to nitrogen input is essential in assessing pollution risks (Gundersen et al., 1998a).

The plant root is an important region of nutrient dynamics. The rhizosphere includes the soil that surrounds and is influenced by plant roots (Wall and Moore, 1999). The mutualistic relationship between plant roots, fungi, and microbes is critical for the growth of the organisms involved. The plant provides shelter and carbon; whereas the symbiont provides access to limiting nutrients such as nitrogen and phosphorus. As indicated above, changes in soil nitrogen influence the mycorrhizal-plant relationship. Mycorrhizal fungal diversity is associated with above-ground plant biodiversity, ecosystem variability, and productivity (Wall and Moore, 1999). Aber et al. (1998) showed a close relationship between mycorrhizal fungi and the conversion of dissolved inorganic nitrogen to soil nitrogen. During nitrogen saturation, soil microbial communities change from being fungal, and probably being dominated by mycorrhizae, to being dominated by bacteria. The loss of mycorrhizal function has been hypothesized as the key process leading to increased nitrification and nitrate mobility. Increased nitrate mobility leads to increased cation leaching and soil acidification (Aber et al., 1998).

The interrelationship of above- and below-ground flora is illustrated by the natural invasion of heathlands by oaks (*Quercus robur*). The soil-forming factors under the heath have been vegetation typed during the last 2000 years; whereas the invasion by oaks has been taking place for only a few decades. Clearly changes in the ground floor and soil morphology takes place when trees colonize heath (Nielsen et al., 1999). The distribution of roots also changed under the three different vegetation types. Under both heather and the Sitka spruce plantation, the majority of roots are confined to the uppermost horizons; whereas under oak, the roots are distributed more homogeneously. There was also a change in the C:N ratio when heather was replaced by oaks. Also, the spontaneous succession of the heath by oaks changed the biological nutrient cycle into a deeper vertical cycle when compared to the heath where the cycle is confined to the upper soil horizons. Soils similar to those described in this study (Jutland, Denmark) with mainly an organic buffer system seem to respond quickly to changes in vegetation (Nielsen et al., 1999).

The affects of changes in root to shoot relationships in plants were observed in studies of the coastal sage scrub (CSS) community in southern California which is composed of the drought-deciduous shrubs *Artemisia californica*, *Encelia farinosa*, and *Eriogonum fasciculatum*. The CSS in California has been declining in land area and in shrub density over the past 60 years and is being replaced in many areas by Mediterranean annual grasses (Allen et al., 1998; Padgett et al., 1999; Padgett and Allen, 1999). Nitrogen deposition was considered as a possible cause. Up to 45 kg/ha/yr are deposited in the Los Angeles Air Basin (Bytnerowicz and Fenn, 1996). Tracts of land set aside as reserves, which in many cases in southern California are surrounded by urbanization, receive large amounts of nitrogenous compounds from polluted air. The CSS is of particular interest because some 200 sensitive plant species and several federally listed animal species are found in the area (Allen et al., 1998). Because changes in plant community structure often can be related to increases in the availability of a limiting soil nutrient or other resource, experiments were conducted to determine whether increased nitrogen availability was associated with the significant loss in native shrub cover. Studies indicated that the three native perennial shrubs (*Artemisia californica*, *Eriogonum fasciculatum,* and *Encelia farinosa* tended to be more nitrophilous than the two exotic annual grasses (*Bromus rubens*, *Avena fatua*) and the weedy pod mustard (*Brassica geniculata*). These results contrast with most models dealing with the adaptation of perennial species to stressful environments (Padgett and Allen, 1999). If nitrogen were the only variable between the invasive annuals and native shrubs, neither shrubs nor grasses have a particular advantage. Although CSS shrubs are able to take up nitrogen at high rates, native grasses have a denser seedbank and earlier germination than native species. The native seedlings are not able to compete with dense stands of exotic grasses, and thus are gradually replaced by the grasses following disturbance such as frequent fire (Eliason and Allen, 1997; Cione et al., 2002; Yoshida and Allen, 2001). In addition, nitrogen-induced changes in arbuscular mycorrhizal fungi may also affect the growth of native seedlings. Nitrogen enrichment of the soils induced a shift in the arbuscular mycorrhizal community composition. Larger-spored fungal species (*Scutellospora* and *Gigaspora*), due to a failure to sporulate, decreased in number with a concomitant proliferation of small-spored species of *Glomus aggregatum*, G. *leptotichum*, and G. *geosporum*, indicating a strong selective pressure for the smaller spores species of fungi (Edgerton-Warburton and Allen, 2000). These results demonstrate that nitrogen enrichment of the soil significantly alters the arbuscular mycorrhizal species composition and richness and markedly decreases the overall diversity of the arbuscular mycorrhizal community. The decline in coastal sage scrub species can, therefore, directly be linked to the decline of the arbuscular mycorrhizal community *(*Edgerton-Warburton and Allen, 2000).

In addition to excess nitrogen deposition effects on terrestrial ecosystems of the types noted above (e.g., dominant species shifts and other biodiversity impacts), direct atmospheric nitrogen deposition and increased nitrogen inputs via runoff into streams, rivers, lakes, and oceans can noticable affect aquatic ecosystems as well (Figure 4-15). Estuaries are among the most intensely fertilized ecosystems on Earth, receiving far greater nutrient inputs than other systems. Chesapeake Bay is a prime example (Fenn et al., 1998). Another illustrative example is recently reported research (Paerl et al., 2001) characterizing the effects of nitrogen deposition on the Pamlico Sound, NC, estuarine complex, which serves as a key fisheries nursery supporting an estimated 80% of commercial and recreational finfish and shellfish catches in the southeastern U.S. Atlantic coastal region. Such direct atmospheric nitrogen deposition onto waterways feeding into the Pamlico Sound or onto the sound itself and indirect nitrogen inputs via runoff from upstream watersheds contribute to conditions of severe water oxygen depletion; formation of algae blooms in portions of the Pamlico Sound estuarine complex; altered fish distributions, catches, and physiological states; and increases in the incidence of disease. Under extreme conditions of especially high rainfall rate events (e.g., hurricanes) affecting watershed areas feeding into the sound, the effects of nitrogen runoff (in combination with excess loadings of metals or other nutrients) can be massive — e.g., creation of the widespread “dead-zone” affecting large areas of the Pamlico Sound for many months after hurricane Fran in 1996 and hurricanes Dennis, Floyd, and Irene in 1999 impacted eastern North Carolina.

The primary pathways of nitrogen loss from forest ecosystems are hydrological transport beyond the rooting zone into groundwater or stream water, or surface flows of organic nitrogen as nitrate and nitrogen loss associated with soil erosion (Fenn et al., 1998). Stream water nitrate concentrations have been related to forest successional stage in the eastern United States. Logging history and fire history of an area are major variables determining the capability of a forest stand to retain nitrogen. Nitrogen concentrations were high in manure ecosystems after disturbances such as clearcutting, but lower in mid-successional forests.

Nitrogen saturation of a high elevation watershed in the southern Appalachian Mountains was observed to affect stream water chemistry. High nitrate concentrations have been observed in streams draining undisturbed watersheds in the Great Smoky Mountains National Park in Tennessee and North Carolina. Nitrate concentrations were highest at higher elevations and in areas around old-growth forests that had never been logged (Fenn et al., 1998).

In the Northeast, nitrogen is the element most responsible for eutrophication in coastal waters of the region (Jaworski et al., 1997). There has been a 3 to 8-fold increase in nitrogen flux from 10 watersheds in the Northeastern United States since the early 1900s. These increases are associated with nitrogen oxide emissions from combustion which have increased

5-fold. Riverine nitrogen fluxes have been correlated with atmospheric deposition onto their landscapes and also with nitrogen oxides emissions into their airsheds. Data from 10 benchmark watersheds with good historical records, indicate that ca., 36-80% of the riverine total nitrogen export, with an average of 64%, was derived directly or indirectly from nitrogen oxide emissions (Jaworski et al., 1997).

Nitrogen saturation of a high elevation watershed in the southern Appalachian Mountains was observed to affect streamwater chemistry. The Great Smoky Mountains in the southeastern United States receive high total atmospheric deposition of sulfur and nitrogen (2,200 Eq/ha/yr of total sulfur and approximately 1,990 Eq/ha/yr of total nitrogen). A major portion of the atmospheric loading is from dry and cloud deposition. Extensive surveys conducted in October 1993 and March 1994 indicated that stream pH values were near or below pH 5.5 and that the acid neutralizing capacity (ANC) was below 50 μeq/L at high elevations. Analysis of streamwater indicated that nitrate was the dominant anion (Flum and Nodvin, 1995; Nodvin et al., 1995). The study was expanded to the watershed scale with monitoring of precipitation, thoughfall, stream hydrology, and stream chemistry. Nitrogen saturation of the watershed resulted in extremely high exports of nitrate and promoted both chronic and episodic stream acidification in which the nitrate was the dominant ion. Significant exports of base cation was also observed. Nitrification of the watershed soils resulted in elevations of soil solution aluminum concentrations to levels known to inhibit calcium uptake in red spruce (Nodvin et al., 1995).

Excessive nitrogen loss is a symptom of terrestrial ecosystem dysfunction and results in the degradation of water quality and potentially deleterious effects on terrestrial and aquatic ecosystems (Fenn and Poth, 1999). Data from a number of hydrologic, edaphic, and plant indicators indicate that the mixed conifer forests and chaparral systems directly exposed to air pollution from greater Los Angeles are nitrogen saturated. Preliminary data suggests that symptoms of nitrogen saturation are evident in mixed conifer or chaparral sites receiving atmospheric deposition of 20 to 25 kg/N/ha/y (Fenn et al, 1996). Available data clearly indicate that ecosystems with a Mediterranean climate have a limited capacity to retain nitrogen within the terrestrial system (Fenn and Poth, 1999). A 3-year study of streamwater NO_3^- concentrations along nitrogen deposition gradients in the San Bernardino Mountains in southern California evaluated streamwater quality and whether the streamwater concentrations covaried with nitrogen deposition across pollution gradients in the San Bernardino Mountains. Streamwater NO_3^- concentrations at Devil Canyon in the San Gabriel Mountains northeast of Los Angeles are the highest reported in North America for forested watersheds (Fenn and Poth, 1999). Five of the six streams monitored maintained elevated NO_3^- throughout the year. Peak nitrate concentrations ranged from 40 to 350 µmol/L. In the San Gorgonio Wilderness, an area of low to moderate deposition where 12 streams were sampled, only the five that had the greatest air pollution exposure had high NO_3^- concentrations. The results of the study suggested a strong association between levels of NO_3^- export in streamwater and the severity of chronic nitrogen deposition to the terrestrial watersheds. However, nitrogen processing within terrestrial and aquatic systems, even in areas with high nitrogen deposition, determine streamwater NO_3^- concentrations (Fenn and Poth, 1999). The Fernow Experimental Forest in West Virginia, the Great Smoky Mountains National park in Tennessee, and watersheds in southwestern Pennsylvania are the only undisturbed forested sites in North America known to have streamwater NO_3^- concentrations within the range of values found at Devil Canyon (Fenn and Poth, 1999).

Effects of Sulfur Deposition. Sulfur is a major component of plant proteins and as such is an essential plant nutrient. The most important source of sulfur is sulfate taken up from the soil by plant roots even though plants can utilize atmospheric SO_2 (Marschner, 1995). The availability of organically bound sulfur in soils depends largely on microbial decomposition, a relatively slow process. The major factor controlling the movement of sulfur from the soil into vegetation is the rate of release from the organic to the inorganic compartment (May et al., 1972; U.S. Environmental Protection Agency, 1982; Marschner, 1995). Sulfur plays a critical role in agriculture as an essential component of the balanced fertilizers needed to grow and increase worldwide food production (Ceccotti and Messick, 1997). Atmospheric deposition is an important component of the sulfur cycle. This is true not only in polluted areas where atmospheric deposition is very high, but also in areas of low sulfur input. Additions of sulfur into the soil in the form of SO_4^{-2} could alter the important organic-sulfur/organic-nitrogen relationship involved in protein formation in plants. The biochemical relationship between sulfur and nitrogen in plant proteins and the regulatory coupling of sulfur and nitrogen metabolism indicate that neither element can be assessed adequately without reference to the other. Sulfur deficiency reduces nitrate reductase and, to a similar extent, also glutamine synthetase activity. Nitrogen uptake in forests, therefore, may be loosely regulated by sulfur availability, but sulfate additions in excess of needs do not necessarily lead to injury (Turner and Lambert, 1980; Hogan et al., 1998).

Only two decades ago, there was little information comparing sulfur cycling in forests with other nutrients, especially nitrogen. With the discovery of deficiencies in some unpolluted regions (Kelly and Lambert, 1972; Humphreys et al., 1975; Turner et al., 1977; Schnug, 1997) and excesses associated with acidic deposition in other regions of the world (Meiwes and Khanna, 1981; Shriner and Henderson, 1978; Johnson et al., 1982a,b), interest in sulfur nutrition and cycling in forests has heightened. General reviews of sulfur cycling in forests have been written by Turner and Lambert (1980), Johnson (1984), Mitchell et al. (1992a,b), and Hogan et al. (1998). The salient elements of the sulfur cycle as it may be affected by changing atmospheric deposition are summarized by Johnson and Mitchell (1998). Sulfur has become the most important limiting factor in European agriculture because of the desulfurization of industrial emissions (Schnug, 1997).

Most studies dealing with the effects of sulfur deposition on plant communities have been conducted in the vicinity of point sources and have investigated above-ground effects of SO_2 or acidifying effects of sulfate on soils (Krupa and Legge, 1998; Dreisinger and McGovern, 1970; Legge, 1980; Winner and Bewley, 1978a,b; Laurenroth and Michunas, 1985; U.S. Environmental Protection Agency, 1982). Krupa and Legge (1986), however, observed a pronounced increase in foliar sulfur concentrations in all age classes of needles of the hybrid pine lodgepole x jack pine (*Pinus contorta* x *P. banksiana*). This vegetation had been exposed to chronic low concentrations of sulfur dioxide (SO_2) and hydrogen sulfide (H_2S) for more than 20 years and, then, to fugitive sulfur aerosol. Observations under the microscope showed no sulfur deposits on the needle surfaces and led to the conclusion that the sulfur in the needles was derived from the soil. The oxidation of elemental sulfur and the generation of protons is well known for the soils of Alberta, Canada. This process is mediated by bacteria of the *Thiobacillus* sp. As elemental sulfur gradually is converted to protonated SO_4, it can be leached downward and readily taken up by plant roots. The activity of *Thiobacillus* sp. is stimulated by elemental sulfur additions (Krupa and Legge, 1986).

Effects of Acidic Deposition on Forest Soils. Acidic deposition over the past quarter of a century has emerged as a critical environmental stress that affects forested landscapes and aquatic ecosystems in North America, Europe, and Asia (Driscoll et al., 2001). Acidic deposition can originate from transboundary air pollution and affect large geographic areas. It is composed of ions, gases, particles derived from gaseous emissions of sulfur dioxide (SO_2), nitrogen oxides (NO_x), ammonia (NH_3), and particulate emissions of acidifying and neutralizing compounds and is highly variable across space and time. It links air pollution to diverse terrestrial and aquatic ecosystems and alters the interactions of the hydrogen ion (H^+) and many elements (e.g., sulfur, nitrogen, calcium, magnesium, aluminum, and mercury). Acidic deposition contributes directly and indirectly to biological stress and the degradation of ecosystems and has played a major role in recent acidification of soil in some areas of Europe and, to a more limited extent, eastern North America (Driscoll et al., 2001).

Substantial and previously unsuspected changes in soils have been observed in polluted areas of eastern North America, the United Kingdom, Sweden, and Central Europe and in less polluted regions of Australia and western North American (reviewed by Johnson et al., 1999 and by Huntington, 2000). In some cases, trends were toward more acidic soils (e.g., Markewitz et al., 1998), and, in others, there were no consistent trends, with some soils showing increases and some showing decreases at different sampling times, and some showing no change (e.g., Johnson and Todd, 1998; Trettin et al., 1999; Yanai et al., 1999).

Significant changes in soil chemistry have occurred at many sites in the eastern United States during recent decades. Patterns of change in tree ring chemistry, principally at high elevations sites in the eastern United States, reflect the changing inputs of regional pollutants to forests. A temporal sequence of changes in uptake patterns, and possibly in tree growth, would be expected if significant base cation mobilization and depletion of base cations from eastern forest soils has occurred. Temporal changes in the chemistry of tree rings of red spruce were examined as indicators of historical changes in the chemical environment of red spruce.

Analysis of changes in wood chemistry from samples across several sites indicated that there have been substantial departures from the expected linear decreases in calcium accumulation patterns in wood. A region-wide calcium increase above expected levels followed by decreasing changes in wood calcium suggest that calcium mobilization began possibly 30 to 40 years ago and has been followed by reduced accumulation rates in wood, presumably associated with decreasing calcium availability in soil (Bondietti and McLaughlin, 1992). The period of calcium mobilization coincides with a region-wide increase in growth rate of red spruce; whereas the period of decreasing levels of calcium in wood corresponds temporally with patterns of decreasing radial growth at high elevation sites throughout the region during the past 20 to 30 years. The decline in wood calcium suggests that calcium loss may have increased to the point at which base saturation of soils has been reduced. Increases in aluminum and iron typically occur as base cations are removed from the soils by tree uptake (Bondietti and McLaughlin, 1992). The changes are spatially and temporally consistent with changes in the emissions of SO_2 and NO_2 across the region and suggest that increased acidification of soils has occurred.

Studies by Shortle and Bondietti (1992) support the view that changes in soil chemistry in eastern North America forest sites occurred many decades ago, "before anybody was looking." Sulfur and nitrogen emissions began increasing in eastern North America in the 1920s and continued to increase into the 1980s when sulfur began to decrease but nitrogen emissions did not (Garner et al., 1989). Shortle and Bondietti (1992) present evidence that, from the late 1940s into the 1960s, the mor humus (organic) layer of acid-sensitive forest sites in eastern North America underwent a significant change that resulted in the loss of exchangeable essential base cations and interrupted the critical base nutrient cycles between mature trees and the root-humus complex. The timing of the effect appears to have coincided with the period when the SO_x and NO_x emissions in eastern North America subject to long-range transport were increasing the most rapidly (see above; Shortle and Bondietti, 1992). Although forest ecosystems other than the high-elevation spruce-fir forests are not currently manifesting symptoms of injury directly attributable to acid deposition, less sensitive forests throughout the United States are experiencing gradual losses of base cation nutrients, which in many cases will reduce the quality of forest nutrition over the long term (National Science and Technology Council, 1998).
In some cases it may not even take decades because these forests already have been receiving sulfur and nitrogen deposition for many years. The current status of forest ecosystems in different U.S. geographic regions varies, as does their sensitivity to nitrogen and sulfur deposition. Variation in potential future forest responses or sensitivity are caused, in part, by differences in deposition of sulfur and nitrogen, ecosystem sensitivities to sulfur and nitrogen

additions, and responses of soils to sulfur and nitrogen inputs (National Science and Technology Council, 1998).

Acidic deposition has played a major role in recent soil acidification in some areas of Europe and, to a more limited extent, eastern North America. Examples include the study by Hauhs (1989) at Lange Bramke, Germany, which indicated that leaching was of major importance in causing substantial reduction in soil-exchangeable base cations over a 10-year period (1974-1984). Soil acidification and its effects result from the deposition of nitrate (NO_3^-) and sulfate (SO_4^{-2}) and the associated hydrogen (H^+) ion. The effects of excessive nitrogen deposition on soil acidification and nutrient imbalances have been well established in Dutch forests (Van Breemen et al., 1982; Roelofs et al., 1985; Van Dijk and Roelofs, 1988). For example, Roelofs et al. (1987) proposed that NH_3 /NH_4^+ deposition leads to heathland changes via two modes: acidification of the soil and the loss of cations K^+, Ca^{+2}, and Mg^{+2}; and nitrogen enrichment that results in “abnormal” plant growth rates and altered competitive relationships. Nihlgård (1985) suggested that excessive nitrogen deposition may contribute to forest decline in other specific regions of Europe. Falkengren-Grerup (1987) noted that, during about 50 years, unexpectedly large increases in growth of beech (*Fagus sylvatica L.*) were associated with decreases in pH and exchangeable cations in some sites in southernmost Sweden.

Likens et al. (1996, 1998) suggested that soils are changing at the Hubbard Brook Watershed, NH, because of a combination of acidic deposition and reduced base cation deposition. They surmised, based on long-term trends in streamwater data, that large amounts of calcium and magnesium have been lost from the soil-exchange complex over a 30-year period from approximately 1960 to 1990. The authors speculate that the declines in base cations in soils may be the cause of recent slowdowns in forest growth at Hubbard Brook. In a follow-up study, however, Yanai et al. (1999) found no significant decline in calcium and magnesium concentrations in forest floors at Hubbard Brook over the period 1976 to 1997. They also found both gains and losses in forest floor calcium and magnesium between 1980 and 1990 in a regional survey. Thus, they concluded that “forest floors in the region are not currently experiencing rapid losses of base cations, although losses may have preceded the onset of these three studies.” The biogeochemistry of calcium at Hubbard Brook is discussed in detail by Likens et al. (1998).

Hydrogen ions entering a forest ecosystem first encounter the forest canopy, where they are often exchanged for base cations that then appear in throughfall (Figure 4-18 depicts a model of H^+ sources and sinks). Base cations leached from the foliage must be replaced through uptake from the soil, or foliage cations will be reduced by the amounts leached. In the former case, the acidification effect is transferred to the soil where H^+ is exchanged for a base cation at the root-soil interface. Uptake of base cations or NH_4^+ by vegetation or soil microorganisms causes the release of H^+ in order to maintain charge balance; uptake of nutrients in anionic form (NO_3^-, SO_4^{-2}, PO_4^{-3}) causes the release of OH^- in order to maintain charge balance. Thus, the net acidifying effect of uptake is the difference between cation and anion uptake. The form of ions taken up is known for all nutrients but nitrogen because either NH_4^+ or NO_3^- can be utilized. In that nitrogen is a nutrient taken up in greatest quantities, the uncertainty in the ionic form of nitrogen utilized creates great uncertainty in the overall H^+ budget for soils (Johnson 1992).

The cycles of base cations differ from those of N, P, and S in several respects. The fact that calcium, potassium, and magnesium exist primarily as cations in solution, whereas N, P, and S exist primarily as anions, has major implications for the cycling of the nutrients and the effects of acid deposition on these cycles. The most commonly accepted model of base cation cycling in soils is one in which base cations are released by weathering of primary minerals to cation exchange sites where they are available for either plant uptake or leaching (Figure 4-18). The introduction of H^+ by atmospheric deposition or by internal processes will affect the fluxes of Ca, K, and Mg via cation exchange or weathering processes. Therefore, soil leaching is often of major importance in cation cycles, and many forest ecosystems show a net loss of base cations (Johnson, 1992).

Two basic types of soil change are involved: (1) a short-term intensity type change resulting from the concentrations of chemicals in soil water and (2) a long-term capacity change based on the total content of bases, aluminum, and iron stored in the soil (Reuss and Johnson, 1986; Van Breemen et al., 1983). Changes in intensity factors can have a rapid affect on the chemistry of soil solutions. Increases in the amounts of sulfur and nitrogen in acidic deposition can cause immediate increases in acidity and mobilization of aluminum in soil solutions. Increased aluminum concentrations and an increase in the Ca/Al ratio in soil solution have been linked to a significant reduction in the availability of essential base cations to plants, an increase

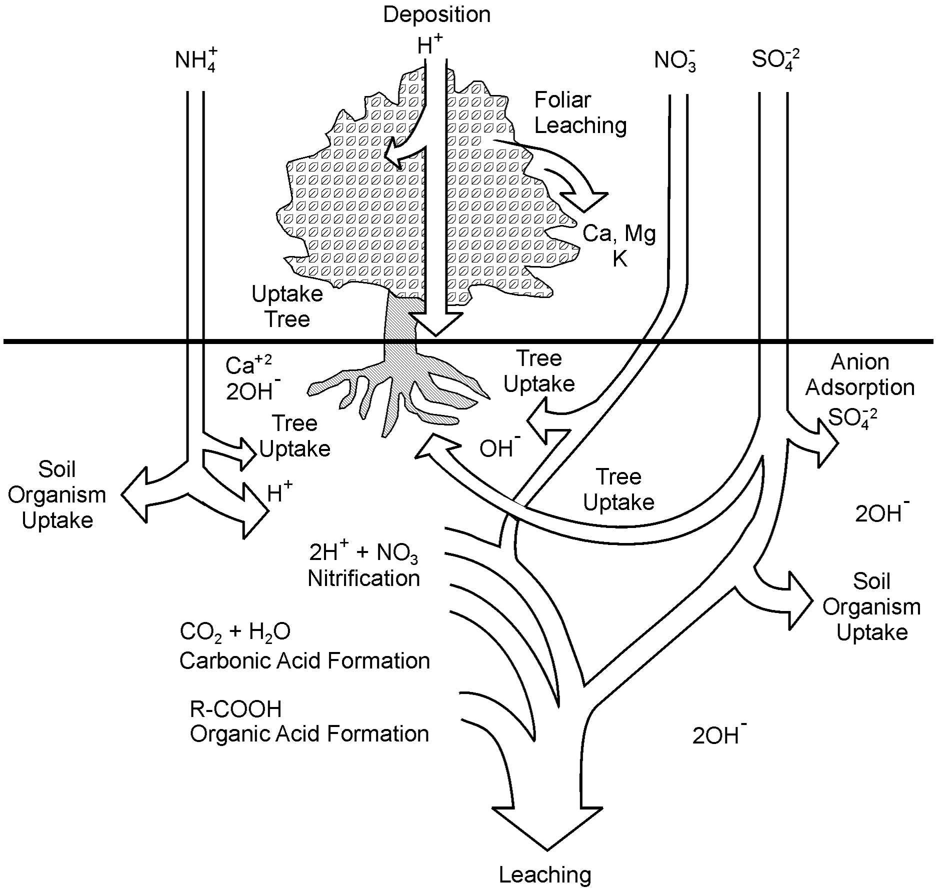


Figure 4-18. Schematic of sources and sinks of hydrogen ions in a forest (from Taylor et al., 1994).

in plant respiration, and increased biochemical stress (National Science and Technology Council, 1998).

Rapid changes in intensity resulting from the addition of increased amounts of nitrogen or sulfur in acidic deposition can have a rapid effect on the chemistry of soil solutions by increasing the acidity and mobilizing aluminum. Increased concentrations of aluminum and an increase in the ratio of calcium to aluminum in soil solution have been linked to a significantly reduced availability of essential cations to plants.

Capacity changes are the result of many factors acting over long time periods. The content of base cations (calcium, magnesium, sodium, and potassium) in soils results from additions from the atmospheric deposition, decomposition of vegetation, and geologic weathering. Loss of base cations may occur through plant uptake and leaching. Increased leaching of base cations may result in nutrient deficiencies in soils as has been happening in some sensitive forest ecosystems (National Science and Technology Council, 1998).

Aluminum toxicity is a possibility in acidified soils. Atmospheric deposition (or any other source of mineral anions) can increase the concentration of Al, especially Al^{3+}, in soil solution without causing significant soil acidification (Johnson and Taylor, 1989). Aluminum can be brought into soil solution in two ways: (1) by acidification of the soil and (2) by an increase in the total anion and cation concentration of the soil solution. The introduction of mobile, mineral acid anions to an acid soil will cause increases in the concentration of aluminum in the soil solution, but extremely acid soils in the absence of mineral acid anions will not produce a solution high in aluminum. An excellent review of the relationships among the most widely used cation-exchange equations and their implications for the mobilization of aluminum into soil solution is provided by Reuss (1983).

A major concern has been that soil acidity would lead to nutrient deficiency. Calcium is essential for root development and the formation of wood, and it plays a major role in cell membrane integrity and cell wall structure. Aluminum concentrations in the soil can influence forest tree growth in regions where acidic deposition and natural acidifying processes increase soil acidity. Acidic deposition mobilizes calcium and magnesium, which are essential for root development and stem growth. Mobilized aluminum can also bind to fine root tips of red spruce, further limiting calcium and magnesium uptake (Shortle and Smith, 1988; Shortle et al., 1997).

There is abundant evidence that aluminum is toxic to plants. Upon entering tree roots, it accumulates in root tissues (Thornton et al., 1987; Vogt et al., 1987a, b). Reductions in calcium uptake have been associated with increases in aluminum uptake (Clarkson and Sanderson, 1971). A number of studies suggest that the toxic effect of aluminum on forest trees could be caused by Ca^{+2} deficiency (Shortle and Smith, 1988; Smith, 1990a). Mature trees have a high calcium requirement relative to agriculture crops (Rennie, 1955). Shortle and Smith (1988) attributed the decline of red spruce in eight stands across northern New England from Vermont to Maine to an imbalance of Al^{3+} and Ca^{+2} in fine root development.

To be taken up from the soil by roots, calcium must be dissolved in soil water (Lawrence and Huntington, 1999). Aluminum in soil solution reduces calcium uptake by competing for binding sites in the cortex of fine roots. Tree species may be adversely affected if high aluminum to nutrient ratios create a nutrient deficiency by limiting uptake of calcium and magnesium (Shortle and Smith, 1988; Garner, 1994). Acid deposition, by lowering the pH of aluminum-rich soil, can increase aluminum concentrations in soil water through dissolution and ion exchange processes. Aluminum is more readily taken up than is calcium because of its greater affinity for negatively charged surfaces. When present in the forest floor, aluminum tends to displace adsorbed calcium and causes it to be more readily leached. The continued buildup of aluminum in the forest floor layer, where nutrient uptake is greatest, can lower efficiency of calcium uptake when the ratio of calcium to aluminum in soil water is less than one (Lawrence and Huntington, 1999). Reduction in calcium uptake suppresses cambial growth and reduces the rate of wood (annual ring) formation, decreases the amount of functional sapwood and live crown, and predisposes trees to disease and injury from stress agents when the functional sapwood becomes less that 25% of cross-sectional stem area (Smith, 1990a). A 1968 Swedish report to the United Nations postulated a decrease in forest growth of ca., 1.5% per year when the ratio of calcium to aluminum in soil water is less than one (Lawrence and Huntington, 1999). The concern that acidification and nutrient deficiency may result in forest decline remains today.

Acidic deposition has been firmly implicated as a causal factor in the northeastern high-elevation decline of red spruce (DeHayes et al., 1999). The frequency of freezing injury of red spruce has increased over the past 40 years, a period that coincides with increase emissions of sulfur and nitrogen oxides and acidic deposition (DeHayes et al., 1999). Studies indicate that there is a significant positive association between cold tolerance and foliar calcium in trees exhibiting deficiency in foliar calcium. Most of the calcium in conifer needles is insoluble calcium oxalate and pectate crystals, which are of little physiological importance. It is the labile calcium ions in equilibrium within the plasma membrane that are of major physiological importance (DeHayes et al., 1999). The membrane-associated pool of calcium (mCa), although a relatively small fraction of total foliar ion pools, strongly influences the response of cells to changing environmental conditions. The plant plasma membrane plays a critical role in mediating cold acclimation and low-temperature injury. Leaching of calcium associated with acidic deposition is considered to be the result of cation exchange due to exposure to the H^+ ion. The studies of DeHayes et al. (1999) demonstrate that the direct deposition of acidic deposition on needles represents a unique environmental stress, in that it preferentially removes mCa which is not readily replaced in autumn. They propose that direct deposition on red spruce foliage preferentially displaces calcium ions specifically associated with plasma membranes of mesophyll cells resulting in the reduction of mCa and the destabilizing of plasma membranes and depletion of messenger calcium. Further, DeHayes et al. (1999) state that their studies raise the strong possibility that acid rain alteration of the mCa and membrane integrity is not unique to red spruce but has been demonstrated in many other northern temperate forest tree species including yellow birch (*Betula alleghaniensis*), white spruce (*Picea glaucus*), red maple (*Acer rubrum*) eastern white pine (Pinus strobus), and sugar maple (*Acer saccharum*). Assessments of mCa, membrane integrity, and the effects of other secondary stresses have not yet been made for these species.

Seasonal and episodic acidification of surface waters have been observed in the eastern United States, Canada and Europe (Hyer et al., 1995). In the Northeast, the Shenandoah National Park in Virginia, and the Great Smoky Mountains, episodic acidification has been associated with the nitrate ion (Driscoll et al., 2001; Hyer et al., 1995 ; Eshleman et al., 1995). The short-term acid episodes occur during spring snowmelts and large precipitation events (Driscoll et al., 2001). Episodic acidification of surface waters has usually been considered to be a transient loss of acid neutralizing capacity associated with snowmelt/rainfall runoff and, as such, represents short-term (hours to weeks) effects considered to be distinguishable from chronic long-term (years to centuries) changes in acidity. Studies of both episodic and chronic acidification of surface waters indicate that acidification can have long-term adverse effects on fish populations, declines of species richness, abundance of zooplankton, and macroinvertebrates (Driscoll et al., 2001; Eshleman et al., 1995). Nitrogen saturation of soils and the slow release of nitrates inhibited the recovery of acid sensitive systems (Driscoll et al., 2001). The acidification of aquatic ecosystems and effects on aquatic biota are discussed in more detail in the EPA document Air Quality Criteria for Nitrogen Oxides (U.S. Environmental Protection Agency, 1993).

Air pollution is not the sole cause of soil change. High rates of acidification are occurring in less polluted regions of the western United States and Australia because of internal soil processes, such as tree uptake of nitrate and nitrification associated with excessive nitrogen fixation (Johnson et al., 1991b). Many studies have shown that acidic deposition is not a necessary condition for the presence of extremely acidic soils, as evidenced by their presence in unpolluted, even pristine, forests of the northwestern United States and Alaska (Johnson et al., 1991b). Soil can become acidic when H^+ ions attached to NH_4^+ or HNO_3 remain in the soil after nitrogen is taken up by plants. For example, Johnson et al. (1982b) found significant reductions in exchangeable K^+ over a period of only 14 years in a relatively unpolluted Douglas fir Integrated Forest Study (IFS) site in the Washington Cascades. The effects of acid deposition at this site were negligible relative to the effects of natural leaching (primarily carbonic acid) and nitrogen tree uptake (Cole and Johnson, 1977). Even in polluted regions, numerous studies have shown the importance of tree uptake of NH_4^+ and NO_3^- in soil acidification. Binkley et al. (1989) attributed the marked acidification (pH decline of 0.3 to 0.8 units and base saturation declines of 30 to 80%) of abandoned agricultural soil in South Carolina over a 20-year period to NH_4^+ and NO_3^- uptake by a loblolly pine plantation.

An interesting example of uptake effects on soil acidification is that of Al uptake and cycling (Johnson et al., 1991b). Aluminum accumulation in the leaves of coachwood (*Ceratopetalum apetalum*) in Australia has been found to have a major effect on the distribution and cycling of base cations (Turner and Kelly, 1981). The presence of C. *apetalum* as a secondary tree layer beneath brush box (*Lophostemon confertus*) was found to lead to increased soil exchangeable Al^{3+} and decreased soil exchangeable Ca^{2+} (Turner and Kelly, 1981). The constant addition of aluminum-rich litter fall obviously has had a substantial effect on soil acidification, even if base cation uptake is not involved directly.

Given the potential importance of particulate deposition for base cation status of forest ecosystems, the findings of Driscoll et al. (1989, 2001) and Hedin et al. (1994) are especially relevant. Driscoll et al. (1989, 2001) noted a decline in both SO_4^{-2} and base cations in both atmospheric deposition and stream water over the past two decades at Hubbard Brook Watershed, NH. The decline in SO_4^{-2} deposition was attributed to a decline in emissions, and the decline in stream water SO_4^{-2} was attributed to the decline in sulfur deposition. Hedin et al. (1994) reported a steep decline in atmospheric base cation concentrations in both Europe and North America over the past 10 to 20 years. The reductions in SO_2 emissions in Europe and North America in recent years have not been accompanied by equivalent declines in net acidity related to sulfate in precipitation. These current declines in sulfur deposition have, to varying degrees, been offset by declines in base cations and may be contributing "to the increased sensitivity of poorly buffered systems." Analysis of the data from the IFS supports the authors' contention that atmospheric base cation inputs may seriously affect ecosystem processes. Johnson et al. (1994) analyzed base cation cycles at the Whiteface Mountain IFS site in detail and concluded that Ca losses from the forest floor were much greater than historical losses, based on historical changes in forest floor Ca observed in an earlier study. Further, the authors suggested that the difference between historical and current net loss rates of forest floor Ca may be caused by sharply reduced atmospheric inputs of calcium after about 1970 and may be exacerbated by sulfate leaching (Johnson et al., 1994b).

The calcium/aluminum molar ratio has been suggested as a valuable ecological indicator of an approximate threshold beyond which the risk of forest injury from Al stress and nutrient imbalances increases (Cronan and Grigal, 1995). The Ca/Al ratio also can be used as an indicator to assess forest ecosystem changes over time in response to acidic deposition, forest harvesting, or other process that contribute to acid soil infertility. This ratio, however, may not be a reliable indicator of stress in areas with both high atmospheric deposition of ammonium and magnesium deficiency via antagonism involving ammonium rather than aluminum and in areas with soil solutions with calcium concentrations greater than 500 micromoles per liter (National Science and Technology Council, 1998). Cronan and Grigal (1995), based on a review of the literature, have made the following estimates for determining the effects of acidic deposition on tree growth or nutrition:

- forests have a 50% risk of adverse effects if the Ca/Al ration is 1.0,
- the risk is 75% if the ratio is 0.5, and
- the risk approaches 100% if the ratio is 0.2.

The Ca/Al ratio of soil solution provides only an index of the potential for Al stress. Cronan and Grigal (1995) state that the overall uncertainty of the Ca/Al ratio associated with a given probability ratio is considered to be approximately ±50%. Determination of thresholds for potential forest effects requires the use of the four successive measurement endpoints in the soil, soil solution, and plant tissue listed below.

(1) Soil base saturation less than 15% of effective cation exchange capacity,
(2) Soil solution Ca/Al molar ratio less than 1.0 for 50% risk,
(3) Fine roots tissue Ca/Al molar ratio less than 0.2 for 50% risk, and
(4) Foliar tissue Ca/Al molar ratio less than 12.5 for 50% risk.

The application of the Ca/Al ratio indicator for assessment and monitoring of forest health risks has been recommended for sites or in geographic regions where the soil base saturation < 15%.

Critical Loads. The critical loads framework for assessing the effects of atmospheric deposition originated in Europe where the concept has generally been accepted as the basis for abatement strategies to reduce or prevent injury to the functioning and vitality of forest ecosystems caused long-range transboundary chronic acidic deposition (Lokke et al., 1996). The critical load has been defined as a "quantitative estimate of an exposure to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment do not occur according to present knowledge" (Lokke et al., 1996).

The concept is useful for estimating the amounts of pollutants that sensitive ecosystems can absorb on a sustained basis without experiencing measurable degradation. The response to pollutant deposition of an ecosystem is a direct function of the level of sensitivity of the ecosystem to the pollutant and its capability to ameliorate change. The estimation of ecosystem critical loads requires an understanding of how an ecosystem will respond to different loading rates in the long term. The approach can be of special value for ecosystems receiving chronic deposition of pollutants such as nitrogen and sulfur. A program was designed to develop and evaluate a framework for setting critical loads of nitrogen and sulfur in the United States in 1989 (Strickland et al., 1993). A flexible six step approach has been outlined for use with the critical load framework (Figure 4-19). These are (1) selection of ecosystem components, indicators, and characterization of the resource; (2) definition of the functional subregions; (3) characterization of deposition within each of the subregions; (4) definition of an assessment endpoint; (5) selection and application of models; and (6) mapping projected ecosystem responses. The approach permits variability in ecosystem characteristic and data availability (Strickland et al., 1993).

Ecological endpoints or indicators are measurable characteristics related to the structure, composition, or functioning of ecological systems (i.e., indicators of condition). One or more measurable endpoints are associated with each element in Table 4-1. These assessment endpoints represent a formal expression of the environmental value that is to be protected. If the assessment endpoint is to be used as a regulatory limit, it should be socially relevant. Selection of a specific ecosystem for study will depend on the severity of the problem of concern for a

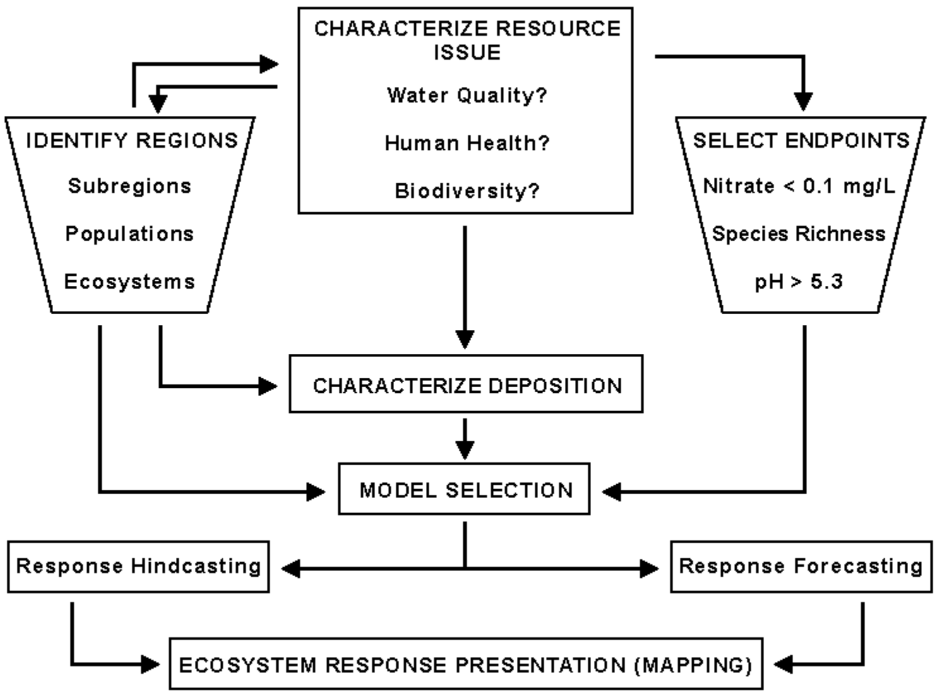


Figure 4-19. Key elements of proposed framework for determining critical loads for nitrogen and sulfur in the United States.

Source: Strickland et al. (1993).

region. Time scales o response must be considered in selecting and evaluating ecosystem response(s) to changes in atmospheric deposition. Responses of aquatic ecosystems to depositions can occur quickly. Surface water acidification associated with nitrate leaching should respond to decreases in nitrogen loading in a short period of time. However, changes in growth responses of vegetation resulting from soil nutrient imbalances may require years or decades to detect. The focus of concern should be the populations within an ecosystem that are sensitive to nitrogen and sulfur deposition (Hunsaker et al., 1993).

Biogeochemicals as indicators for monitoring forest nitrogen status have been proposed by Fenn and Poth (1998). Because nitrogen is a major constituent of all forms of life and is cycled through a complex web of processes involving many biotic and abiotic mechanisms, evaluating forest nitrogen status is a challenge. Indicators of ecosystems at risk of nitrogen saturation should include those that can be identified when nitrogen availability exceeds biotic demand.

Such indicators typically should monitor parameters that are normally at background or low levels in nitrogen-limited systems and should be those that commonly respond to excess nitrogen in a wide range of ecosystems (Fenn and Poth, 1998). Such indicators include foliar nitrogen; nutrient ratios (N:P,N:cation); foliar nitrate; foliar δ^{15} N; arginine concentration; soil C:N ratio; NO_3^- in soil extracts or in soil solution; and flux rates of nitrogenous trace gasses from soil (Fenn et al., 1998). The cardinal indicator or manifestation of nitrogen saturation in all ecosystem types, including California forests and chaparral, is increased and prolonged NO_3^- loss below the main rooting zone and in stream water. Seasonal patterns of stream water nitrate concentrations are especially good indicators of watershed nitrogen status (see sections on nitrate, sulfur and acidic deposition; Fenn and Poth, 1998).

In Europe, the elements used in the critical load concept are: a biological indicator, a chemical criterion, and a critical value. The biological indicator is the organism used to indicate the status of the receptor ecosystem; the chemical criterion is the parameter that results in harm to the biological indicator; and the critical value is the value of the chemical criterion below which no significant harmful response occurs to the biological indicator (Lokke et al., 1996). Trees, and sometimes other plants, are used as the biological indicators in the case of critical loads for forests. The critical load calculation using the current methodology, is essentially an acidity/alkalinity mass balance calculation. The chemical criterion must be expressible in terms of alkalinity. Initially, the Ca/Al ratio was used; but, recently, the (Ca+Mg+K)/Al ratio has been used (Lokke et al., 1996).

Ideally, changes in acidic deposition should result in changes in the status of the biological indicator used in the critical load calculation. However, the biological indicator is the integrated response to a number of different stresses. Furthermore, there are other organisms more sensitive to acid deposition than trees. At high concentrations, Al^{+3} is known to be toxic to plants, inhibiting root growth and, ultimately, plant growth and performance (Lokke et al., 1996; National Science and Technology Council, 1998). Sensitivity to Al varies considerably between species and within species because of changes in nutritional demands and physiological status that are related to age and climate. Experiments have shown that there are large variations in Al sensitivity, even among ecotypes.

Mycorrhizal fungi as possible biological indicators have been suggested by Lokke et al. (1996) because they are intimately associated with tree roots, depend on plant assimilates, and play an essential role in plant nutrient uptake influencing the ability of their host plants to tolerate different anthropogenically generated stresses. Mycorrhizas and fine roots are an extremely dynamic component of below-ground ecosystems and can respond rapidly to stress. They have a relatively short life span, and their turnover appears to be strongly controlled by environmental factors. Changes in mycorrhizal species composition or the loss of dominant mycorrhizal species in areas where diversity is already low may lead to increased susceptibility of plant to stress (Lokke et al., 1996). Stress affects the total amount of carbon fixed by plants and modifies carbon allocation to biomass, symbionts, and secondary metabolites. The physiology of carbon allocation has also been suggested as an indicator of anthropogenic stress (Andersen and Rygiewicz, 1991). Because mycorrhizal fungi are dependent for their growth on the supply of assimilates from the host plants, stresses that shift the allocation of carbon reserves to the production of new leaves at the expense of supporting tissues will be reflected rapidly in decreased fine root and mycorrhizzal biomass (Winner and Atkinson, 1986). Decreased carbon allocation to roots also affects soil carbon and rhizosphere organisms. Soil dwelling animals are important for decomposition, soil aeration, and nutrient redistribution in the soil. They contribute to decomposition and nutrient availability mainly by increasing the accessibility of dead plant material to microorganisms. Earthworms decrease in abundance and in species number in acidified soils (Lokke et al., 1996).

Effects of Wet and Dry Deposition on Biogeochemical Cycling — The Integrated Forest Study. The Integrated Forest Study (IFS; Johnson and Lindberg, 1992a) has provided the most extensive data set available on wet and dry deposition and deposition effects on the cycling of elements in forest ecosystems. The overall patterns of deposition and cycling have been summarized by Johnson and Lindberg (1992a), and the reader is referred to that reference for details. The following is a summary of particulate deposition, total deposition, and leaching in the IFS sites.

Particulate deposition in the IFS was separated at the 2-μm level; a decision was made to include total particulate deposition in this analysis and may include the deposition of particles larger than 10 μm. Particulate deposition contributes considerably to the total impact of base cations to most of the IFS sites. On average, particulate deposition contributes 47% to total calcium deposition (range: 4 to 88%), 49% of total potassium deposition (range: 7 to 77%), 41% to total magnesium deposition (range: 20 to 88%), 36% to total sodium deposition (range: 11 to 63%), and 43% to total base cation deposition (range: 16 to 62%). Of total particulate deposition, the vast majority (> 90%) is > 2 μm.

Figures 4-20 through 4-23 summarize the deposition and leaching of calcium, magnesium, potassium, and total base cations for the IFS sites. As noted in the original synthesis (Johnson and Lindberg, 1992a), measurements indicated annual gains of base cations for some sites (i.e., total deposition > leaching), some losses (total deposition < leaching), and some are approximately in balance. Not all cations follow the same pattern at each site. For example, a net accumulation of calcium occurs at the Coweeta, TN, Durham (Duke), NC, and Florida sites (Figure 4-20), whereas accumulation of potassium was noted at the Duke, Florida, Thompson, WA, Huntington Forest, NY, and White Face Mountain, NY, sites (Figure 4-22). Magnesium accumulated only at the Florida sites (Figure 4-21), and only at the Florida site is there a clear net accumulation of total base cations (Figure 4-23).

As noted previously, the factors affecting net calcium accumulation or loss include the soil-exchangeable cation composition; base cation deposition rate; the total leaching pressure because of atmospheric sulfur and nitrogen inputs, as well as natural (carbonic and organic) acids; and biological demand (especially for potassium). At the Florida site, which has a very cation-poor, sandy soil (derived from marine sand), the combination of all these factors leads to net base cation accumulation from atmospheric deposition (Johnson and Lindberg, 1992a). The site showing the greatest net base cation losses, the red alder stand in Washington state, is one that is under extreme leaching pressure by nitrate produced because of excessive fixation by that species (Van Miegroet and Cole, 1984). In the red spruce site in the Smokies, the combined effects of SO_4^{-2} and NO_3^- leaching are even greater than in the red alder site (Figure 4-24), but a considerable proportion of the cations leached from this extremely acid soil consist of H^+ and Al^{+3} rather than of base cations (Johnson and Lindberg, 1992a). Thus, the red spruce site in the Smokies is approximately in balance with respect to calcium and total base cations, despite the very high leaching pressure at this site (Figures 4-20 and 4-23).

The relative importance of particulate-base-cation deposition varies widely with site and cation and is not always related to the total deposition rate. The proportion of calcium deposition in particulate form ranges from a low of 4% at the Whiteface Mountain site to a high of 88% at the Maine site (Figure 4-20). The proportion of potassium deposition as particles

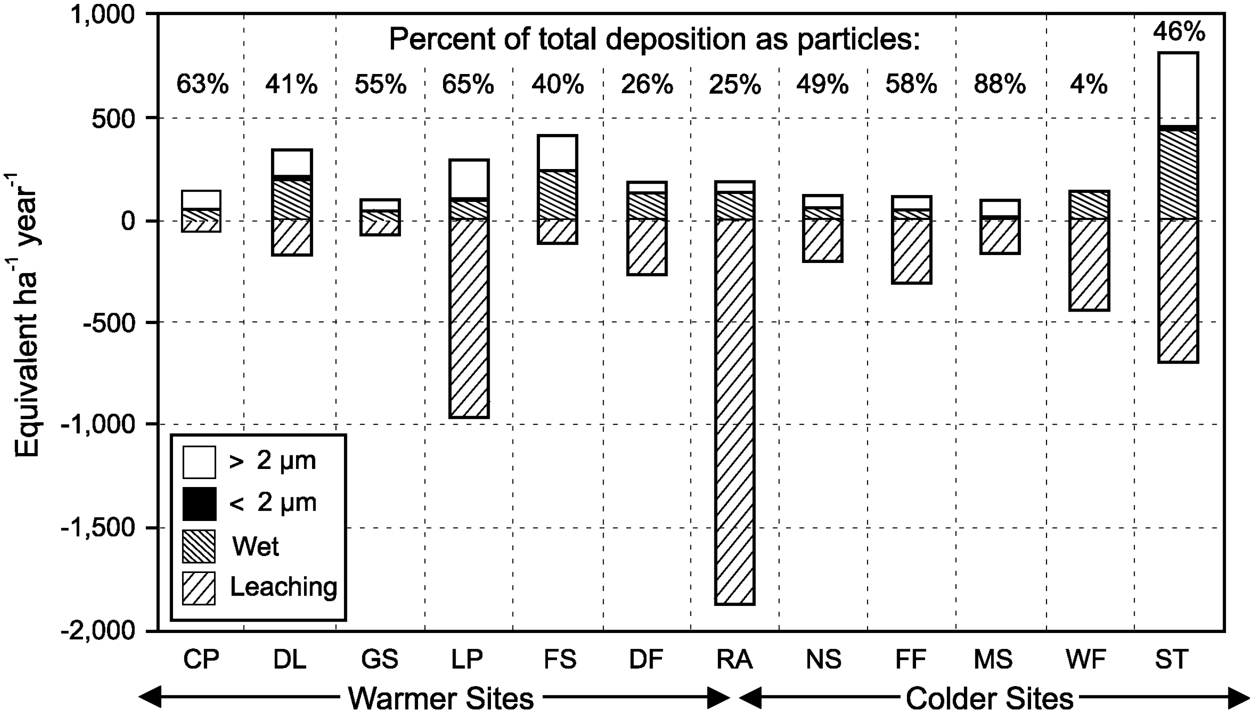


Figure 4-20. Calcium deposition in > 2-µm particles, < 2-µm particles, and wet forms (upper bars) and leaching (lower bars) in the Integrated Forest Study sites. CP = *Pinus strobus*, Coweeta, TN; DL = *Pinus taeda*, Durham (Duke), NC; GS = *Pinus taeda*, B. F. Grant Forest, GA; LP = *Pinus taeda*, Oak Ridge, TN; FS = *Pinus eliottii*, Bradford Forest, FL; DF = *Psuedotsuga menziesii*, Thompson, WA; RA = *Alnus rubra*; Thompson WA; NS = *Picea abies*, Nordmoen, Norway; HF = northern hardwood, Huntington Forest, NY; MS = *Picea rubens*, Howland, ME; WF = *Picea rubens*, Whiteface Mountain, NY; and ST = *Picea rubens*, Clingman's Dome, NC.

ranges from 7% at the Smokies site to 77% at the Coweeta site (Figure 4-22), and the proportion of total base cation deposition ranges from 16% at the Whiteface site to 62% at the Maine site (Figure 4-23). Overall, particulate deposition at the site in Maine accounted for the greatest proportion of calcium, magnesium, potassium, and base cation deposition (88, 88, 57, and 62%, respectively) even though total deposition was relatively low. At some sites, the relative importance of particulate deposition varies considerably by cation. At the Whiteface Mountain site, particulate deposition accounts for 4, 20, and 40% of calcium, magnesium, and potassium

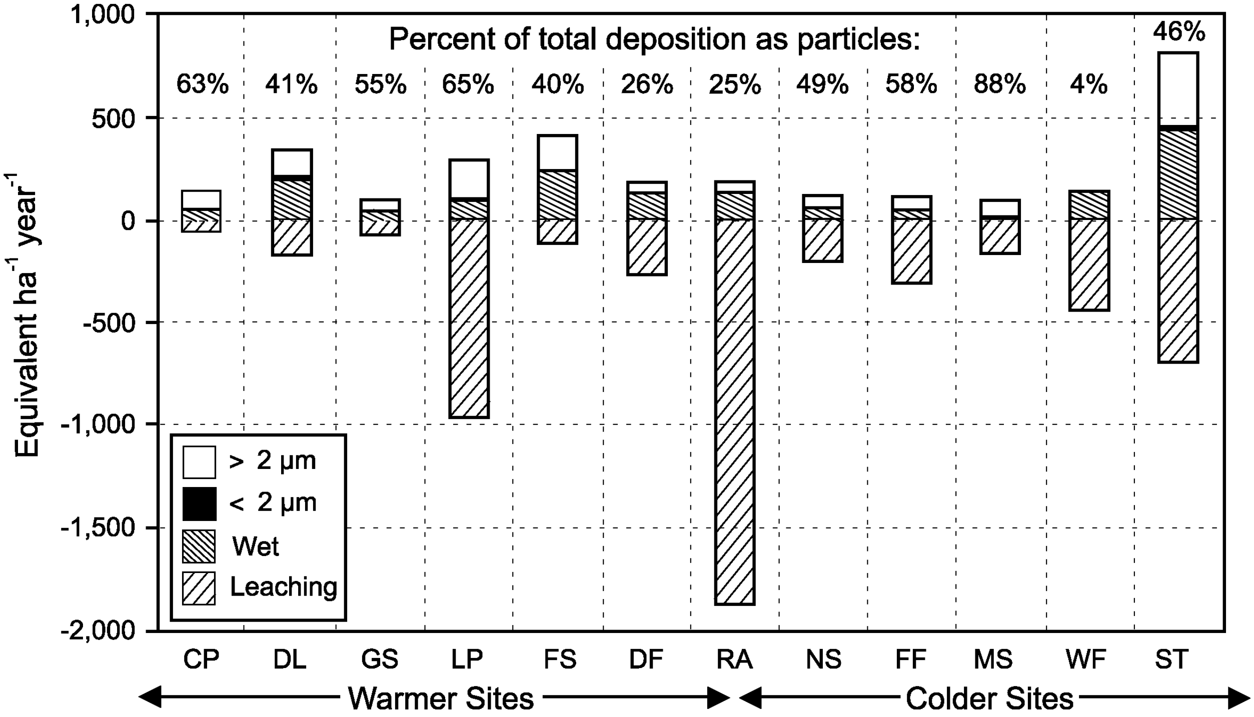


Figure 4-21. Magnesium deposition in > 2-µm particles, < 2-µm particles, and wet forms (upper bars) and leaching (lower bars) in the Integrated Forest Study sites. See Figure 4-20 for site abbreviations.

deposition, respectively. At the red spruce site in the Smokies, particulate deposition accounts for 46, 26%, 7% of calcium, magnesium, and potassium deposition, respectively.

As indicated in the IFS synthesis, SO_4^{-2} and NO_3^- leaching often are dominated by atmospheric sulfur and nitrogen (Johnson and Lindberg, 1992a). The exceptions to this are in cases where natural nitrogen inputs are high (i.e.,the nitrogen-fixing red alder stand), as are NO_3^- leaching rates even though nitrogen deposition is low, and where soils adsorb much of the atmospherically deposited SO_4^{-2} thus reducing SO_4^{-2} leaching compared to atmospheric sulfur input.

Sulfate and NO_3^- leaching have a major effect on cation leaching in many of the IFS sites (Johnson and Lindberg, 1992a). Figure 4-24 shows the total cation leaching rates of the IFS sites and the degree to which cation leaching is balanced by SO_4^{-2} + NO_3^- deposition. The SO_4^{-2} and NO_3^- fluxes are subdivided further into that proportion potentially derived from particulate sulfur

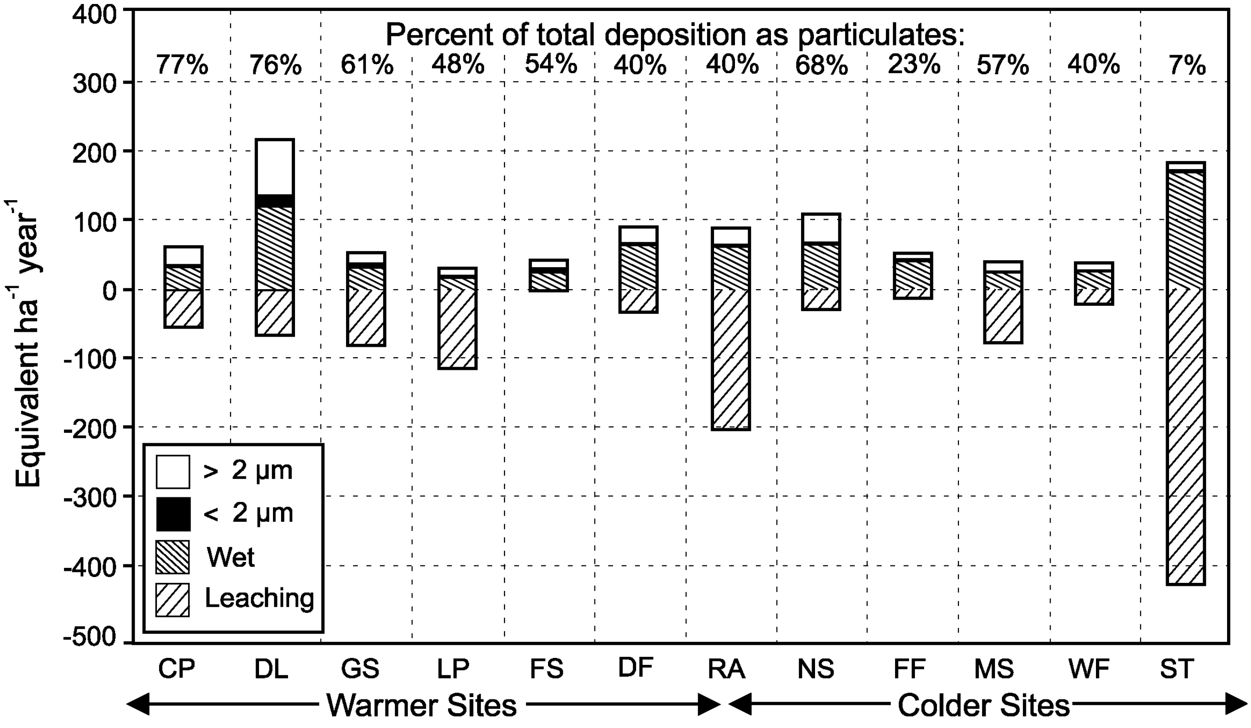


Figure 4-22. Potassium deposition in > 2-µm particles, < 2-µm particles, and wet forms (upper bars) and leaching (lower bars) in the Integrated Forest Study sites. See Figure 4-20 for site abbreviations.

and nitrogen deposition (assuming no ecosystem retention, a maximum effect) and other sulfur and nitrogen sources (wet and gaseous deposition, internal production).

As noted in the IFS synthesis, total SO_4^{-2} and NO_3^- inputs account for a large proportion (28 to 88%) of total cation leaching in most sites. The exception is the Georgia loblolly pine site where there were high rates of HCO_3^- and Cl^- leaching (Johnson and Lindberg, 1992a). The role of particulate sulfur and nitrogen deposition in this leaching is generally very small (< 10%), however, even if it is assumed that there is no ecosystem sulfur or nitrogen retention.

It was noted previously in this chapter that the contribution of particles to total deposition of nitrogen and sulfur at the IFS sites is lower than that for base cations. On average, particulate deposition contributes 18% to total nitrogen deposition (range: 1 to 33%) and 17% to total sulfur deposition (range: 1 to 30%). Particulate deposition contributes only a small amount to total H^+ deposition (average = 1%; range: 0 to 2%). (It should be noted, however, that particulate H^+ deposition in the > 2 µm fraction was neglected.)

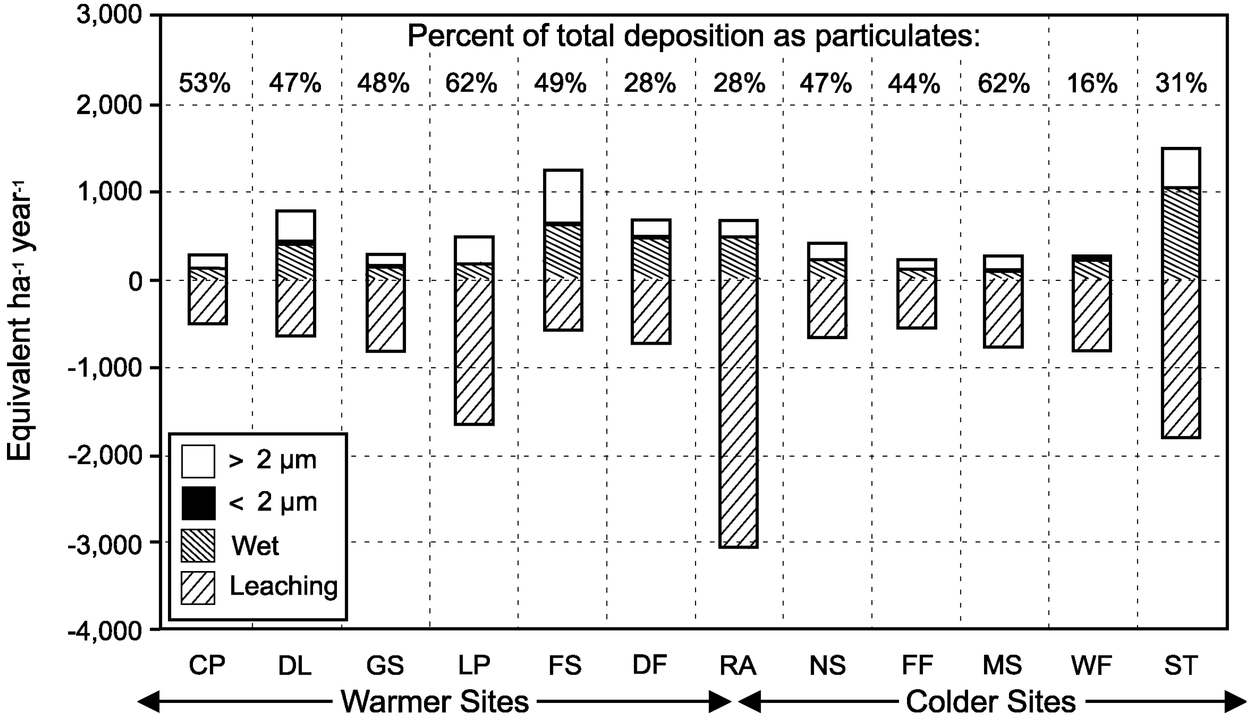


Figure 4-23. Base cation deposition in > 2-µm particles, < 2-µm particles, and wet forms (upper bars) and leaching (lower bars) in the Integrated Forest Study sites. See Figure 4-20 for site abbreviation.

Based on the IFS data, it appears that the particulate deposition has a greater effect on base cation inputs to soils than on base cation losses associated with inputs of sulfur, nitrogen, and H^+. It cannot be determined what fraction of the mass of these particles are < 10 µm, but only a very small fraction is < 2 µm. These inputs of base cations have considerable significance, not only to the base cation status of these ecosystems, but also to the potential of incoming precipitation to acidify or alkalize the soils in these ecosystems. As noted above, the potential of precipitation to acidify or alkalize soils depends on the ratio of base cations to H^+ in deposition, rather than simply on the inputs of H^+ alone. In the case of calcium, the term "lime potential" has been applied to describe this ratio; the principle is the same with respect to magnesium and potassium. Sodium is a rather special case, in that it is a poorly absorbing cation and leaching tends to balance input over a relatively short term.

Net balances of base cations tell only part of the story as to potential effects on soils; these net losses or gains must be placed in the perspective of the soil pool size. One way to express

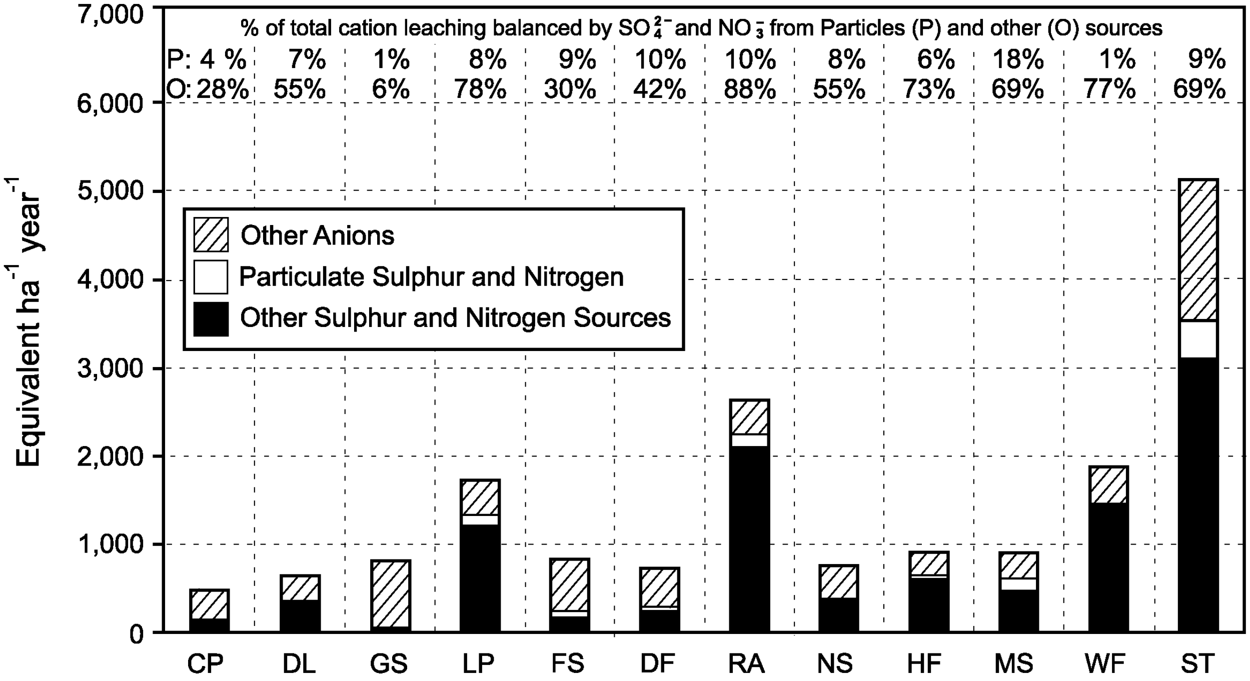


Figure 4-24. Total cation leaching (total height of bar) balanced by sulfate and nitrate estimated from particulate deposition (assuming no ecosystem retention, particulate sulfur and nitrogen) and by other sources (both deposition and internal) of sulfate and nitrate (other sulfur and nitrogen sources) and by other anions in the Integrated Forest Study sites. See Figure 4-20 for site abbreviations.

this perspective is to simply compare soil pool sizes with the net balances. This comparison is made for exchangeable pools and net balances for a 25-year period in Figures 4-25 to 4-27. It readily is seen that net leaching losses of cations pose no threat in terms of depleting soil-exchangeable Ca^{+2}, K^+, or Mg^{+2} within 25 years at the Coweeta, Duke, Georgia, Oak Ridge, or Douglas-fir sites. However, there is a potential for significant depletion at the red alder, Whiteface Mountain (magnesium), and Smokies red spruce sites.

The range of values for soil-exchangeable turnover is very large, reflecting variations in both the size of the exchangeable pool and the net balance of the system. Soils with the highest turnover rates are those most likely to experience changes in the shortest time interval, other things being equal. Thus, the Whiteface Mountains, Smokies, and Maine red spruce sites; the Thompson red alder site; and the Huntington Forest northern hardwood site appear to be most

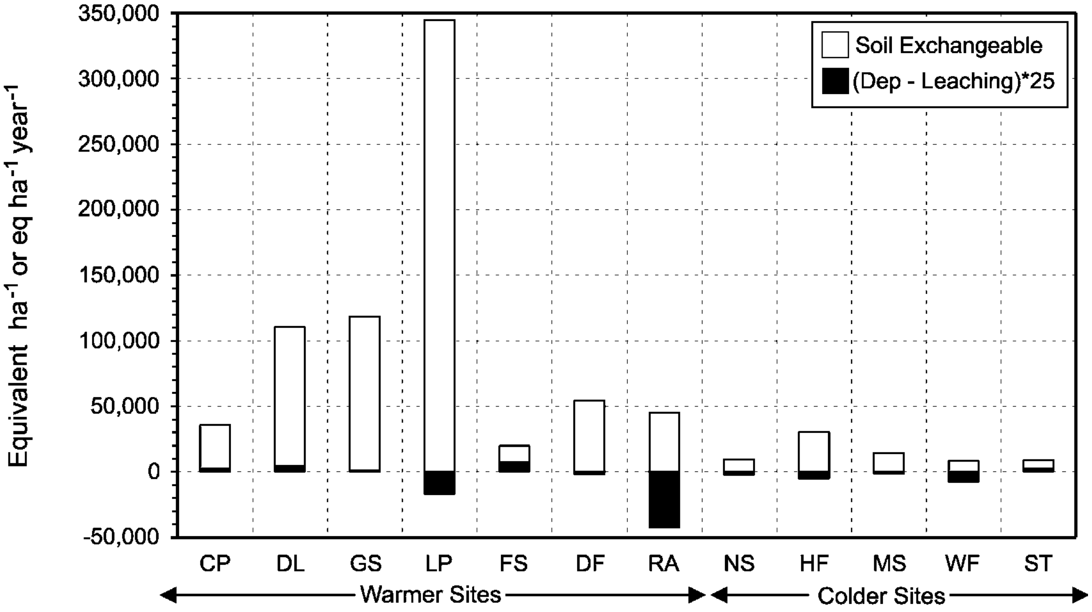


Figure 4-25. Soil exchangeable Ca^{+2} pools and net annual export of Ca^{+2} (deposition minus leaching times 25 years) in the Integrated Forest Study sites. See Figure 4-20 for site abbreviations.

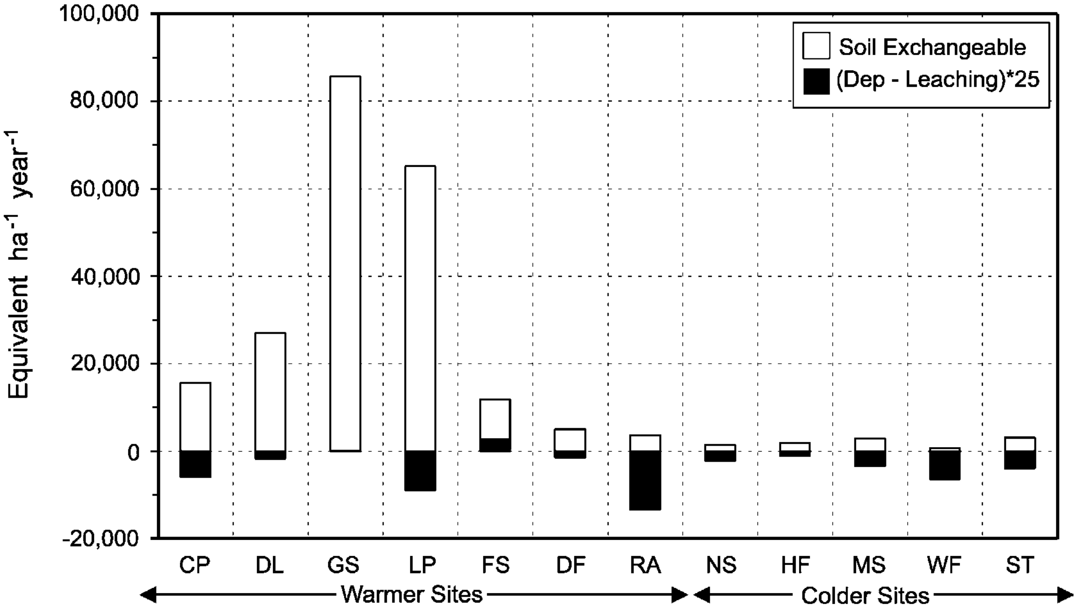


Figure 4-26. Soil exchangeable Mg^{+2} pools and net annual export of Mg^{+2} (deposition minus leaching times 25 years) in the Integrated Forest Study sites. See Figure 4-20 for site abbreviations.

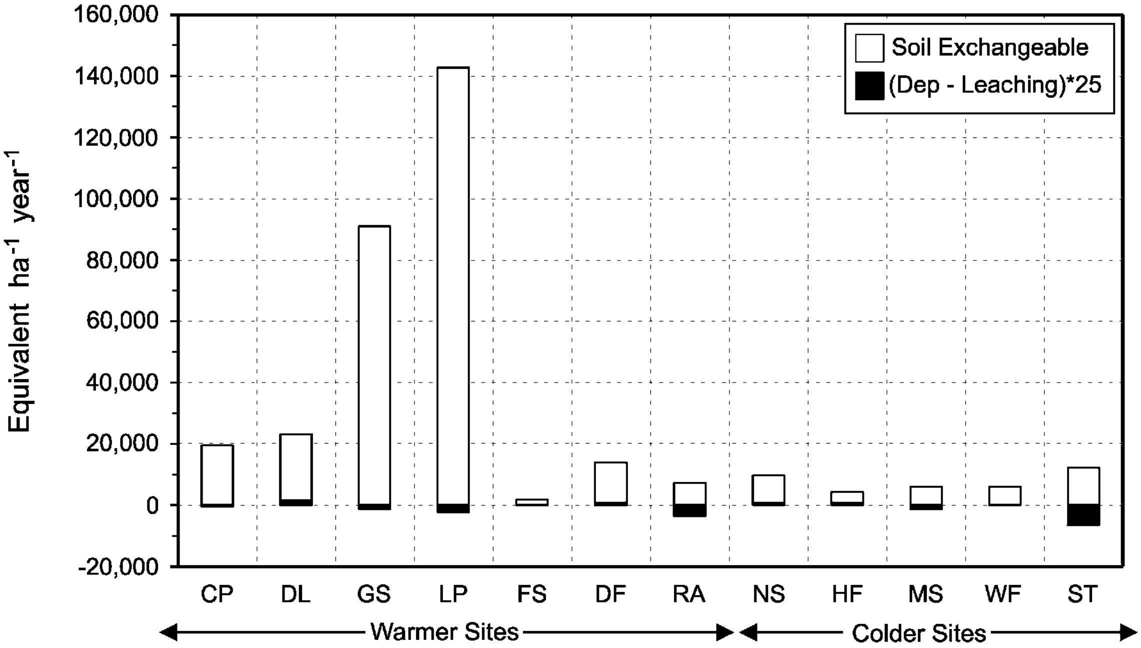


Figure 4-27. Soil exchangeable K^{2+} pools and net annual export of K^{2+} (deposition minus leaching times 25 years) in the Integrated Forest Study sites. See Figure 4-20 for site abbreviations.

sensitive to change. The actual rates, directions, and magnitudes of changes that may occur in these soils (if any) will depend on weathering inputs and vegetation outputs, in addition to deposition and leaching. It is noteworthy that each of the sites listed above as sensitive has a large store of weatherable minerals; whereas many of the other soils, with larger exchangeable cation reserves, have a small store of weatherable minerals (e.g., Coweeta white pine, Duke loblolly pine, Georgia loblolly pine, and Oak Ridge loblolly pine; Johnson and Lindberg, 1992a; April and Newton, 1992).

Base cation inputs are especially important to the Smokies red spruce site because of potential aluminum toxicity and calcium and magnesium deficiencies. Johnson et al. (1991a) found that soil- solution aluminum concentrations occasionally reached levels found to inhibit calcium uptake and cause changes in root morphology in solution culture studies of red spruce (Raynal et al., 1990). In a follow-up study, Van Miegroet et al. (1993) found a slight but significant growth response to calcium and magnesium fertilizer in red spruce saplings near the Smokies red spruce site. Joslin et al. (1992) reviewed soil and solution characteristics of red spruce in the southern Appalachians, and it appears that the IFS site is rather typical.

Wesselink et al. (1995) reported on the complicated interactions among changing deposition and soils at this site (including repeated sampling of soil exchangeable base cation pools) from 1969 to 1991 and compared these results with those of a simulation model. They identified three basic stages of change in this ecosystem. During Stage 1, there was increased deposition of sulfur and constant deposition of base cations, causing increased base cation leaching and reduced base saturation in the soils. During Stage II, sulfur deposition is reduced; soil solution sulfate and base cation leaching decline accordingly, but base saturation continues to decrease. During Stage III, two alternative scenarios are introduced: (a) sulfur deposition continues to decline, whereas base cation deposition says constant; or (b) both sulfur and base cation deposition decline. Under Stage III-a, sulfate and base cation leaching continue to decline, and base saturation begins to increase as base cations displace exchangeable aluminum and cause it to transfer to the gibbsite pool. Under Stage III-b, this recovery in base saturation is over-ridden by the reduction in base cation deposition.

The IFS project, for the first time, accurately quantified atmospheric deposition inputs to nutrient cycles using state-of-the-art techniques to measure wet and dry deposition. The principal aim of the project was to determine the effects of atmospheric deposition on the nutrient status of a variety of forest ecosystems and to determine if these effects are in any way related to current or potential forest decline. Acidic deposition is having a significant effect on nutrient cycling in most of the forest ecosystems studied in the IFS project. The exceptions were the relatively unpolluted Douglas fir, red alder, and Findley Lakes in Washington state. The nature of the effects, however, varies from one location to another (Johnson,1992). In all but the relatively unpolluted Washington sites, atmospheric deposition was having a significant, often overwhelming effect on cation leaching from the soils. In general, nutrient budget data from IFS and the literature suggest that the susceptibility of southeastern sites to base-cation-depletion from soils and the development of cation deficiencies by that mechanism appears to be greater than in northern sites (Johnson, 1992).

Atmospheric deposition may have affected significantly the nutrient status of some IFS sites through the mobilization of Al. Soil-solution Al levels in the Smokies sites approach and sometimes exceed levels noted to impede cation uptake in solution culture studies. It is therefore possible that the rates of base cation uptake and cycling in these sites have been reduced because of soil solution Al. To the extent that atmospheric deposition has contributed to these elevated soil-solution Al levels, it has likely caused a reduction in base cation uptake and cycling rates at these sites. Nitrate and sulfate are the dominant anions in the Smokies sites, and nitrate pulses are the major cause of Al pulses in soil solution (Johnson, 1992). The connection between Al mobilization and forest decline is not clear. The decline in red spruce certainly has been more severe in the Northeast than in the Southeast, yet all evidence indicates that Al mobilization is most pronounced in the southern Appalachians. However, at the Whiteface Mountain site selected for study because it was in a state of decline, and soil solution levels were lower than in the Smokies, which are not in a visibly obvious state of decline (there was no dieback other than the fir killed by the balsam wooly adelgid, no needle yellowing). Thus, Al mobilization constitutes a situation worthy of further study (Johnson, 1992).

The simple calculations shown above give some idea of the importance of particulate deposition in these forest ecosystems, but they cannot account for the numerous potential feedbacks between vegetation and soils nor for the dynamics through time that can influence the ultimate response. One way to examine some of these interactions and dynamics is to use simulation modeling. The nutrient cycling model (NuCM) has been developed specifically for this purpose and has been used to explore the effects of atmospheric deposition, fertilization, and harvesting on some of the IFS sites (Johnson et al., 1993). The NuCM model is a stand-level model that incorporates all major nutrient cycling processes (uptake, translocation, leaching, weathering, organic matter decay, and accumulation).

Johnson et al. (1999) used the NuCM model to simulate the effects of reduced S, N, and base cation (C_B) deposition on nutrient pools, fluxes, soil, and soil solution chemistry in two contrasting southern Appalachian forest ecosystems: the red spruce and Coweeta hardwood sites from the IFS project. The scenarios chosen for these simulations included "no change"; 50% N and S deposition; 50% C_B deposition; and 50% N, S, and C_B deposition (50% N, S, C_B). The NuCM simulations suggested that, for the extremely acid red spruce site, S and N deposition is the major factor affecting soil-solution Al concentrations and C_B deposition is the major factor affecting soil solution C_B concentrations. The effects of S and N deposition were largely through changes in soil solution SO_4^{-2} and NO_3^- and, consequently, mineral acid anion (MAA) concentrations rather than through changes in soils. This is illustrated in Figures 4-28a,b and 4-29a,b, which show simulated soil-solution mineral-acid anions, base cations, Al, and soil base saturation in B horizon from in the red spruce site. The 50% S and N scenario caused reductions

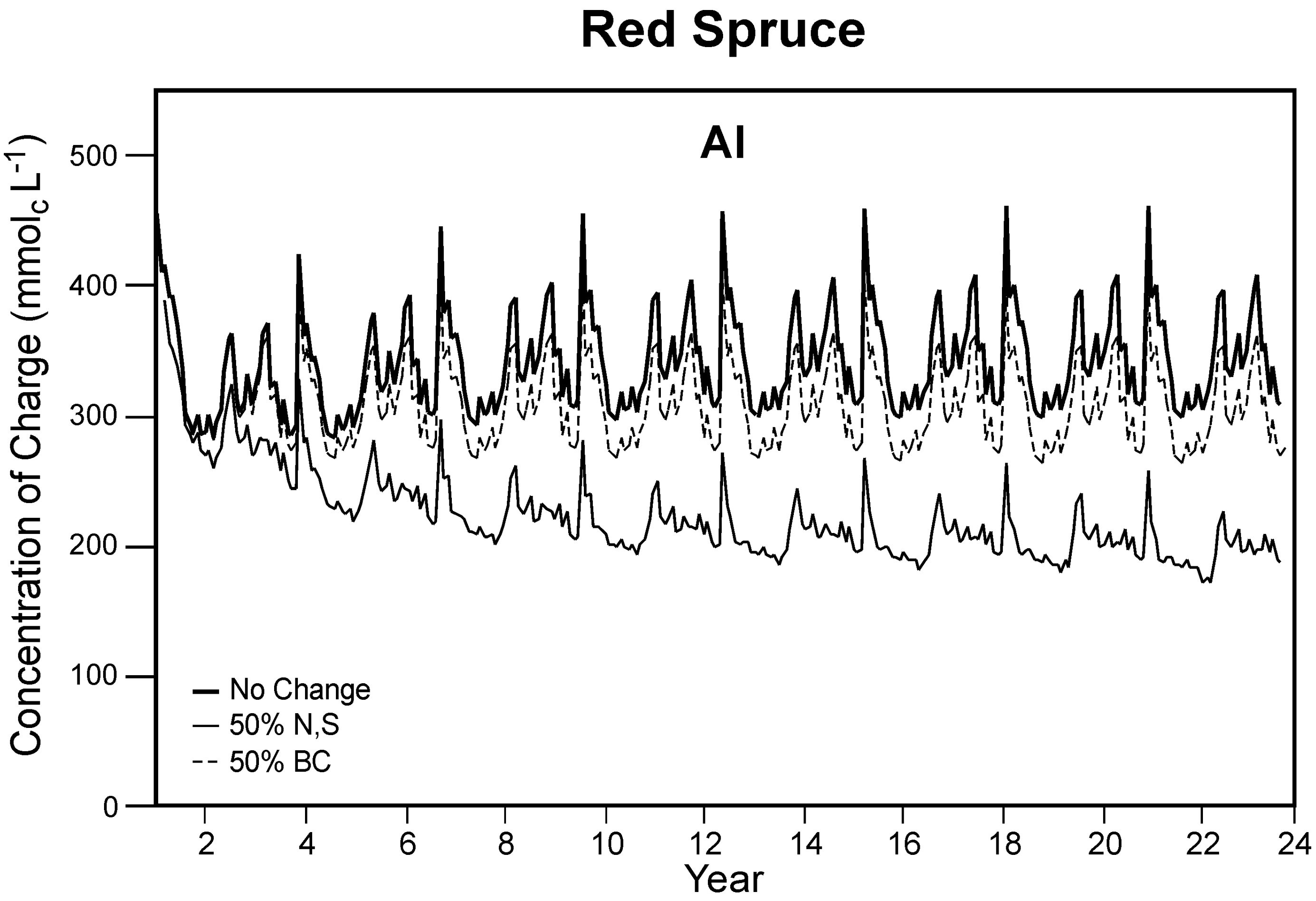


Figure 4-28a. Simulated soil solution mineral acid anions and base cations in the red spruce site with no change, 50% N and S deposition, and 50% base cation deposition. Redrawn from Johnson et al. (1999).

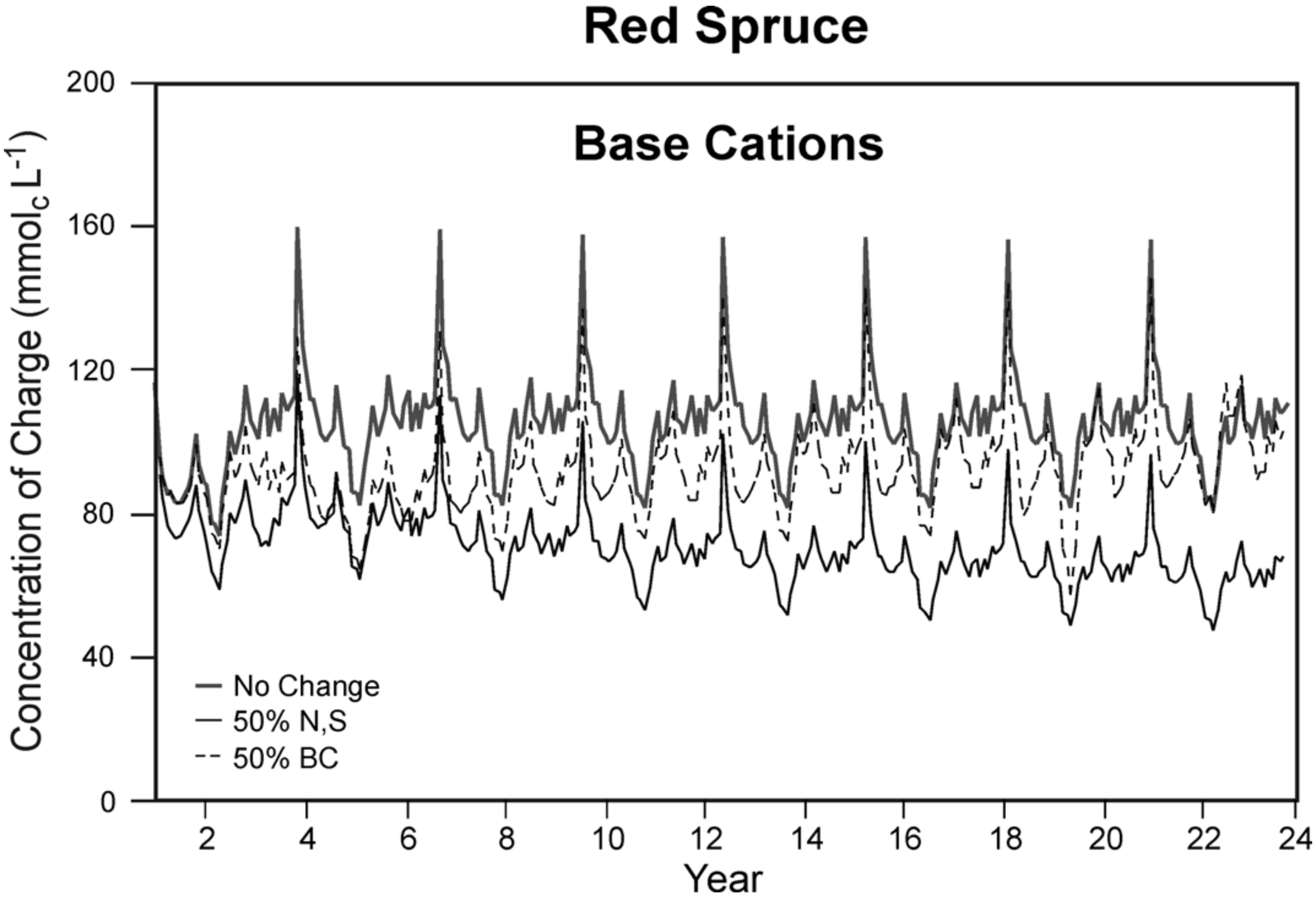


Figure 4-28b. Simulated soil solution mineral acid anions and base cations in the red spruce site with no change, 50% N and S deposition, and 50% base cation deposition. Redrawn from Johnson et al. (1999).

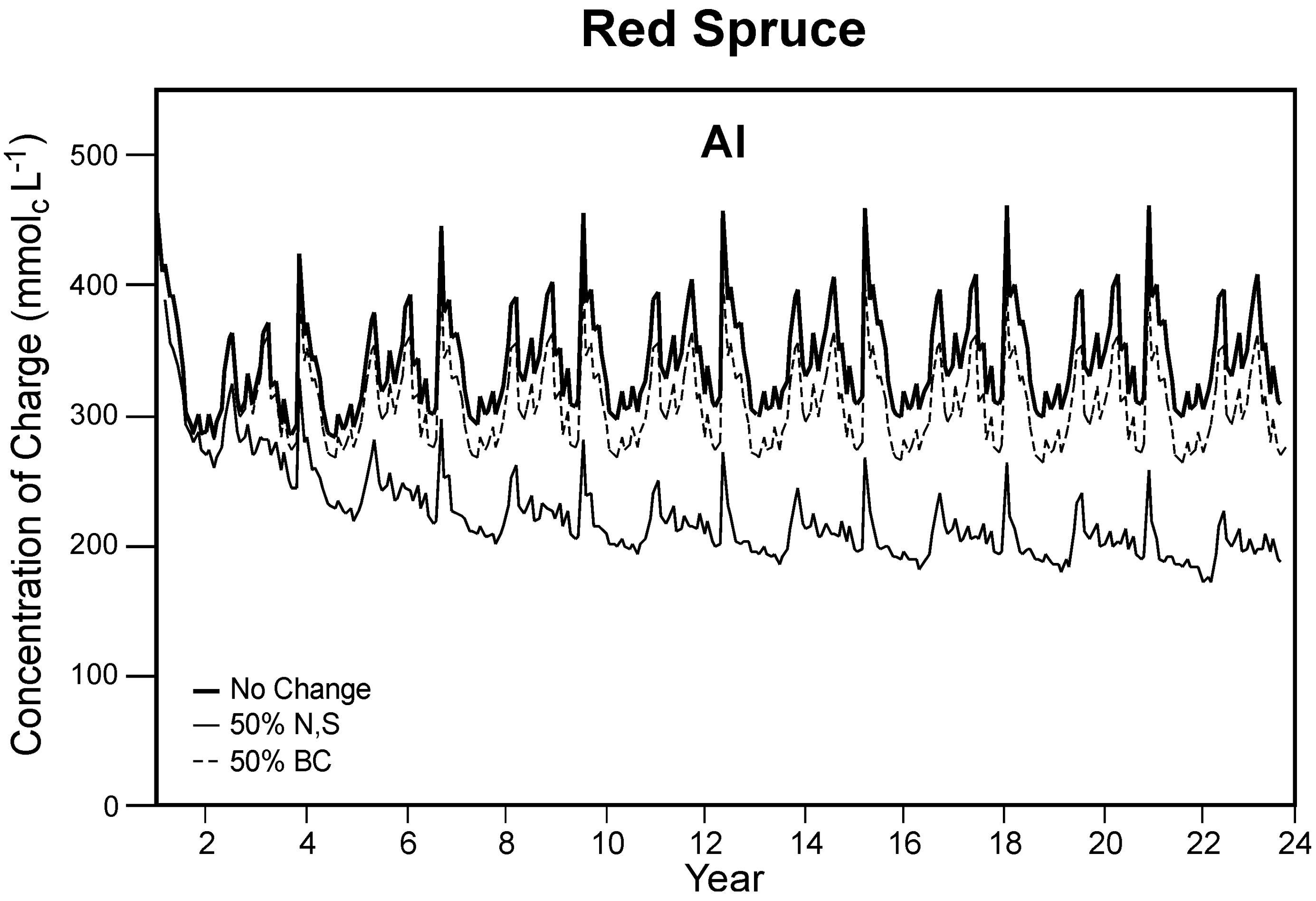


Figure 4-29a. **Simulated soil solution A1 and soil base saturation in the red spruce site with no change, 50% N and S deposition, and 50% base cation deposition. Redrawn from Johnson et al. (1999).**

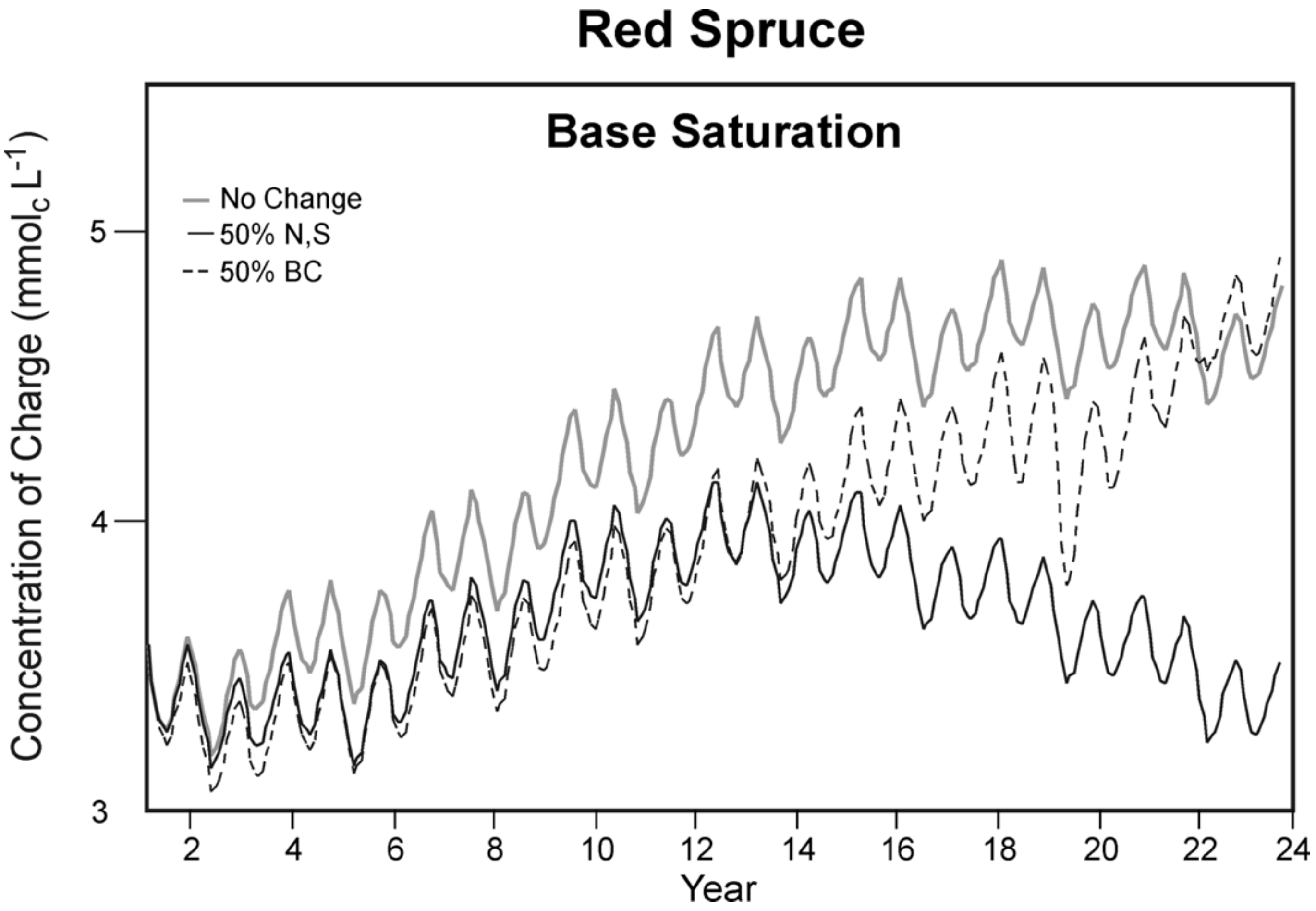


Figure 4-29b. Simulated soil solution A1 and soil base saturation in the red spruce site with no change, 50% N and S deposition, and 50% base cation deposition. Redrawn from Johnson et al. (1999).

in soil solution SO_4^{-2}, NO_3^- and, therefore, MAA concentrations, as expected. This, in turn, caused short-term reductions in base cation concentrations. However, by the end of the 24-year simulation, base cations in the 50% S, N scenario were nearly as high as in the no change scenario because base saturation had increased and the proportion of cations as Al decreased. The 50% C_B scenario had virtually no effect on soil solution SO_4^{-2}, NO_3^- and, therefore, MAA concentrations, as expected, but did cause a long-term reduction in base cation concentrations. This was caused by a long-term reduction in base saturation (Figure 4-29a,b). Thus, the effects of C_B deposition were solely through changes in soils rather than through changes in soil solution MAA, as postulated by Driscoll et al. (1989). In the less acidic Coweeta soil, base saturation was high and little affected by the scenario (cited above); Al was unimportant; and S and N deposition had a much greater effect than C_B deposition in all respects (Figure 4-30a,b).

In summary, Johnson et al. (1999) found that the results of the red spruce simulations support the hypothesis of Driscoll et al. (1989) in part: C_B deposition can have a major effect on C_B leaching through time in an extremely acid system. This effect occurred through changes in the soil exchanger and not through changes in soil solution MAA concentration. On the other hand, S and N deposition had a major effect on Al leaching at the Noland Divide site. This occurred primarily because of changes in soil solution MAA concentration. At the less acidic Coweeta site, C_B deposition had a minor effect on soils and soil solutions; whereas S and N deposition had delayed but major effects on C_B leaching because of changes in SO_4^{-2} and MAA concentrations.

Effects of Trace Elements

Trace metals are natural elements that are ubiquitous in small (trace) amounts in soils, ground water, and vegetation. Many are essential elements required for growth by plants and animals as micronutrients. Naturally occurring surface mineralizations can produce metal concentrations in soils and vegetation that are as high, or higher, than those in the air and deposited near man-made sources (Freedman and Hutchinson, 1981). The occurrence and concentration of trace metals in any ecosystem component depend on the sources of the metal (i.e., via the soil or as a particulate). Even when air pollution is the primary source, continued deposition can result in the accumulation of trace metals in the soil (Martin and Coughtrey,

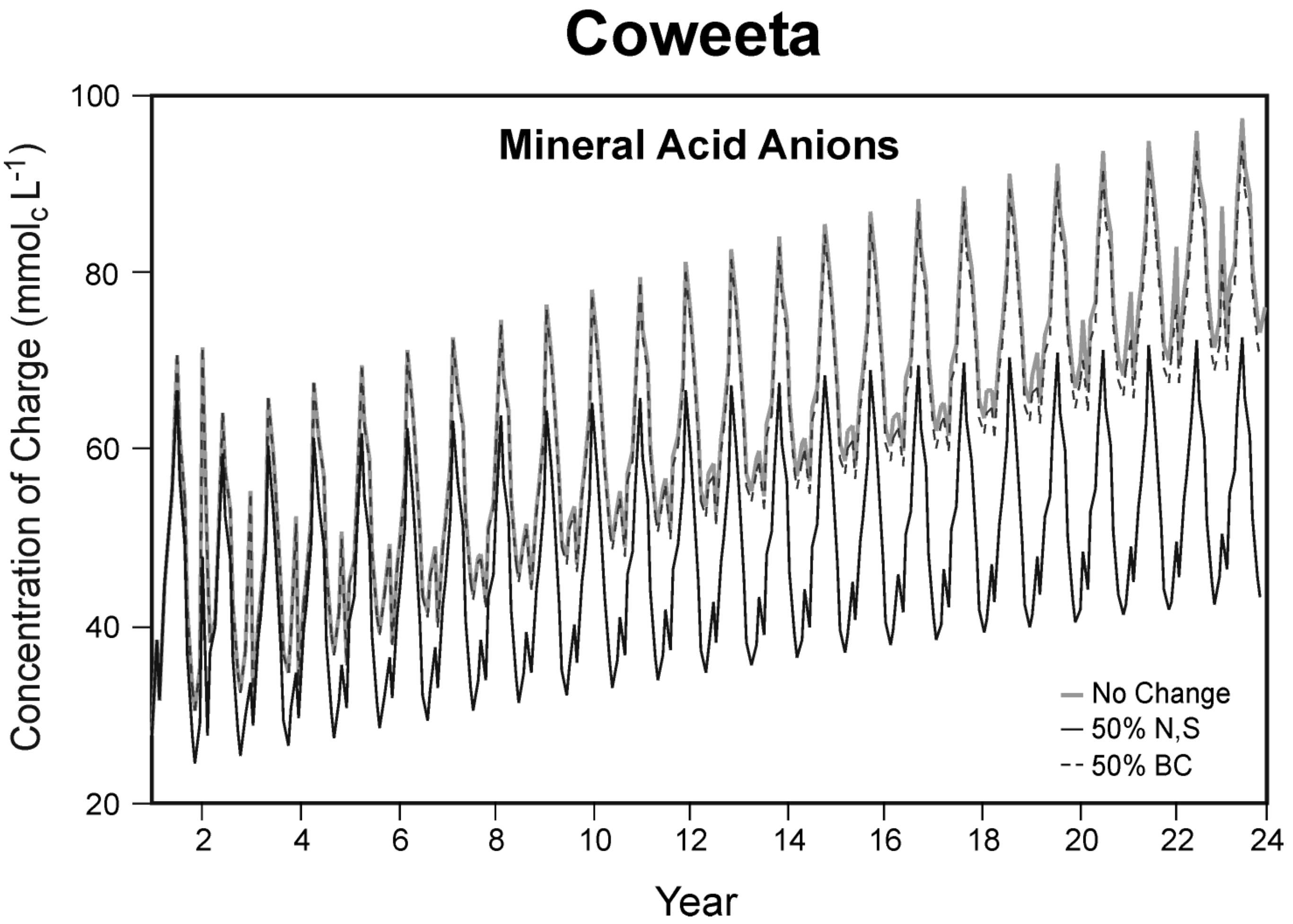


Figure 4-30a. Simulated soil solution mineral acid anions and base cations in the Coweeta site with no change, 50% N and S deposition, and 50% base cation deposition. Redrawn from Johnson et al. (1999).

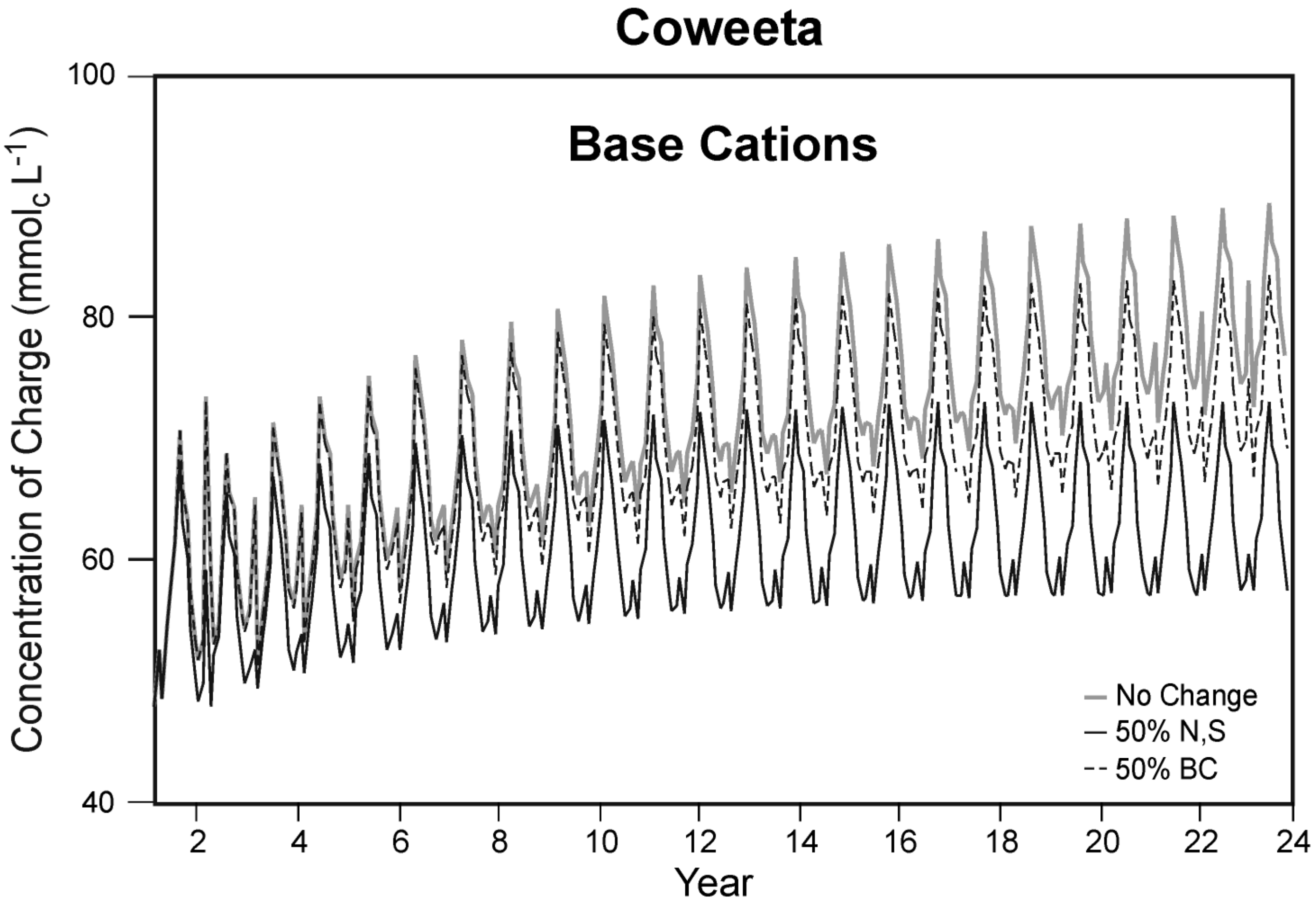


Figure 4-30b. **Simulated soil solution mineral acid anions and base cations in the Coweeta site with no change, 50% N and S deposition, and 50% base cation deposition. Redrawn from Johnson et al. (1999).**

1981). Many metals are deposited into soils by chemical processes and are not available to plants (Saunders and Godzik, 1986).

When aerial deposition is the primary source of metal particles, both the chemical form and particle size deposited determine the heavy metal concentration in the various ecosystem components (Martin and Coughtrey, 1981). Human activities introduce heavy metals into the atmosphere and have resulted in the deposition of antimony, cadmium, chromium, copper, lead, molybdenum, nickel, silver, tin, vanadium, and zinc (Smith, 1990c). Extensive evidence indicates that heavy metals deposited from the atmosphere to forests accumulate either in the richly organic forest floor or in the soil layers immediately below, areas where the activity in roots and soil is greatest. The greater the depth of soil, the lower the metal concentration. The accumulation of metal in the soil layers where the biological activity is greatest, therefore, has the potential to be toxic to roots and soil organisms and to interfere with nutrient cycling (Smith, 1990c). The shallow-rooted plant species are those most likely to take up metals from the soil (Martin and Coughtrey, 1981). Though all metals can be directly toxic at high levels, only toxicity from copper, nickel, and zinc have been documented frequently. Toxicity of cadmium, cobalt, and lead has been seen only under unusual conditions (Smith, 1990c). Exposures at lower concentrations have the potential, over the long-term, to interfere with the nutrient-cycling processes when they affect mycorrhizal function.

Biological accumulation of metals through the plant-herbivore and litter-detrivore chains can occur. A study of the accumulation of cadmium, lead, and zinc concentrations in earthworms suggested that cadmium and zinc were concentrated, but not lead. Studies indicate that heavy metal deposition onto the soil, via food chain accumulation, can cause excessive levels and toxic effects in certain animals. Cadmium appears to be relatively mobile within terrestrial food chains; however, the subsequent mobility of any metal after it is ingested by a herbivorous animal depends on the site of accumulation within body tissues. Although food chain accumulation may not in itself cause death, it can reduce the breeding potential in a population (Martin and Coughtrey, 1981).

In actual case studies, it was observed that the deposition of copper and zinc particles around a brassworks resulted in an accumulation of incompletely decomposed litter. In one study, litter accumulation was reported up to 7.4 km from the stack of a primary smelter in southeastern Missouri. Similar results were reported around a metal smelter at Avonmouth, England. In the latter case, litter accumulation was associated closely with concentrations specifically of cadmium, as well as with those of lead, copper, and zinc (Martin and Coughtrey, 1981). Experimental data (using mesh bags containing litter) supports the hypothesis that reduced decomposition occurs close to heavy metal sources.

Accumulations of metals emitted in particulate matter also were reported in soil litter close to a metal smelter at Palmerton, PA, in 1975 and 1978. The continued presence of cadmium, lead, zinc, and copper in the upper soil horizons (layers) were observed 6 years after the smelter terminated operation in 1980. Metal levels were highest near the smelter. The relationship of decreasing amounts of metal in body tissues also held true for amphibians and mammals. Levels of cadmium in kidneys and liver of white-tailed deer (*Odocoileus virginaus*) were five times higher at Palmerton than in those collected 180 km southwest downwind. The abnormal amounts of metal in the tissues of terrestrial vertebrates and the absence or low abundance of wildlife at Palmerton indicated that ecological processes within 5 km of the zinc smelter continued to be markedly influenced even 6 years after its closing (Storm et al., 1994).

Accumulation of heavy metals in litter presents the greatest potential for interference with nutrient cycling. Microorganisms are essential for decomposition of organic matter and soil fertility. Toxic effects on the microflora can be caused by Zn, CD, and Cu. Addition of a few mg/kg of soil of Zn can inhibit the more sensitive microbial processes (van Beelen and Doelman, 1997). Experiments by Kandeler et al. (1996) indicated that microbial biomass and enzyme activities decreased with increasing heavy metal concentrations. The amount of decrease varied among the enzymes with those involved in carbon cycling least affected, whereas the activities of the enzymes involved in the cycling of N, P and S, especially arylsulfatase and phosphatase were dramatically affected.

Accumulation of metals in the litter occurs chiefly around brass works and lead and zinc smelters. There is some evidence that invertebrates inhabiting soil litter do accumulate metals. Earthworms from roadsides were shown to contain elevated concentrations of cadmium, nickel, lead, and zinc; however, interference with earthworm activity was not cited (Martin and Coughtrey, 1981). It has been shown, however, that when soils are acidic, earthworm abundance decreases, and bioaccumulation of metals from soil may increase exponentially with decreasing pH (Lokke et al, 1996). Organisms that feed on earthworms living in soils with elevated levels of Cd, Ni, Pb, and Z for extended periods could accumulate lead and zinc to toxic levels (Martin and Coughtrey, 1981). Increased concentrations of heavy metals have been found in a variety of small mammals living in areas with elevated heavy metal concentrations in the soils.

Studies by Babich and Stotsky (1978) support the concept that increased accumulation of litter in metal-contaminated areas is due to the effects on the microorganismal populations. Cadmium toxicity to microbial populations was observed to decrease and prolong logarithmic rates of microbial population increase, to reduce microbial respiration and fungal spore formation and germination, to inhibit bacterial transformation, and to induce abnormal morphologies. Additionally, the effects of cadmium, copper, nickel, and zinc on the symbiotic activity of fungi, bacteria, and actinomycetes were reported by Smith (1991). The formation of mycorrhizae by *Glomus mosseae* with onions was reduced when zinc, copper, nickel, or cadmium was added to the soil. The relationship of the fungus with white clover, however, was not changed. It was suggested that the effect of heavy metals on vesicular-arbuscular mycorrhizal fungi will vary from host to host (Gildon and Tinker, 1983). Studies with ericoid plants indicated that, in addition to *Calluna vulgaris*, mycorrhizae also protect *Vaccinium macrocarpa* and *Rhodendron ponticum* from heavy metals (Bradley et al., 1981). Heavy metals tend to accumulate in the roots, and shoot toxicity is prevented.

The effects of sulfur deposition on litter decomposition in the vicinity of smelters also must be considered. Metal smelters emit SO_2 as well as heavy metals. Altered litter decomposition rates have been well documented near SO_2 sources (Prescott and Parkinson, 1985). The presence of sulfur in litter has been associated with reduced microbial activity (Bewley and Parkinson, 1984). Additionally, the effects on symbiotic activity of fungi, bacteria, and actinomycetes were reported by Smith (1990d).

The potential pathways of accumulation of trace metals in terrestrial ecosystems, as well as the possible consequences of trace metal deposition on ecosystem functions, is summarized in Figure 4-31. The generalized trophic levels found in an ecosystem and the various physiological and biological processes that could be affected by trace metals are shown in the figure. Reduction in physiological processes can affect productivity, fecundity, and mortality (Martin and Coughtrey, 1981). Therefore, any effects on structure and function of an ecosystem are likely to occur through the soil and litter (Tyler, 1972).

Certain species of plants are tolerant of metal-contaminated soils (e.g., soils from mining activities) (Antonovics et al., 1971). Certain species of plants also have been used as

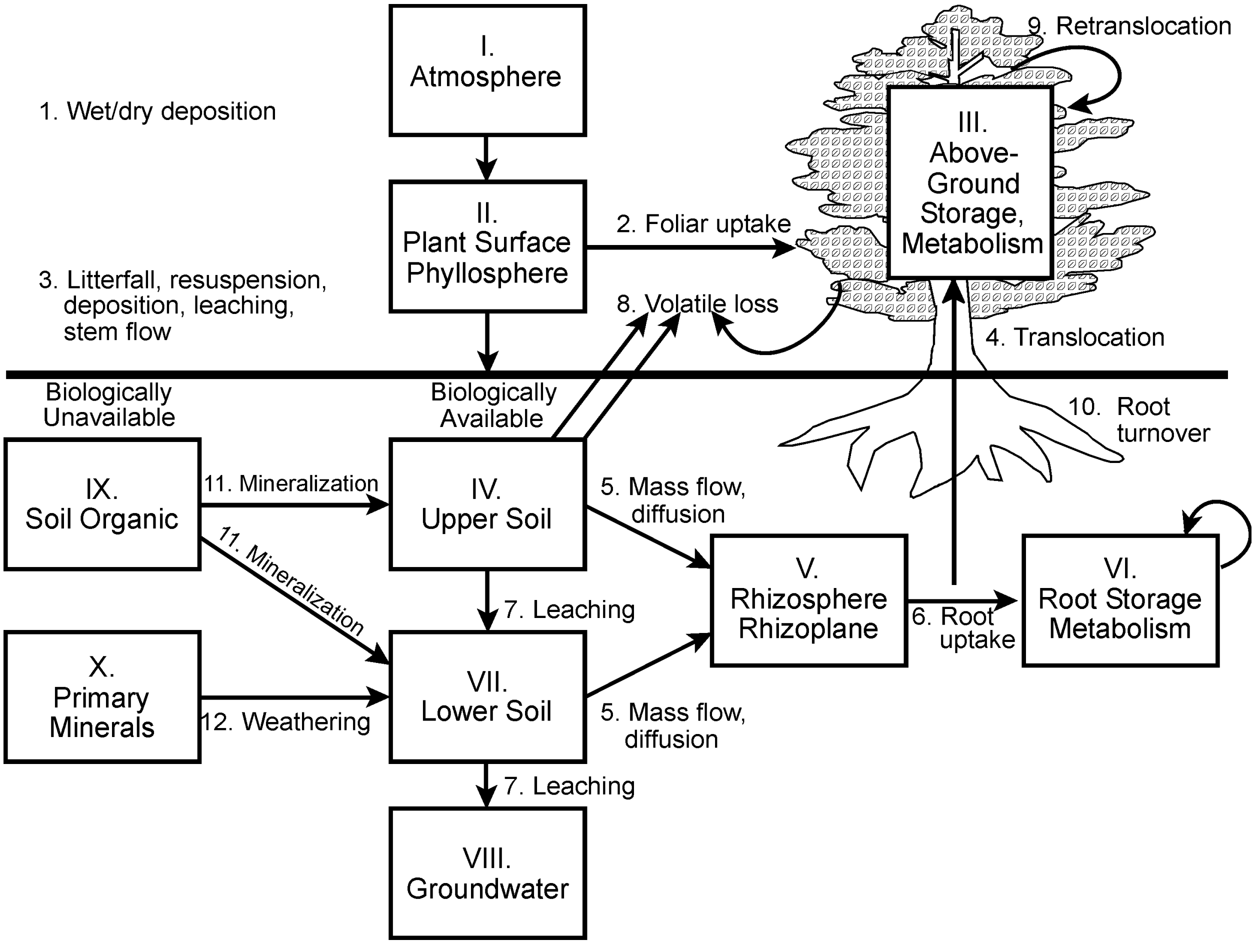


Figure 4-31. Relationship of plant nutrients and trace metals with vegetation. Compartments (roman numerals) represent potential storage sites; whereas arrows (arabic numerals) represent potential transfer routes.

bioindicators of metals (e.g., *Astragalus* is an accumulator of selenium). The sources of both macroelements and trace metals in the soil of the Botanical Garden of the town of Wroclow, Poland, were determined by measuring the concentrations of the metals in Rhododendron *catawbiense, Ilex aquifolium*, and *Mahonia aquifolium* growing in a garden and comparing the results with the same plant species growing in two botanical gardens in nonpolluted areas. Air pollution deposition was determined as the source of metals in plants rather than the soil (Samecka-Cymerman and Kempers, 1999).

The effects of lead in ecosystems are discussed in the EPA document *Air Quality Criteria for Lead* (U.S. Environmental Protection Agency, 1986). Studies have shown that there is cause for concern in three areas in which ecosystems may be extremely sensitive to lead: (1) delay of decomposition because the activity of some decomposer microorganisms and invertebrates is inhibited by lead, (2) subtle shifts toward plant populations tolerant of lead, and (3) lead in the soil and on the surfaces of vegetation which may circumvent the processes of biopurification. The problems cited above arise because lead is deposited on the surface of vegetation, accumulates in the soil, and is not removed by the surface and ground water of the ecosystem (U.S. Environmental Protection Agency, 1986).

4.2.4 Urban Ecosystems

Humans dominate Earth's ecosystems. Their influence on the environment has been pervasive for thousands of years. Evidence has been accumulating from anthropological and archeological research that human influence has been pervasive for thousands of years (Grimm et al., 2000). Major human effects on the environment probably began as early as 12,000 to 15,000 years ago and continue to be a major influence on all natural ecosystems. Nowhere has human action been more intense than in cities, suburbs, exurbs and in the supporting hinterlands (Grimm et al., 2000). This fact has lead to much recent interest in the study of urban ecological systems.

Vitousek et al. (1997) point out that understanding a human-dominated planet requires that the human dimensions of global change — the social, cultural, and other drivers of human actions — need to be included within ecological analyses. Therefore, humans must be integrated into models for a complete understanding of extant ecological systems. Development of more realistic models for ecological systems will lead to greater success in finding solutions to environmental problems.

In the past, ecological plant or animal studies conducted in urban settings used traditional ecological approaches and considered humans as agents of disturbance. Although the term urban ecosystem has been used to describe human-dominated ecosystems, it does not adequately take into account the developmental history, sphere of influence, and potential impacts required in order to understand the true nature of an urban ecosystem (McIntyre, et al., 2000). Because urbanization is both an ecological and a social phenomenon, urban ecology implicitly recognizes the role humans play in developing unique systems. Therefore, if urban ecology is to be a truly interdisciplinary field, it is crucial that it integrate both social and natural sciences into the study of urban ecosystems (McIntyre, et al., 2000).

Although the study of ecological phenomena in urban environments is not a new area of science, the concept of the city as an ecosystem is relatively new for the field of ecology (Grimm et al., 2000). There is a wealth of information on the terrestrial components of urban ecological systems. However, much of it is organized from the perspective of ecology *in* cities while the more comprehensive perspective identified as ecology *of* cities is needed (Pickett et al., 2001). The basic questions addressed by the literature of ecology *in* cities are how do ecological patterns and processes differ in cities as compared with other environments? What is the effect of the city (i.e., a concentration of human population and activities) on the ecology of organisms inside and outside of its boundary and influence? The concept of ecology *of* cities has to do with how aggregated parts make up the whole (i.e., how cities process energy or matter relative to their surroundings; Grimm et al., 2000). The latter concept includes primary production, species richness, biogeophysical budgets, ecosystem patterns and processes, and an open definition of urban ecosystems that incorporates the exchanges of materials and influence between cities and surrounding landscapes (Pickett et al., 2001). If ecosystems are to be understood, there is a need for a new integrative ecology that explicitly incorporates human decisions, culture, institutions, and economic systems (Grimm et al., 2000). This fact makes an ecological approach to land use planning not only necessary but essential to maintain long-term sustainability of ecosystem benefits, services, and resources (Zipperer et al., 2000). The ecological and social effects of "edge city" need to be studied as they may be greater than the previous patterns of suburbanization. The classical ecosystem approach and a patch dynamic approach are needed to understand and manage the dynamics of urban and urbanizing ecosystems (Zipperer et al., 2000).

There has been little work on the rates of atmospheric deposition to urban ecosystems despite the large body of knowledge on concentrations and chemical reactions of air pollutants in cities. A search of the abundant literature produced no references that dealt with the effects of PM deposition. Lovett et al. (2000), however, reported that urban ecosystems are likely to be subjected to large rates of deposition of anthropogenic pollutants. Decades of research on urban air quality indicate that cities are often sources of nitrogen oxides, sulfur oxides, and dust, among many other pollutants. Some of these air pollutants are major plant nutrients (e.g., nitrogen) and may be affecting nutrient cycles in plant-dominated areas in and around cities. The gases and particles in urban air can increase atmospheric deposition within and downwind of the city. Studying the deposition rates of atmospheric pollutants in urban areas can provide a quantitative estimate of the amounts of gaseous and particulate air pollutants that are removed by urban vegetation.

To determine the patterns of atmospheric deposition and throughfall in the vicinity of a large city, Lovett et al. (2000) measured bulk deposition, oak forest throughfall, and particulate dust at sites along a transect within and to the north of New York City. They observed that concentrations and fluxes of NO_3^-, NH_4^+, Ca^{+2}, Mg^{+2}, SO_4^{-2}, and Cl^- in throughfall all declined significantly with distance from the city, while hydrogen ion concentration and flux increased significantly with distance from the city. Most of the change in concentrations and fluxes occurred within 45 km of the city. Additionally, it was observed that throughfall nitrogen was twice as high in the urban areas when compared with the suburban and rural sites. Most of the dry deposition of nitrate was from gaseous nitrogen oxides. As mentioned above, the effects of the atmospheric deposition of the particulate pollutants was not mentioned.

McDonnell et al. (1997) in a 10-year study of ecosystem processes along an urban-rural gradient included plant litter dynamics and nitrogen cycling of two key components of a forest ecosystem: litter decomposition and heavy metal levels in soil and foliar litter. Foliar litter decomposition integrates many features of the abiotic and biotic environment. It is an important site of heavy metal incorporation into ecosystems and provides a both a habitat and a resource for fungi, bacteria, and invertebrates. Litter decomposition integrates the effects of resource quality, environmental factors, and activities of decomposer organisms on nutrient cycling and serves as an easily measured indicator of the effect of urbanization on an important ecosystem function. McDonnell et al. (1997) noted that levels of heavy metals in the foliar litter in urban forest soils were higher than in rural forest soils. The levels in urban forest stands approached or exceeded the levels reported to affect soil invertebrates, macrofungi, and soil microbial processes. The urban forests exhibited reduced fungal biomass and microarthropod densities when compared to rural stands. These results supported the concept that urban forests have depauperate communities because of anthropogenic stress resulting from poor air quality due to high levels of SO_2, sulfate, ozone, and nitrogen; elevated levels of soil- and forest-floor-heavy metals; and low water availability such as those caused by hydrophobic soils (McDonnell et al.,1997). Thus, forests at the urban end of the gradient exhibited reduced fungal and microarthropod populations and poorer leaf quality than the more rural forests. The potential effect of these conditions on the ecosystem processes of decomposition and nitrogen cycling in urban forests appeared to be ameliorated by two other anthropogenic factors: increased average temperatures caused by the heat island effect and the introduction and successful colonization of earthworms in the urban forests (McDonnell et al.,1997).

McDonnell et al. (1997) observed that the changes in forest nitrogen dynamics were related to increased anthropogenic nitrogen deposition in an urban environment. The studies of Aber et al. (1989) in the northeastern United States on forest nitrogen dynamics demonstrated that elevated nitrogen deposition over many years results in increased nitrification and the mineralization of more nitrogen than can be taken up by plants and microorganisms. Nitrification can precipitate decreases in fine root biomass and increases in nitrate leaching below the root zone. These effects of nitrogen deposition were not related to inputs from a specific source such as PM.

There have also been studies of heavy metal deposition in or near cities; but the studies do not cite the effects of metals in the soil. Pouyat and McDonnell (1991) discuss heavy metal accumulations in forest soils along an urban-rural gradient in southeastern New York. Variations in the amounts of Zn, Cu, Ni, and Cd appeared indicative of a pattern of atmospheric deposition near point sources (Section 4.3.2.6). The concentrations of heavy metals in forest floor and soils corresponded closely with the urban-rural land use gradient. Again, as in the study by Lovett et al. (2000), the pollutants were highest near the urban end of the gradient and declined toward rural sites, with Pb, Ni and Cu highest near the urban end.

The air quality of the region around East St. Louis has been of concern due to industries in the area (Kaminski and Landsberger, 2000a), which include ferrous and nonferrous metal smelters (Pb, Zn, Cu, and Al), coal-fired power plants, producers of organic and inorganic chemicals, municipal waste incinerators, and petroleum refineries. The city is also in the path of diverse plumes from refineries to the north, coal-fired power plants to the west, and nonferrous smelters to the south. Concentrations of heavy metals and metalloids (As, Cd, Cu, Hg, Pb, Sb, Zn) in the soil provided a basis for analysis (Kaminski and Landsberger, 2000b). These studies of the extent of long-term metal deposition on the soil surface and depth of soil contamination, as well as the leaching dynamics of heavy metals were made to determine possible effects on biota uptake or groundwater contamination. The effects on biota are not mentioned; however, the soils in the area acted as a sink and there was little groundwater mobility (Kaminski and Landsberger, 2000b).

Overall, the above assessment of new information leads to the clear conclusion that atmospheric PM at levels currently found in the United States have the potential to alter ecosystem structure and function in ways that may reduce their ability to meet societal needs. The possible direct effects of airborne PM on individual plants were discussed in Section 4.2.2.1.

4.3 AIRBORNE PARTICLE EFFECTS ON VISIBILITY

4.3.1 Introduction

Visibility may be thought of as the degree to which the atmosphere is transparent to visible light (National Research Council, 1993). The beauty of scenic vistas in many parts of the U.S. is often diminished by haze that reduces contrast, washes out colors, and renders distant landscape features indistinct or invisible. This degradation of visibility is due primarily to the scattering and absorption of light by fine particles suspended in the atmosphere. One quantitative measure of visibility, used traditionally by meteorologists, is the visual range, defined as the farthest distance at which a large black object can be distinguished against the horizon sky (U.S. Environmental Protection Agency, 1979).

In August 1977, Congress amended the Clean Air Act (CAA) to establish as a national goal “the prevention of any future and remedying of any existing impairment of visibility in mandatory Class I Federal areas (many national parks and wilderness areas), which impairment results from manmade air pollution” (Title I Part C Section 169A, U.S. Code [1990]). The 1977 Amendments also included provisions requiring applicants for new major source permits to assess the potential for their projects to cause adverse effects on air quality-related values, including visibility, in nearby Class I areas. In 1980, the EPA established regulatory requirements under Section 169A to address Class I protection from “reasonably attributable” visibility impairment; i.e., visibility impairment attributable to a single source or small group of sources.

The CAA, as amended in 1990 (section 169B), required the U.S. Environmental Protection Agency to conduct research on regional visibility impairment and to establish the Grand Canyon

Visibility Transport Commission (GCVTC). The GCVTC was charged with assessing and providing recommendations to help preserve clear days and to improve visibility in the 16 national parks and wilderness areas located on the Colorado Plateau. The GCVTC also was mandated to provide recommendations to the U.S. Environmental Protection Agency for the reduction of visibility impairment due to regional haze, described as any perceivable change in visibility (light extinction, visual range, contrast, or coloration) from that which would have existed under natural conditions that is caused predominantly by a combination of many anthropogenic sources over a wide geographical area (U.S. Environmental Protection Agency, 1999a). In July 1999, the U.S. Environmental Protection Agency published the Regional Haze Rule (Federal Register, 1999). The regulation established a program for the improvement and protection of visibility in the 156 protected Class I parks and wilderness areas and included the establishment of baseline and current visibility conditions and the tracking of changes in visibility conditions over time. Implementation of the regional haze regulations is supported by the U.S. Environmental Protection Agency's $PM_{2.5}$ monitoring network and an expanded Interagency Monitoring of Protected Visual Environments (IMPROVE) network. The $PM_{2.5}$ monitoring network and the IMPROVE network are described briefly later in this section and in more detail elsewhere (National Park Service, 1998; Evans and Pitchford, 1991; U.S. Environmental Protection Agency, 2000b; U.S. Environmental Protection Agency, 2001).

The objective of the visibility discussion in this section is to provide a brief description of the fundamentals of atmospheric visibility and to summarize the linkage between particulate matter and visibility. Visibility is an effect of air quality and, unlike the particulate matter concentration, is not a property of an element of volume in the atmosphere. Visibility can be quantified only for a sight path and depends on the illumination of the atmosphere and the direction of view. However, the concentration of particles in the atmosphere plays a key role in determining visibility. Therefore, visibility impairment may be controlled by control of particle concentrations. The relationships between particles, other factors, and visibility impairment are described in this section. For a more detailed discussion on visibility, the reader is referred to the 1996 Air Quality Criteria for Particulate Matter (1996 PM AQCD; U.S. Environmental Protection Agency, 1996a); the Recommendations of the Grand Canyon Visibility Transport Commission (Grand Canyon Visibility Transport Commission, 1996); the National Research Council (National Research Council, 1993); the National Acid Precipitation Assessment

Program (Trijonis et al., 1991); Interim Findings on the Status of Visibility Research (U.S. Environmental Protection Agency, 1995a); Visibility: Science and Regulation (Watson, 2002), and reports summarizing visibility science and data from the IMPROVE visibility monitoring network (Malm et al., 2000; Sisler, 1996; Sisler et al., 1993).

4.3.2 Factors Affecting Atmospheric Visibility

The visual perception of a distant object is influenced by a large number of factors including human vision (the eye), the brain's response to signals received from the eye, the interaction of light with the atmosphere (e.g., atmospheric illumination, path and transmitted radiance, contrast, and optical properties), and atmospheric pollution from natural and anthropogenic sources. Detailed discussion of this full range of topics can be found in the 1996 PM AQCD (U.S. Environmental Protection Agency, 1996a) and other general references (Malm, 1999, Watson, 2002). This section focuses only on those topics that have been addressed by more recent research, including atmospheric illumination, the optical properties of gases and particles in the atmosphere, and the effects of relative humidity on the optical properties of particles.

4.3.2.1 Optical Properties of the Atmosphere and Atmospheric Particles

Atmospheric particles and gases attenuate image-forming light as it travels from a viewed object to an observer. The fractional attenuation of light per unit distance is known as the light extinction coefficient. The light extinction coefficient, b_{ext}, is expressed in units of one over length, for example inverse kilometers (km^{-1}) or inverse megameters (Mm^{-1}). The light extinction coefficient can be expressed as the sum of the light scattering and light absorption coefficients of particles and gases.

$$b_{ext} = b_{ap} + b_{ag} + b_{sg} + b_{sp} \tag{4-7}$$

where the subscripts *p* and *g* signify particles and gases, and *s* and *a* signify scattering and absorption.

The light extinction coefficient can be measured with a reasonable degree of accuracy or can be calculated with the size, composition, shape, and the orientation of the particles. The light extinction coefficient is influenced by meteorological conditions and optical properties along the sight path.

Relationship Between Light, Targets, and Objects in a Sight Path

The appearance of a distant object is determined by light from two sources: the light reflected from the object itself (initial radiance) and the light reflected by the intervening atmosphere (path radiance). Human vision and the brain's response to signals received from the eye distinguishes between objects by contrast or differences in the radiance of adjacent objects. Light reflected by objects is attenuated by scattering and absorption as it travels through the atmosphere toward the observer. The portion that reaches the observer is the transmitted radiance. During the daytime, the sight path is illuminated by the direct rays of the sun, diffuse skylight, light that has been reflected from the surface of the Earth, etc. Some of this illumination is scattered toward the observer by the air molecules and particulate matter in the sight path. The accumulation of the light scattered into the sight path is the path radiance or air light. The path radiance significantly influences the light transmitted by the object being viewed. As the path radiance increases, the light transmitted by an object decreases.

The transmitted radiance carries the information about the object; the path radiance only carries information about the intervening atmosphere and is often quite featureless. When the transmitted radiance is dominant, visibility is good. Conversely, when the path radiance is dominant, visibility is poor. In a dense fog, the transmitted radiance from nearby objects can be seen, but the transmitted radiance from more distant objects is completely overwhelmed by the path radiance (i.e., the light scattered by the fog). Distant objects are lost in the white (or gray) of the fog (Gazzi et al., 2001).

Figure 4-32 illustrates the radiance seen by an observer looking at a hillside or through the aperture of a measurement instrument. The radiance that enters the eye of the observer (or the aperture of a measurement instrument) is known as the apparent radiance (i.e., the sum of the transmitted and path radiance). The competition between the transmitted radiance and the path radiance determines visibility.

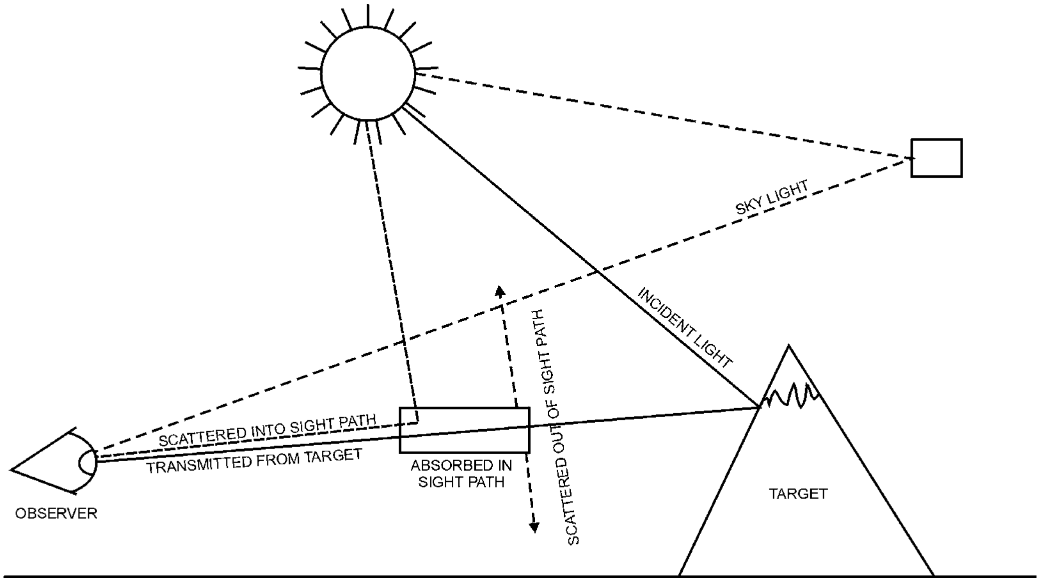


Figure 4-32. Light reflected from a target toward an observer. The intervening atmosphere scatters a portion of this light out of the sight path and scatters light from the sun into the sight path. Some particles and gases also absorb a portion of the light from the target. The light scattered into the sight path increases with distance from the target, whereas the light transmitted from the target decreases with distance from the target. The visual range is the closest distance between the target and the observer at which the transmitted light no longer can be distinguished from the light scattered into the sight path.

Source: Watson and Chow (1994).

Light Absorption and Scattering by Gases

In the ambient atmosphere the only visible-light-absorbing gas of any consequence is nitrogen dioxide (NO_2), which primarily absorbs blue light and, if present in sufficient concentration across a sight path, causes yellow or brown color seen in urban hazes. Usually the absorption by NO_2 is much smaller than the scattering by particles that are typically present in polluted environments, such as urban areas. The most common exception to this situation of relatively small NO_2 absorption is in effluent plumes from combustion facilities where the particles are effectively removed but the nitrogen oxide (NO), which can convert rapidly to NO_2, is not removed. Except for such particle-depleted NO plumes, the light absorption coefficient for gases is usually ignored in determinations of the light extinction.

Scattering by gases in the atmosphere is described by the Rayleigh scattering theory (van de Hulst, 1981) and is referred to as Rayleigh scattering. The magnitude of the Rayleigh scattering depends on the gas density of the atmosphere and varies from about 9 Mm^{-1} to 11 Mm^{-1} for most locations of interest, depending primarily on site elevation. To simplify comparisons of light extinction coefficient values among sites at a variety of elevations, a standard value of 10 Mm^{-1} is often used for the Rayleigh scattering component (Malm, 2000).

Light Absorption and Scattering by Particles

Particle scattering tends to dominate light extinction except under pristine atmospheric conditions when Rayleigh scattering by gas molecules is the largest contributor. If the particle size, refractive index, and shape are known, the extinction coefficient can be calculated. For particles of sizes similar to the wavelength of visible light, Mie equations for homogeneous spheres can be used to calculate the scattering and absorption of individual particles.

Absorption by particles is primarily caused by elemental carbon (also referred to as soot or light-absorbing carbon) generated by the incomplete combustion of fossil fuels. Some minerals in crustal particles also absorb light and can be a significant factor during fugitive dust episodes.

Most particle absorption data are determined by measuring light transmission or reflection of particles captured on filter media. Absorption estimates made in this way are sensitive to the filter substrate used, the optical configuration of the transmission measurement, particle loading on the filter, and particle scattering albedo with the result that there are significant uncertainties for measurements of filtered particles (Horvath, 1993). Another approach to estimating aerosol light absorption is by subtracting concurrent light scattering measurements made with a nephelometer from light extinction measurements made with a transmissometer. Substantial uncertainty in this difference approach results from the assumption that the point measurement of scattering is representative of the scattering over a long path (1 to 10 km) that is typically required for transmissometers measurements. A recently field-tested prototype photoacoustic spectrometer designed to determine absorption of suspended aerosol and an enclosed-folded path transmissometer offers hope of resolving the problems of the filter-based and difference approaches to the measurement of light absorption by particles (Arnott et al., 1999).

The relationship between elemental carbon concentration and particle absorption can be calculated using Mie equations for particles with known size distribution, particle density, index of refraction, shapes, and for various internal mixtures with non-absorbing aerosol materials (Fuller et al., 1999). Mie equations are used to determine the efficiency factors for extinction $Q_{ext,}$ $Q_{scat,}$ and Q_{abs}. The efficiency factors represent the fraction of light falling on a circle with the same diameter and index of refraction as the particle. While such application of this theory can provide a range of absorption efficiencies for various model aerosol distributions, it is rare that sufficiently detailed particle characterization data for ambient aerosols are available. Also, although elemental carbon is the strongest and most common of the absorbing particles, light absorption by elemental carbon particles can be reduced when the particle is covered by other chemical species (Dobbins et al., 1994) or may be enhanced when coated with a non-absorbing refractive material such as ammonium sulfate (Fuller et al., 1999).

More commonly, estimates of elemental carbon absorption efficiency are empirically determined from the ratios of or the slopes of regression analysis fits to absorption coefficient and corresponding elemental carbon concentration measurements. Use of the regression approach permits the inclusion of crustal component concentrations as a second dependent parameter, so that crustal absorption can also be estimated. Uncertainties in the absorption efficiency determined empirically are a combination of the measurement uncertainties for the absorption coefficients, elemental carbon concentrations, and where used, the crustal concentrations. In reviews of estimates of elemental carbon light absorption mass efficiency (i.e., the absorption coefficient per carbon mass concentration), Horvath (1993) and Liousse et al. (1993) found values ranging from 2 to 17 m^2/g. Moosmüller et al. (1998) showed that by limiting the absorption coefficient estimates to those using photoacoustic methods, the absorption efficiency shows a wavelength dependence with highest values (17 m^2/g) at the shortest wavelength used ($\lambda = 0.42$ μm) and lowest values (3 m^2/g) at the longest wavelengths used ($\lambda = 0.8$ μm). The center of the visible light wavelength ($\lambda = 0.53$ μm) yielded elemental carbon absorption efficiencies values of approximately 10 m^2/g, a commonly used value for elemental carbon absorption efficiency. Fuller et al. (1999) suggested that isolated spheres of light absorbing carbon have a specific absorption of less than 10 m^2/g. Light absorption by carbon particles will be greater than 10 m^2/g only if the particles are internally mixed and the occluding particles are sufficiently large. Absorption values for graphitic and amorphous carbon for primary sizes typical of diesel soot are approximately 5 m^2/g.

Particle scattering tends to dominate light extinction except under pristine atmospheric conditions when Rayleigh scattering by gas molecules is the largest contributor. Light-scattering by particles has been reported to account for 68 to 86% of the total extinction coefficient in several cities in California (Eldering et al., 1994). When light-scattering increases, visibility is impaired because of a decrease in the transmitted radiance and an increase in the path radiance. The single most important factor that determines the amount of light scattered by a particle is its size, as shown in Figure 4-33 (based on Mie calculations). The maximum single-particle scattering efficiency (i.e., scattering per cross-sectional area of a particle) is associated with particles with diameters of about the wavelength of visible light (centered at 0.53 μm). For particles that are small compared to the wavelength of light, the single- particle scattering efficiency is low. For particles larger than the wavelength, the single particle scattering efficiency initially decreases with diameter and then fluctuates around a value of two as size increases. However, a larger particle always scatters more light than a smaller particle because particle cross-sectional area increases faster with diameter than does the decrease in single-particle scattering efficiency at any point on the scattering efficiency curve. The mass scattering efficiency (i.e., the scattering per mass concentration) peaks for particles that are about 0.5 μm to 0.8 μm in diameter. Smaller particles are much less efficient at scattering light, while larger particles have mass that increases with particle size faster than the increase in the amount of light they scatter.

Use of the Mie equation to calculate light scattering or the light scattering efficiency of particles in the atmosphere is severely limited by the general lack of sufficiently detailed particle characterization data. At a minimum, size-resolved particle composition data (e.g., aerosol collected on an 8-stage impactor) are needed to permit meaningful Mie scattering calculations. The chemical composition provides clues to the appropriate particle density and index of refraction, while the size distribution is inferred by fitting a distribution function to the concentration for each stage. Assumptions are still necessary to address the particle component mixture characteristics of the aerosol. Resulting scattering calculations can be compared to directly measured particle extinction to assess the reasonableness of the Mie calculations.

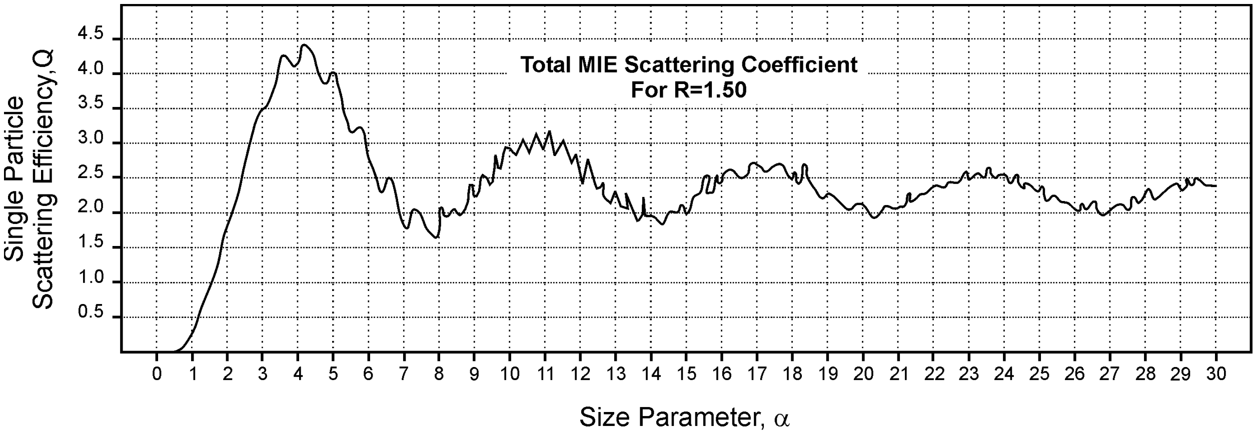


Figure 4-33. Light-scattering efficiency factor (per cross sectional area), Q, for a homogeneous sphere with an index of refraction of 1.50 as a function of the size parameter, $\alpha = \pi D/\lambda$.

Source: Penndorf (1958).

Reported calculated scattering efficiencies for sulfates range from 1.2 to 5.6 m^2/g. Sulfate scattering efficiencies have been reported to increase by a factor of two when the size distribution increased from 0.15 to 0.5 μm (McMurry et al., 1996). Calculated scattering efficiencies for carbon particles ranged from 0.9 to 8.1 m^2/g. A scattering efficiency of 1.0 and 0.6 m^2/g was reported for soil and coarse mass, respectively (U.S. Environmental Protection Agency, 1996a; Sisler and Malm, 2000).

Figure 4-34 gives the volume-specific light scattering efficiency in units of μm^{-1} as a function of particle diameter. The light scattering coefficient is derived by multiplying the volume-specific light scattering efficiency factor by the volume concentration. The mass-specific light scattering efficiency can be obtained by dividing the values for the curves by the density of the particulate matter.

Similar results have been produced in field nephelometer measurements of ambient particle scattering. A variety of nephelometer configurations, unrestricted or size selective inlets and the control of sample air temperature and relative humidity, permit the composite scattering properties of ambient aerosol to be directly observed (Day et al., 1997). When sample-controlled nephelometer data are combined with collocated particle speciation data, composite

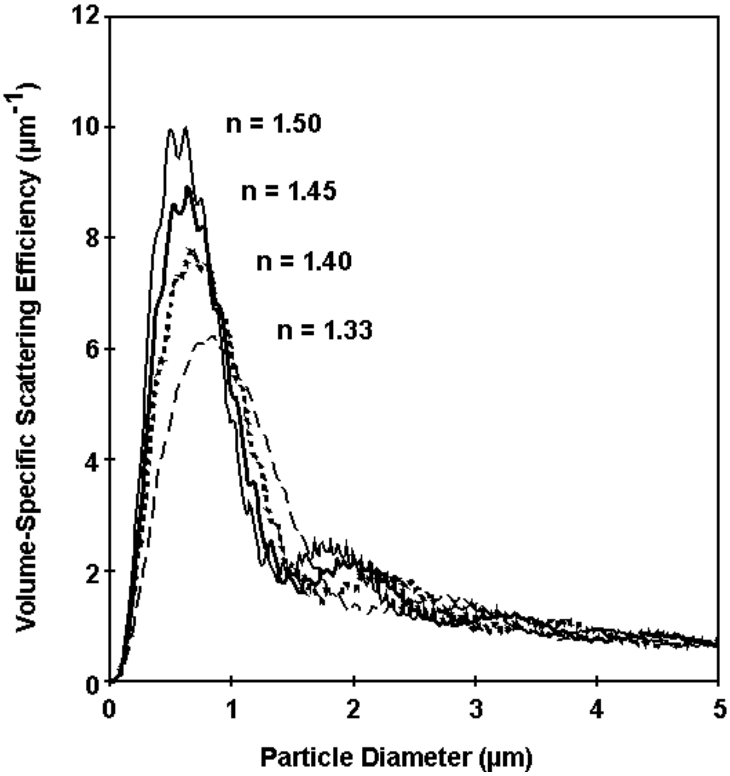


Figure 4-34. Volume-specific light-scattering efficiency as a function of particle diameter D_p. The calculations were performed for the indicated indices of refraction and a wavelength of 550 nm. For large particle diameters the scattering efficiencies tend toward a value of $3/D_p$. Mass-specific light-scattering efficiencies (in units of m^2/g) can be obtained by dividing the values of the curves by the particle density (in units of g/cm^3).

Source: U.S. Environmental Protection Agency (1996a).

particle scattering efficiency values for ambient aerosol can be empirically derived (Malm et al., 2000).

The scattering efficiency for particles have been reported by White et al. (1994) for dry particles less than 2.5 µm (2.4 and 2.5 m^2/g) and coarse particles 0.34 to 0.45 m^2/g). Other reported values for coarse particles include 0.4 and 0.6 m^2/g (White and Macias, 1990 and Trijonis and Pitchford, 1987). Nephelometer measurements for light scattering by coarse particles is underestimated (White et al., 1994). Chow et al. (2002a) reported scattering efficiencies of 2 to 3 m^2/g but in some cases > 5 m^2/g for dry particles less than 2.5 µm.

4.3.2.2 Relative Humidity Effects on Particle Size and Light-Scattering Properties

The ability of some commonly occurring chemical components of atmospheric aerosol to absorb water from the vapor phase has a significant effect on particle light scattering. Hygroscopic particulate materials, which typically include sulfuric acid, the various ammonium sulfate salts, ammonium nitrate, and sodium chloride, change size by the accumulation and loss of water as they maintain equilibrium with the vapor phase as a function of changes in relative humidity. For some materials (e.g., sulfuric acid), the growth is continuous and reversible over the entire range of relative humidity. For other materials, water absorption begins abruptly for a dry particle at a specific relative humidity known as the deliquescent point (e.g., ~80% for ammonium sulfate) and continues as relative humidity increases. There is a hysteresis effect with these materials in that, once wet, the relative humidity can be reduced below the deliquescent point until crystallization occurs at a substantially lower relative humidity (e.g., ~30% for ammonium sulfate). Figure 4-35 shows the water vapor growth curve for ammonium sulfate.

Water growth behavior for hygroscopic materials commonly found in atmospheric aerosol in pure form or in some mixtures is generally well known as a result of laboratory measurements (Tang and Munkelwitz, 1994; Tang, 1997). Models that calculate water growth of mixtures from known solubility properties of many common water-soluble chemicals have long been available (Zdanovskii, 1948) and have been successfully applied to determine growth for particles with known composition (Saxena and Peterson, 1981; Pilinis et al., 1995; Saxena et al., 1993).

The water growth of individual ambient particles can be directly measured using a humidity-controlled tandem differential mobility analyzer or TDMA (McMurry and Stolzenburg, 1989; Zhang et al., 1993). Inferences can be made about the mixtures of soluble and insoluble particle components by comparing TDMA measured growth and size-resolved aerosol composition data with water growth model predictions (Pitchford and McMurry, 1994; Zhang et al., 1993; Saxena et al., 1995). A practical limitation of TDMA measurements in investigating aerosol optical properties is that particles with diameter greater than 0.5 μm are not well measured by this approach.

Accounting for water growth of atmospheric aerosols is important in determining visibility because particles containing hygroscopic or deliquescent materials change size, index of

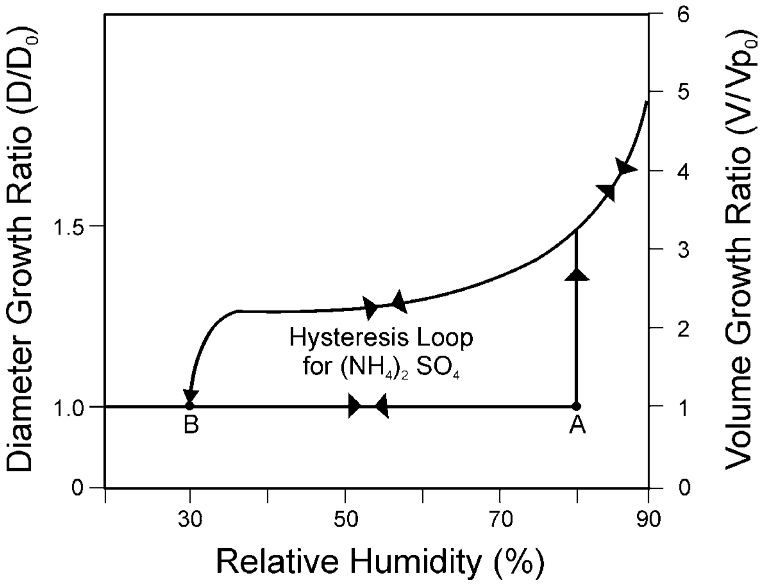


Figure 4-35. Particle growth curve as a function of relative humidity showing deliquescent growth of ammonium sulfate [$(NH_4)_2$ SO_4] particles at the deliquescent point (A, about 80% relative humidity [RH]), reversible hygroscopic growth of ammonium sulfate solution droplets at RH greater than 80%, and hysteresis (the droplet remains supersaturated as the RH decreases below 80%) until the crystallization point (B, about 38% RH) is reached.

Source: Adapted from National Research Council (1993) and Tang (1980).

refraction, and hence scattering efficiency, with changing relative humidity. The nonlinear nature of particle growth curves for hygroscopic aerosols means that substantial light scattering changes result from modest relative humidity changes under humid conditions (relative humidity > 90%). The magnitude of the water growth effect on light scattering for ambient aerosols can be directly measured with humidity-controlled nephelometer measurements (Day et al., 1997). Measurements of water growth effects on scattering are compared to results of water growth and Mie scattering models applied to size-resolved composition data using various mixture assumptions to infer average mixture and other aerosol characteristics (Malm et al., 2000).

While the importance of inorganic hygroscopic particles is well understood, the role of organic compounds in particle water growth has been the subject of recent investigations. In their interpretation of TDMA and particle composition data from two locations, Saxena et al. (1995) made the case that organic components of the aerosol enhanced water absorption by particles at a remote desert location and retarded water absorption at an urban location. They speculated that the latter might be due to hydrophobic organic material coatings on inorganic hygroscopic particles.

While some of the thousands of organic compounds that are in atmospheric aerosols are known to be hygroscopic and while a significant fraction of the organic aerosol material is known to be water soluble, there is a lack of water absorption data for most organic compounds. The incomplete water solubility data combined with incomplete data on the abundance of the numerous organic compounds in ambient aerosols means that organic water growth model calculations are not a reasonable approach to assessing the importance of water growth by organic aerosol components in the atmosphere. To overcome this constraint, Saxena et al. (1995) compared organic concentration to the difference between total aerosol water measured by TDMA and model-estimated water for the inorganic hygroscopic aerosol components. In contrast, Pitchford and McMurry (1994) used the same remote location data set and showed that on six of the eight sampling days water uptake by the sulfates and nitrates could account for all of the measured water absorption.

Swietlicki et al. (1999) made TDMA measurements in northern England and found that growth takes place in two modes, one mode being less hygroscopic that the other. They concluded that growth could be attributed to the inorganic content of the aerosol. Cocker et al. (2001) measured hygroscopic properties of Pasadena, California aerosol and concluded that growth factors increased when forest fires were present. McDow et al. (1995) measured water uptake by diesel soot, automobile exhaust, and wood smoke particles. They found all three emission types absorbed water: the wood smoke sample weight increased by about 10% as sample relative humidity was increased; whereas diesel soot sample weight increased by only 2% to 3%. Chughtai et al. (1999) examined hydration characteristics of a number of anthropogenic and natural organic materials. They found surface water adsorption increased with age and surface oxidation. Hemming and Senfield (2001) evaluated the relative hygroscopicity of different organics, the differences in the amount of water taken up by mixtures, and the individual components of the mixtures in their pure state using the UNIFAC. They found that mixtures take up less water than the individual components in the pure state. The relative hygroscopicity of atmospheric organics was diacids > monoacids > alcohols > carbonyls. Analysis of humidity-controlled and size-resolved chemistry data from Great

Smoky Mountains and Grand Canyon National Parks (Malm et al., 1997; Malm and Kreidenweis, 1996; Malm et al., 2000) show that ambient organic aerosol are at most weakly hygroscopic to within the measurement uncertainty and modeling assumptions.

A more detailed discussion of the effects of relative humidity on the size distribution of ambient particles appears in Chapter 2 of this document.

4.3.3 Relationships Between Particles and Visibility

Visibility, referring to the appearance of scenic elements in an observer's line of sight, depends on more than the optical characteristics of the atmosphere. Numerous scene and lighting characteristics are important to this broad definition of visibility. However, under a variety of viewing conditions, visibility reduction or haziness is directly related to the extinction coefficient.

Light extinction, the sum of the light scattered and absorbed by particles and gases, is frequently used to estimate the effect of air pollution on visibility. Light extinction is usually quantified using the light extinction coefficient, that is the sum of the light scattering and absorption coefficients for gases and particles (see Section 4.3.2.1).

The influence of particles on visibility degradation is dependent on the particle size, composition, and solubility (Pryor and Steyn, 1994). Fine particles (particles with mass mean diameters less than or equal to 2.5 μm) scatter more light than coarse particles. Fine particle species included sulfates (assumed to be ammonium sulfate), nitrates (assumed to be ammonium nitrate), organics, light- absorbing carbon and soil (Malm et al., 1994). Of the fine particle species, sulfates and nitrates are the most hygroscopic and require the use of a relative humidity adjustment factor. The effect of particle light extinction can be determined by totaling the scattering and absorption of light by multiplying the mass-specific efficiency values and the mass concentration for each of the particle species. The effect of relative humidity and the relative humidity adjustment factors are discussed in Section 4.3.2.2. Visibility is measured by human observation, the light extinction coefficient (light scattering and absorption by particles and gases), and parameters related to the light extinction coefficient (visual range, deciview) and fine particle mass concentrations. Using the equation for the light extinction coefficient, light extinction by particles can be expressed as

$$b_{ext} = b_{ap}\,(b_{EC}) \;+\; b_{sp}\,(b_{SO4} \;+\; b_{NO3} \;+\; b_{OC} \;+\; b_{Soil} \;+\; b_{Coarse} + \; b_{sg}) \qquad (4\text{-}8)$$

where

b_{ap} = 10[mass of elemental carbon]

b_{SO} = 3[mass concentration of $(NH_4)_2SO_4$]f(RH)

b_{NO_3} = 3[mass concentration of $(NH_4)_2SO_4$]f(RH)

b_{OC} = 4[OC]

b_{soil} = 1[Soil]

b_{sg} = 10 [Rayleigh scattering by gases]

The visual range method of visibility measurement, commonly taken to be the greatest distance that a large dark object (e.g., a mountain in shadow) can be seen against the background sky (Middleton, 1952), was developed for and continues to function well as an aid in military operations and transportation safety. Visual range is inversely proportional to the light extinction. Visual range can be calculated from a point measurement of light, assuming that the atmosphere and the illumination over the sight path is uniform and the threshold contrast is 2% of the extinction coefficient

$$\text{Visual Range} = K/b_{ext} \qquad (4\text{-}9)$$

where visual range is in kilometers, b_{ext} is in km^{-1}, and a threshold contrast of 2% is assumed. If b_{ext} is in Mm^{-1}, the Koschmieder constant becomes 3,912.

A new index of haziness, expressed in deciview (dv) units, is also very simply related to the light extinction coefficient (Pitchford and Malm,1994).

$$\text{Haziness (dv)} = 10 \ln(\, b_{ext}/10\ Mm^{-1}) \qquad (4\text{-}10)$$

An important characteristic of this visibility index is that it is more nearly linearly related to perceived changes in haze level than either visual range or light extinction. A change of 1 or

2 dv in uniform haze under many viewing conditions will be seen as a small but noticeable change in the appearance of a scene regardless of the initial haze condition.

Figure 4-36 illustrates the relationship of light extinction in Mm^{-1}, deciview index, and visual range in kilometers. Although the deciview is related to extinction, it is scaled in such a way that is perceptually correct (Fox et al., 1999).

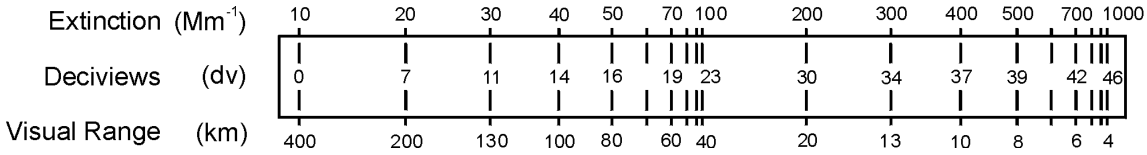


Figure 4-36. Comparison of extinction (Mm^{-1}) and visual range (km).

Source: Fox et al. (1999).

Several early studies have demonstrated a relationship between enclosed nephelometer light scattering measurements and fine particle mass collected on a filter (Waggoner et al., 1981; Samuels et al., 1973). However, the relationship between fine particle mass and light scattering may differ between locations and for different times of the year. The relationship is improved by using the same size selective inlet on both the nephelometer and filter sampler (White et al., 1994) and by minimizing the effect of high relative humidity on filter specimens and in the neplelometer scattering chamber. When particle speciation data for the major aerosol components are available, the relationship between particles and light extinction can be further improved by treating the individual major components separately. A recent study by Chow et al. (2002a) also suggested that continuous light scattering measurements may be useful as an indicator of short-term variations in $PM_{2.5}$ mass concentrations when the measurements are made under dry conditions. Figure 4-37 shows the relationship between fine particle mass and calculated light extinction.

Most routine aerosol monitoring programs and many special study visibility characterization programs were designed to measure the major aerosol components (Malm et al., 1994; Tombach and Thurston, 1994; Watson et al., 1990); they were not designed to determine

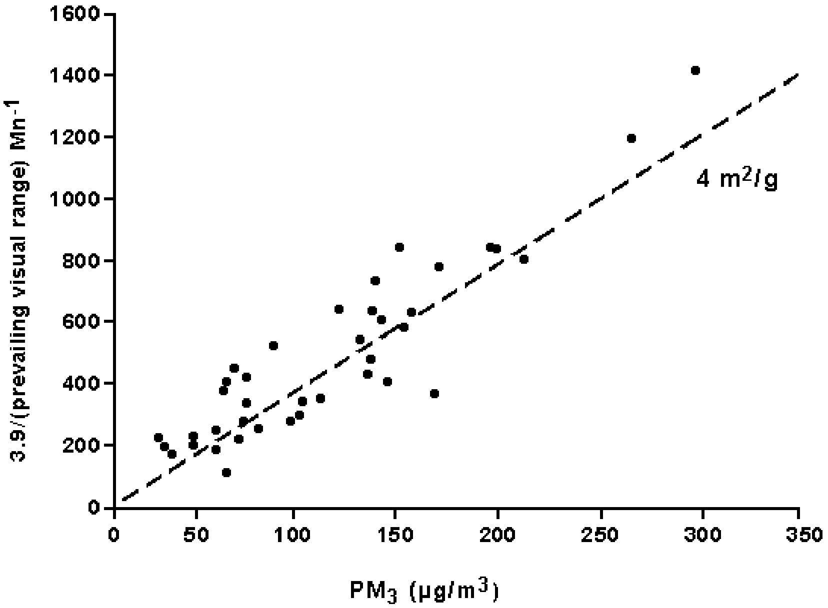


Figure 4-37. Proportionality of observed daytime haziness to fine particle mass concentration in Los Angeles. Visual ranges are 8-h averages of hourly human observations, plotted as extinction according to Koschmieder formula. Mass concentrations are from 8-h samples collected behind a cyclone with 3-µm cut point. Relative humidities were ≤ 70%.

Source: Chow et al. (2002b).

the microphysical and chemical characteristics of these species. However, the inherent limitations of estimating aerosol optical properties from bulk aerosol measurements have been addressed, at least in part, by a number of authors. For instance, Ouimette and Flagan (1982) have shown from basic theoretical considerations that if an aerosol is mixed externally (i.e., separate particles contain the major aerosol components) or if in an internally mixed aerosol the index of refraction is not a function of composition or size and the aerosol density is independent of volume, then

$$b_{sp} = \sum \alpha_i m_i \qquad (4\text{-}11)$$

where α_i is the specific mass scattering efficiency and m_i is the mass of the individual aerosol species.

Sloane (1983, 1984, 1986), Sloane and Wolff (1985), and more recently Lowenthal et al. (1995) and Malm and Kreidenweiss (1997) have shown that differences in estimated specific scattering between external and internal model assumptions are usually less than about 10%. In the absence of detailed microphysical and chemical information of ambient particles, the above studies demonstrate that a reasonable estimate of aerosol extinction can be achieved by assuming each species is externally mixed.

The latest IMPROVE Program report (Malm, 2000) includes calculated aerosol light extinction for each of the five major fine fraction particle ($PM_{2.5}$) components, coarse fraction mass ($PM_{10\text{-}2.5}$), and Rayleigh scattering by gases and sums them for an estimate of total light extinction in Mm^{-1} using the following algorithm:

$$\begin{aligned} b_{ext} = {} & (3)\, f(RH)\, [SULFATE] + \\ & (3)\, f(RH)\, [NITRATE] \\ & +(4)\, [ORGANIC\ CARBON] \\ & +(10)\, [LIGHT\ ABSORBING\ CARBON] \\ & +(1)\, [SOIL] \\ & +(0.6)\, [COARSE\ PM] \\ & +10\ \textit{(for Rayleigh scattering by gases)} \end{aligned} \tag{4-12}$$

where each PM term is the product of a constant dry extinction efficiency for that species, the mass concentration of the species, and, for sulfate and nitrate, an adjustment factor that is a function of relative humidity to account for their hygroscopic behavior. The relative humidity adjustment term for sulfate and nitrate, shown in Figure 4-38, is based upon the ammonium sulfate growth curve, shown in Figure 4-28, smoothed between the upper and lower curves of the hysteresis loop for the relative humidity range of 30-80%. The extinction efficiencies for soil and coarse mass used in this algorithm are taken from a literature review by Trijonis et al. (1987). The extinction efficiency for light absorbing (elemental) carbon of 10 m^2/g is consistent with the value reported by Moosmüller et al. (1998) corresponding to $\lambda = 0.53$ in the middle of the visible light spectrum. The dry extinction efficiencies of 3 m^2/g for sulfate and nitrate species and 4 m^2/g for organic species are based on literature reviews by Trijonis et al. (1991) and by White (1991). Trijonis' best estimate for sulfates is 2.5 m^2/g with an uncertainty of a

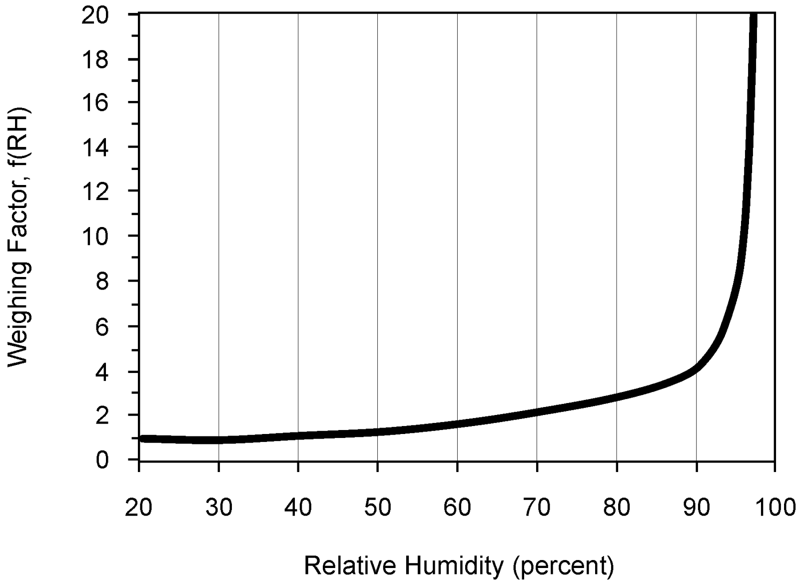


Figure 4-38. Relative humidity adjustment factor, f(RH), for ammonium sulfate as a function of relative humidity.

Source: Malm et al. (2000).

factor of 2, while White's average low and high estimates for the rural West are 3.0 and 3.7 m^2/g. For organics, Trijonis estimates a dry extinction efficiency of 3.75 m^2/g with an uncertainty of a factor of 2, and White's range for the rural West is 1.8 to 4.1 m^2/g. Malm et al. (1996) and Malm (2000) used this algorithm to successfully reconstruct scattering at a total of eleven IMPROVE monitoring sites.

Malm (2000) used additional sophisticated aerosol size, composition, and microphysical data from a special study at the Great Smoky Mountain National Park to compare the performance of a number of models for calculating light extinction. He found that the simplist approach adequately predicted for periods of low light scattering but under-predicted by about 30% during periods of high sulfate concentration. The greatest improvement over the simple model was obtained by including the degree of sulfate ammoniation in the model. This produced better estimates of the extinction coefficient over the entire range. Table 4-15 lists various visibility metrics and methods for visibility measurement.

TABLE 4-15. VISIBILITY MEASUREMENT TECHNIQUES

Visibility Metric and Method	Measurement Principle
Visual Range	Human observation of prevailing visibility. Targets are selected at known distances from an observer. Nighttime targets require lights and may differ from daytime targets. Each hour, the observer records the distance (i.e., VR) corresponding to the furthest target that is visible. This method provides the longest history of visibility measurements in the United States, as it was used at most U.S. airports from 1948 to 1995.
Light extinction (b_{ext})	Directly measures the radiance of a constant light source (transmitter) after the light travels over a finite atmospheric path.
Long-path transmissometer	The transmittance of the path is calculated by dividing the measured radiance by the calibrated initial intensity of the light source. The average extinction of the path is calculated from the transmittance and length of the path.
Short-path transmissometer	Starting in the early 1990s, many sites replaced human observations with automated sensors (i.e., Automated Surface Observing System [ASOS], Automated Weather Observing System [AWOS]) to measure 1-min-average light extinction. The visibility sensor measures forward scattering using a xenon flash lamp source. Instruments can provide measurements up to 48 km, but they are not recorded beyond 16 km.
Contrast transmittance: Teleradiometer	A telescope is focused on a distant target and the background. Changes in radiance are measured by photodiode detectors. Measurements can be made at different wavelengths (e.g., 450, 550, and 630 nm) using narrow band filters. Measures effects of particles of all sizes. Sensitive to variations in inherent contrast (e.g., bright or dark cloud behind the target) and nonuniform illumination conditions. Because path radiance depends on how the atmosphere is illuminated, contrast transmittance represents human perception better than air quality.
Photographs and time-lapse film	A densitometer measures light transmitted through different portions of a color slide. The film's light-response function (the gamma curve) determines target-sky contrast. Computerized photographic simulations can change contrast transmittance for different meteorological and atmospheric conditions, and can be used to judge how people react to these changes.
Particle scattering ($b_{scat,p}$) Integrating nephelometer	Air is drawn into a nephelometer chamber that is illuminated with white or filtered (typically 500-550 nm) light. Light is detected at 90° to the direction of illumination to measure the amount scattered out of the light path. Chamber dimensions limit the integrated arc to ~ 10-170° instead of a full 0-180°, which results in some forward scattering from coarse particles being underestimated. Nephelometers are calibrated with gases of known indices of refraction. Particles (especially hygroscopic and volatile species) may be modified as they pass through the chamber, which is inadvertently heated by the illumination source.

TABLE 4-15 (cont'd). VISIBILITY MEASUREMENT TECHNIQUES

Visibility Metric and Method	Measurement Principle
Particle absorption ($b_{abs,p}$): Aethalometer or particle soot absorption photometer	Particles are collected on a quartz-fiber filter tape. The change in transmittance at selected wavelengths (e.g., 880 nm) across the filter before and after sampling is measured or compared with the reference area. When the filter spot darkens, a new portion of the tape is moved into the sampling position. Assumes a constant relationship between BC mass and quartz filter transmittance of ~19m^2/g. Assumes a relationship of 10m^2/g between BC absorption and concentration.
Photoacoustic spectroscopy	Particles absorb energy from a modulated laser (~514.5 nm) and transfer heat to the surrounding air. Expansion of the heated gas produces sound waves (acoustic signals) that are proportional to the amount of absorbed energy. These are detected by a high-sensitivity microphone. Absorption appears to vary with illumination wavelength.
Filter transmittance, reflectance	Uses densitometer, integrating plate, or integrating sphere spectrophotometer to measure how much light is transmitted or reflected. The difference in the logarithms of light transmission through the filter before and after sampling is proportional to the particle deposit. Light transmission of particles collected on a filter may overestimate light absorption because some of the incident light is scattered within the filter and by other particles in the deposit. There are no absolute calibration standards for densitometry, integrating plate, or sphere methods.
Suspension of insoluble elemental carbon	Particles collected on a Nuclepore polycarbonate-membrane filter are extracted in 30% isopropanol/70% distilled deionized water to form a suspension of insoluble EC particles. Using a spectrophotometer, light transmission (e.g., 400-650 nm, peaking at 575 nm) is measured through the liquid extract.
Component extinction (b_{ext}) (sum of $b_{scat,p}$, $b_{scat,g}$, $b_{abs,p}$, and $b_{abs,g}$)	The sum of clean air scattering estimated from temperature and pressure, NO_2 absorption estimated from NO_2 concentrations, particle scattering measured by nephelometer, and particle absorption ($b_{abs,p}$) measured by one of the $b_{abs,p}$ methods. Measurements are at a single location rather than along a sight path.
Chemical extinction (b_{ext}): Filter measurements for SO_4^{-2}, NO_3^-, organics, EC, fine soil, and coarse mass, plus clear air scattering	Six aerosol chemical components are used to calculate chemical extinction.

Adapted from: Watson (2002).

4.3.4 Photographic Modeling of Visibility Impairment

None of the visibility indices communicate visibility associated with various aerosol conditions as well as directly seeing their effects on a scene. However, photographic modeling for the representation of haze can be useful in portraying changes in visibility specifically due to changes in air pollutant concentrations. Photographic modeling holds constant the effects of sun angle, cloud cover, and relative humidity and is a cost-effective method of evaluating various air quality scenarios. Photographic modeling is difficult to do with actual photographs because of the range of possible conditions in the same scene over multiple days; and, over time, photographs can be expensive to produce. Another limitation in using photographic models for representation of haze is that haze is assumed to be uniformly distributed throughout the scene and selected conditions are idealized, so the full range of conditions that occur in a scene are not represented.

Eldering et al. (1996) proposed the use of a model that uses simulated photographs from satellite and topographic images to evaluate the effect of atmospheric aerosols and gases on visibility. Use of this model requires ground-based photography and data concerning the size distribution and chemical composition of atmospheric aerosols, NO_2 concentration, temperature, and relative humidity for a clear day. Light extinction and sky color are then calculated based on differences in aerosol size distribution, NO_2 concentration, temperature, and relative humidity. The images created represent natural landscape elements.

Molenar et al. (1994) provides a discussion of existing visual air quality simulation methods based on techniques under development for the past 20 years. A photograph taken on a very clean, cloud-free day serves as the base image. The photograph is taken during the season and at the same time of day as the scene to be modeled. The light extinction represented by the scene is derived from aerosol and optical data associated with the day the image was taken, or it is estimated from contrast measurements of features in the image. The image is then digitized to assign an optical density to each picture element (pixel) for the wavelength bands of interest. A detailed topographic map and an interactive image-processing display system is used to determine the specific distance, elevation angle, and azimuth angle for each element in the picture with respect to the observer's position.

Various models are employed to allow the presentation of different air quality scenarios. The output from atmospheric aerosol models (e.g., extinction, scattering coefficients, single scattering albedo, and scattering phase matrix) is incorporated into radiative transfer models to calculate the changes in radiant energy (path radiance, image radiance, sky radiance, terrain radiance) caused by scattering and absorption by gases and particles as it passes through the atmosphere. Atmospheric aerosol models are also use to model the effect of relative humidity on the visual air quality (Molenar et al., 1994).

Molenar et al. (1994) has developed a system call WinHaze that permits the viewing of computer-generated uniform hazes superimposed on digitized scenic photographs of both remote and urban scenes. The program simulates changes in visual air quality imagery from user-specified changes in optical parameters (e.g., σ_{ext}, visual range, or deciview values) or aerosol species concentrations. WinHaze includes imaging for various Class I national parks and wilderness areas and Boston, MA; Dallas, TX; Denver, CO; Fort Collins, CO; Phoenix, AZ; and Tucson, AZ. The computer software is available through the IMPROVE website (http://vista.cira.colostate.edu/ improve/).

4.3.5 Visibility Monitoring Methods and Networks

Visibility monitoring studies measure the properties of the atmosphere either at the sampler inlets (point measurements), as is the case with air quality measurements, or by determining the optical properties of a sight path through the atmosphere (path measurements). Instrumental methods for measuring visibility are generally of three types: (1) direct measurement of light extinction of a sight path using a transmissometer, (2) measurement of light scattering at one location using an integrating nephelometer, and (3) measurement of ambient aerosol mass concentration and composition (Mathai, 1995).

The largest instrumental visibility monitoring network in the United States is the Automated Surface Observing System (ASOS), commissioned by the National Weather Service, Federal Aviation Administration, and Department of Defense at more than 900 airports. The system is designed to objectively measure the clarity of the air versus the more subjective evaluations of human observations. The system provides real-time data for airport visibility.

The visibility sensor, instead of measuring how far one can see, measures the clarity of the air using a forward-scatter visibility meter. The clarity is then converted to what would be perceived by the human eye using a value called Sensor Equivalent Visibility (SEV). Values derived from the sensor are not affected by terrain, location, buildings, trees, lights, or cloud layers near the surface. The amount of moisture, dust, snow, rain, and particles in the light beam will affect the amount of light scattered. The sensor transmits 1-min values based on rolling 10-min periods. Hourly visibility range data are available only at a quantized resolution of 18 binned ranges with a visual range of up to 10 miles. The value provides a generally accurate and representative visibility measurement within a 2 to 3 mile radius of the site. The forward scatter meter was found to correlate fairly well with extinction coefficient measurements from the Optec Transmissometer (National Weather Service, 1998).

Visibility data from the ASOS network is reported in terms of visual range in increments of 1/4 to 1 statute mile. Visual range conditions exceeding 10 miles are truncated to 10 miles for real-time reporting purposes. Data is not extensively archived at ASOS locations; however, researchers are able to download the raw data directly from certain sites. In addition, since 1998, the raw visibility data (including light extinction measurements corresponding to visual ranges exceeding 10 miles) have been archived for a number of sites. Visual range measurements beyond 10 miles may be used to derived particulate matter concentrations except in clean environments. These data are available from the National Climatic Data Center.

The largest monitoring network that includes both visibility and aerosol conditions is the Interagency Monitoring of Protected Visual Environments (IMPROVE) network. This network was formed in 1987 as a collaborative effort between Federal, regional, and state organizations responsible for protection of visibility in the 156 mandatory Class I Federal areas (national parks and wilderness areas) and other areas of interest to land management agencies, states, tribes, and other organizations (National Park Service, 1998; U.S. Environmental Protection Agency, 1996a; U.S. Environmental Protection Agency, 1995b; Eldred et al., 1997; Perry et al., 1997; Sisler and Malm, 2000; U.S. Environmental Protection Agency, 1999b). It is predominantly a rural-based network with more than 140 sites across the country. The primary monitoring objectives of the IMPROVE program are to document current visibility conditions in the mandatory Class I areas, to identify anthropogenic chemical species and emission sources of visibility impairment through the collection of speciated $PM_{2.5}$ data, and to document long-term trends for assessing progress towards elimination of anthropogenic visibility impairment. The IMPROVE network has also been involved in visibility related research, including the advancement of visibility monitoring instrumentation and analysis techniques and visibility monitoring and source attribution field studies (National Park Service, 1998; Evans and Pitchford, 1991).

Visibility monitoring under the IMPROVE network can be divided into three categories: aerosol, optical, and scene. Twenty-four hour $PM_{2.5}$ and PM_{10} aerosol samples are collected by filters at least every third day. The $PM_{2.5}$ samples are analyzed to determined the mass concentration of the major particulate constituents (sulfates, nitrates, organic carbon compounds, elemental carbon, chlorides, and crustal elements) and for elements that indicate sources of visibility-impairing particles (trace elements and ions). Optical monitoring provides a direct measurement of light scattering and absorption. Color photographic imaging documents the appearance of the scene under a variety of air quality and illumination conditions (U.S. Environmental Protection Agency, 1999b). It is anticipated that all data generated by the IMPROVE network will be added to the AIRS database.

The U.S. Environmental Protection Agency has deployed a new national monitoring network (Federal Reference Method Monitoring network) designed to assess $PM_{2.5}$ concentrations and composition. There are over 1,000 monitoring sites in operation and many sites report data to the Aerometric Informational Retrieval System (AIRS). Analyses of these data are expected to provide a more complete understanding of visibility conditions, in particular urban visibility, across the country. The $PM_{2.5}$ monitoring effort has been coordinated with visibility monitoring efforts currently in place to maximize the benefits of all of the monitoring programs (U.S. Environmental Protection Agency, 1997b; U.S. Environmental Protection Agency, 2000b; U.S. Environmental Protection Agency, 2001).

The Northeast States for Coordinated Air Use Management (NESCAUM) has established a real-time visibility monitoring network (CAMNET) using digital photographic imaging. Currently, there is digital photographic imaging for five urban locations (Boston, MA; Burlington, VT; Hartford, CT; Newark, NJ; and New York City, NY), and two rural locations (Acadia National Park, ME and Mt. Washington, NH). The visibility images are updated every 15 minutes. Near real-time air pollution and meteorological data are updated every hour. Archived images will be available for studies of the visual effects of particulate matter air pollution in the Northeast. CAMNET may be accessed at www.hazecam.net (Northeast States for Coordinated Air Use Management, 2002; Leslie, 2001).

The Midwest Regional Planning Organization, in cooperation with a number of other groups, has also developed a real-time visibility camera network (hazecam). The camera network includes several urban (Chicago, IL; Indianapolis, IN; and Cincinnati, OH) and rural locations (Seney NWR, MI; Mayville, WI; and Isle Royale National Park, MI/Grand Portage, MN). The Midwest hazecam can be found at http://www.mwhazecam.net.

4.3.6 Visibility Impairment: Trends and Current Conditions

In the United States, visibility impairment is caused by particles primarily composed of sulfates, nitrates, organic compounds, carbon soot, and crustal dust. Visibility is best in Alaska and the western Great Basin. Moderate levels of light extinction are common on the Pacific Coast, including the western slopes of the Sierra Nevadas in California and the Cascade Range in Oregon and Washington. Visibility is most impaired in the areas encompassing and adjacent to the Ohio and Tennessee River Valleys. Visibility gradually improves along the Atlantic seaboard northeast of New York City (Watson, 2002). Estimates of natural visibility for the eastern and western United States are 26 ± 7 Mm^{-1} natural extinction, 12 Mm^{-1} for clean air and 17 ± 2.5 Mm^{-1} natural extinction, 11 Mm^{-1} for clean air, respectively (Watson, 2002).

4.3.6.1 Trends in Visibility Impairment

Trends in visibility impairment or haziness often are used as indicators of trends in fine particles mass. Observations of visual range, obtained by the National Weather Service and available through the National Climatic Data Center of the National Oceanic and Atmospheric Administration provide one of the few truly long-term, daily records of impairment related to air pollution. After some manipulation including correction for relative humidity effects, the visual range data can be used as an indicator of fine mode particle pollution. The data reduction process and analyses of resulting trends have been reported by Schichtel et al. (2001), Husar et al. (1994), Husar and Wilson (1993), and Husar et al. (1981).

There are many statistical approaches to estimating trends. These approaches include simple correlation and regression analyses, time series analyses, and methods based on non-parametric statistics. A discussion and comparison of the methods for the detection of linear trends is provided in Hess et al. (2001). Schimek (1981) provides a discussion of nonlinear trends. In its annual air quality trends report, the U.S. Environmental Protection Agency characterized trends using a non-parametric regression analysis approach commonly referred to as the Theil test (U.S. Environmental Protection Agency, 1998; Hollander and Wolfe, 1973).

Regional Trends and Class I Areas

The two largest contributors to visibility impairment are sulfates and carbon-based particles. In the east, sulfates are responsible for 60 to 86% of the visibility impairment. The sulfate contribution decreases further west but is still responsible for between 25 to 50% of the visibility impairment. Carbon-based particles are responsible for 10 to 18% of the visibility impairment in the East and 25 to 40% in the West. Nitrates account for only 7 to 16% of the light extinction in the East but are responsible for between 5 to 45% of the light extinction in the West. Crustal material can be a major contributor in the West, accounting for 5 to 25% of the light extinction. Elemental carbon also is contributor to light extinction but to a much lesser degree (U.S. Environmental Protection Agency, 2001).

The U.S. Environmental Protect Agency designated five regional groupings as part of the regional haze program. The regions are Northeast (Mid-Atlantic/Northeast Visibility Union), Southeast (Visibility Improvement State and Tribal Association of the Southeast), Central (Central States Regional and Air Partnership), Midwest (Midwest Regional Planning Organization), and West (Western Regional Air Partnership). The regional groupings serve as concensus organizations comprised of states, tribes, and federal agencies coordinating the implementation of the regional haze rule.

Using hourly prevailing daytime visibility data from human observations at weather stations, Schichtel et al. (2001) observed that haziness declined approximately 10% across the United States between 1980 and 1995. The decrease in haziness was highest in the southeastern United States with a 20% decrease in the 90th percentile light extinction and a 12% decrease in the 75th percentile over the 15 year period. There was a 17% decrease in the 90th percentile and a 9% decrease in the 75th percentile over the eastern United States. Over the eastern United States, haziness was greatest during the summer months. The greatest visibility impairment was adjacent to the Appalachian Mountains in Tennessee and the Carolinas (extinction coefficient of > 0.2 km^{-1} equivalent to 6 miles). During the cold season, elevated haze (extinction coefficient of > 0.2 km^{-1}) was seen between the Great Lakes and the Ohio River Valley, over the Gulf States between Texas and Florida, along the coast from North Carolina to New Jersey, and along the Pacific coast, particularly central and south California.

Visibility impairment or haziness in the southeastern United States from sulfate emissions is greatest in the humid summer months because of the ability of sulfate to absorb atmospheric water vapor. Summer haziness increased in the southeastern United States from the 1950s to 1980 along with increasing SO_2 emissions. A statistically significant increase in summer sulfate concentrations was noted in two Class I areas in the eastern United States (Shenandoah and the Great Smoky Mountains) from 1982 to 1992 (Eldred et al., 1993; Cahill et al., 1996). During that time, the majority of the Southwest showed decreasing sulfur concentrations (Eldred et al., 1993; Eldred and Cahill, 1994). Increasing summer sulfate concentrations were later shown at those two locations by Iyer et al. (2000).

Limited visibility measurements are available for the upper Midwest region (Illinois, Indiana, Michigan, Ohio, and Wisconsin and the tribal lands located in the states). The Midwest Regional Planning Organization conducted an initial assessment of the regional haze problem in this region using existing reports and available air quality data for four major urban areas (St. Louis, Chicago, Detroit, Cincinnati) and Class I areas. The “worst” and “best” visibility days occur throughout the year. Particulate sulfates were the major contributors to light extinction during the summer months, and nitrates dominated on the worst visibility days during the winter and fall in both urban and Class I areas. Organics also were significant contributors to light extinction in urban areas. Higher $PM_{2.5}$ concentrations were correlated with poorer visibility in the southern portion of the regional (Midwest Regional Planning Organization, 2001).

The U.S. Environmental Protection Agency’s National Air Quality and Emission Trends Report summarized an estimated of the regional trends and current conditions in 35 Class I areas and one urban area (Washington, DC), using chemical concentrations data from the IMPROVE network (U.S. Environmental Protection Agency, 2001). The visibility trends analysis is an aggregate of 10 eastern Class I areas and 26 western Class I areas. Trends were presented for annual average values for the clearest (“best”) 20% , middle (“typical”) 20%, and haziest (“worst”) 20% of the days monitored each year. The visibility trends, given in changes in deciview values, for the eastern and western sites are illustrated in Figures 4-39a and 4-39b. From the figures it can be seen that the haziest days in the West are equivalent to the best days in the East. In the East, there was a 16% (1.5 deciview) improvement in haziness on the clearest

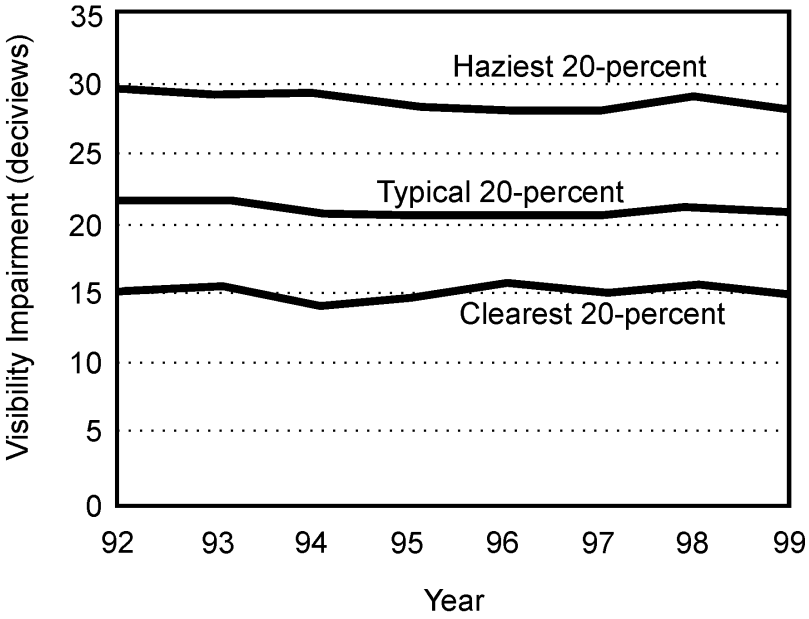


Figure 4-39a. Aggregate visibility trends (in deciviews) for 10 eastern Class 1 areas.

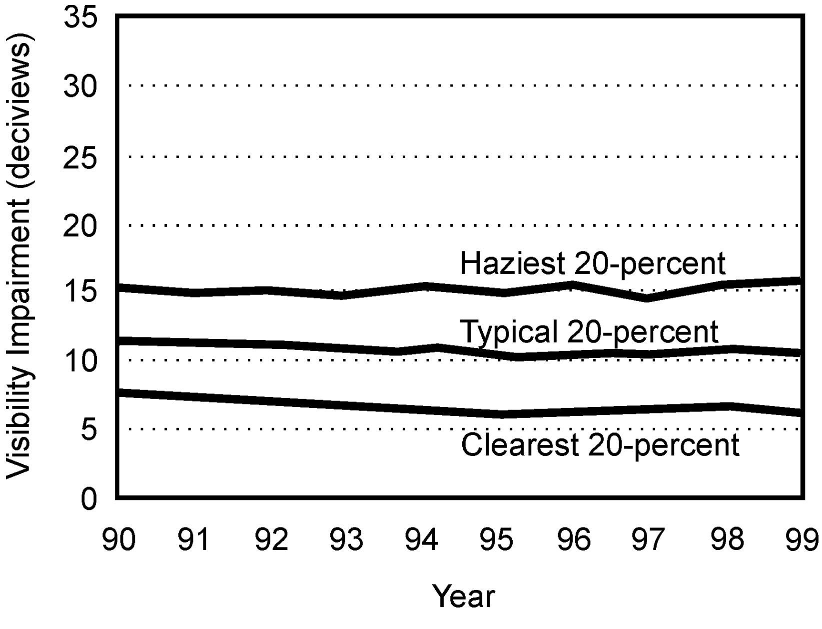


Figure 4-39b. Aggregate visibility trends (in deciviews) for 26 western Class 1 areas.

Source: U.S. Environmental Protection Agency (2001).

days since 1992. Improvements in visibility were noted in the East for the haziest days; however, based on monitoring data for 1999, visibility remains significantly impaired, with a visual range of 23 km for the haziest days compared to a mean visual range of 84 km for the clearest days. A 25% and a 14% improvement in visibility impairment were seen for the clearest and middle days in the West, respectively; whereas conditions for the haziest days degraded by 18.5% (1.7 deciviews) between 1997 and 1999, but were relatively unchanged compared to 1990 conditions (U.S. Environmental Protection Agency, 2001).

Figures 4-40a and 4-40b illustrate aggregate trends in aerosol light extinction, including trends by major aerosol component for the haziest 20% of days monitored for the 10 eastern Class I areas from 1992 to 1999 and the haziest 20% of days monitored for the 26 western Class I areas from 1990 to 1999. The report also includes a number of maps characterizing aerosol light extinction and key components at 36 IMPROVE sites (all rural except Washington, DC) for 1997 through 1999 (U.S. Environmental Protection Agency, 2001).

Urban Trends

Most of the available visibility measurements, with the exception of the airport visual range measurements, focus on the impact of pollution on visibility in scenic vistas and regional haze (Class I areas). Many urban metropolitan areas are monitoring daily visibility conditions. These findings are generally not available in a published form and may not distinguish between pollution- and weather-related effects. Although the EPA Regional Haze Rule addresses visibility impairment in Class I areas and calls for states to establish goals for improving visibility in these areas and to develop long-term strategies for reducing emissions of air pollutants that cause visibility impairment, the steps states take to implement the regulation will also improve visibility and health in broad areas across the country.

Kleeman et al. (2001), citing previously published studies, provided an historical description of visibility conditions in Southern California from the early 1930s. Based on airport observation data for 1932 to 1949, visibility conditions began to decrease in Los Angeles with the advent of industrialization and population growth. Visibility conditions were worse during the 1940s than the 1930s, and the lowest visibility conditions occurring between 1944 and 1947. During this period, there was nearly a complete loss of extremely good visibility days. Between

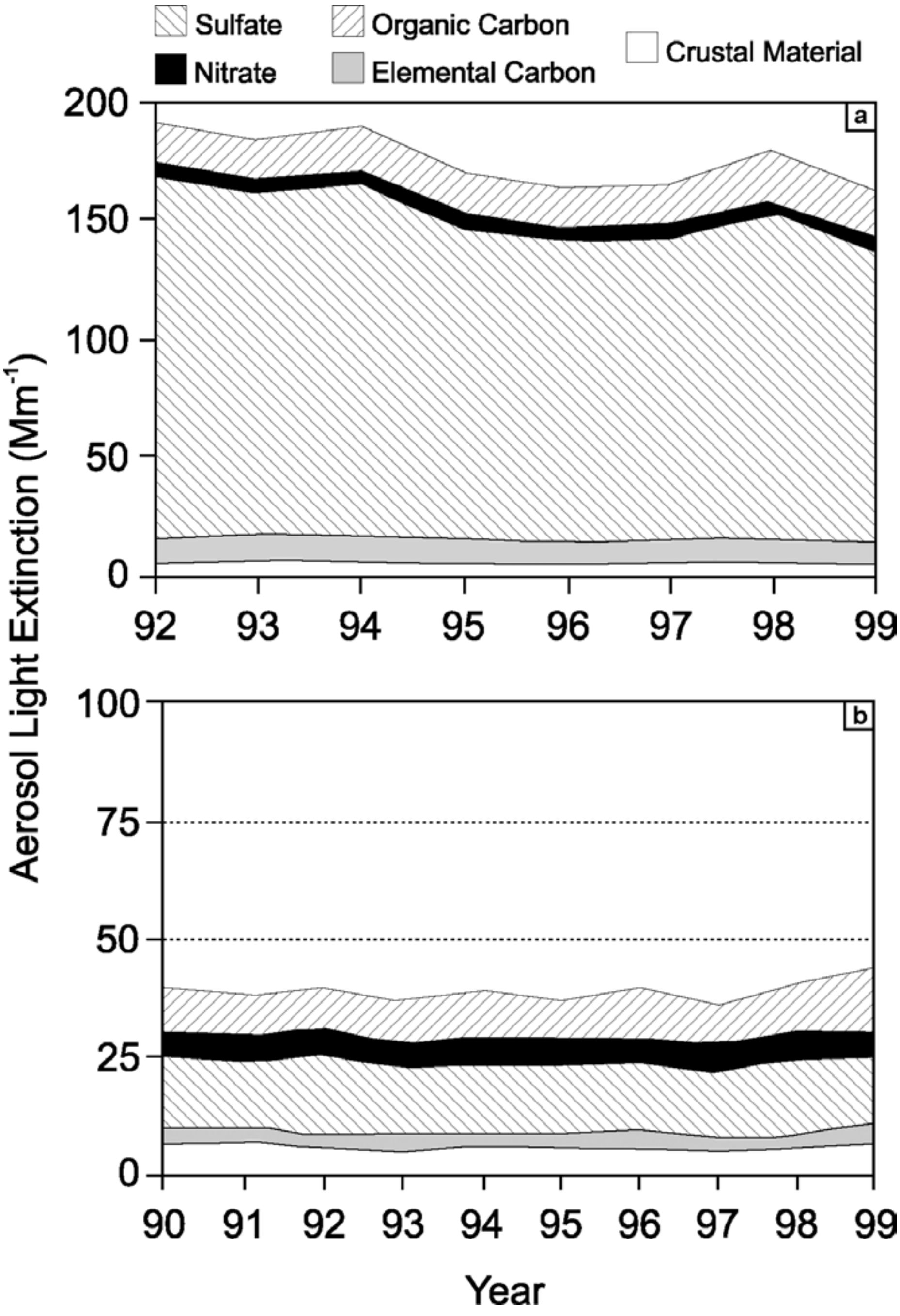


Figure 4-40. (a) Eastern class I area aggregate trends in aerosol light extinction on the 20% haziest days, including trends by major aerosol component; (b) Western class I area aggregate trends in aerosol light extinction on the 20% haziest days, including trends by major aerosol component.

Source: U.S. Environmental Protection Agency (2001).

1943 and 1947, the number of extremely good visibility days during the summer season dropped to 0.2% from 21%.

Between 1950 and 1961, deteriorating visibility conditions extended eastward from Los Angeles along the corridor adjacent to the foothills of the San Gabriel and San Bernardino Mountains. The visual range in the areas nearest Los Angeles was ≤3 miles for more than 140 days per year when the relative humidity was < 70%. Further east of Los Angeles, past Ontario and San Bernardino, the visibility was ≤ 3 miles for 110 days per year during the same time period.

Improvements in visibility conditions have been made since the 1970s. The largest have been made in the western Los Angeles Basin. In Ontario, the average number of days per year when visual range was greater than 10 miles was 99 between 1976 and 1978 and increased to 113 between 1988 and 1990 (Kleeman et al., 2001). In contrast to the Los Angeles Basin and Ontario, Denver and surrounding areas have experienced high pollution episodes since the 1970s. Climate changes trap cooler air under a cover of warm air causing the pollution to remain stagnant over the area producing a brown cloud comprised of a variety pollutants including nitrogen and sulfur oxides, and the grit and dust.

Debate over the cause of the increasing pollution in the Denver area and the controversy over converting coal-fired power plants to a cleaner natural gas system led to initiation of the 1973 Denver Air Pollution Study, 1978 Denver Winter Haze Study, 1987-1988 Metro Denver Brown Cloud Study, and the 1993 Denver Brown Cloud Modeling Study. In 1990, in an effort to improve air quality, Denver adopted a visibility standard of 0.076/km (units of atmospheric extinction per kilometer; 20.1 deciviews) averaged over 4 h. While this is a step towards reducing air pollution, the Denver region still exceeds the visibility standard 50 to 80 times per year (Lloyd, 2002).

A major air quality study was conducted in Phoenix, AZ, during the fall and winter of 1988 to 1990 to address degrading visibility conditions in Phoenix and other urban areas. The objectives were to (1) develop a data base of visibility, air quality, and meteorological measurements; (2) establish quantitative relationships between light extinction and emission sources; and (3) evaluate measurement systems for short-term and long-term monitoring in Phoenix. The major contributors to light extinction in Phoenix were residual wood burning, primary mobile source emissions, and secondary ammonium nitrate (Chow et al., 1990).

The Arizona Department of Environmental Quality has conducted optical measurements of visibility in Tucson since 1993 and in Phoenix since 1994. The measurements are divided into the mean of the "dirtiest" 20% of all hours, the mean of all hours, and the mean 20% "cleanest" of all hours for the entire day and for the 5:00 to 11:00 a.m. period. Figures 4-41a,b represent the trends in visibility conditions from 1993 to 2001 for Tucson and from 1994 to 2001 for Phoenix. Visibility on the dirtiest days in the Phoenix metropolitan area has not changed since visibility monitoring started; but, visibility on the best days has significantly degraded. There is a seasonally related effect on visibility in Phoenix: the mean and the dirtiest 20% of all hourly light extinction are more pronounced during the winter and fall months (Arizona Department of Environmental Quality, 2002). Daytime visibility is worst during the morning. Samples taken from 1994 to 1996 showed that organic and elemental carbon dominated visibility impairment during the dirtiest and cleanest days, whereas ammonium nitrate was an important contributor during the 20% dirtiest days (Neuroth and Heisler, 2000).

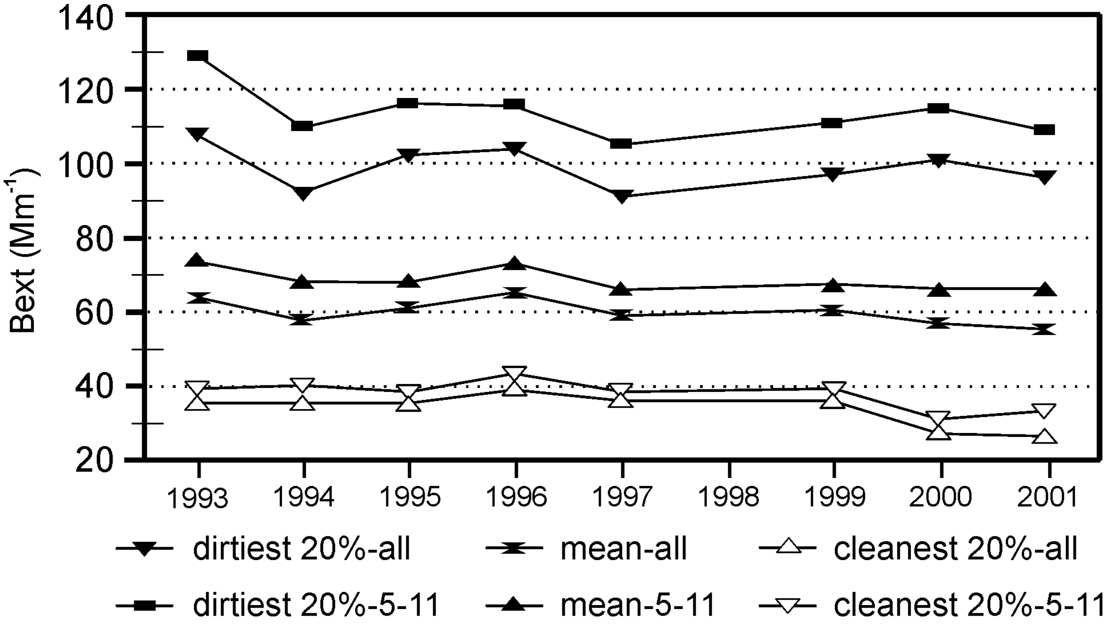


Figure 4-41a. Light extinction trends in Tucson, Arizona from 1993 to 2002.

Source: Arizona Department of Environmental Quality (2002).

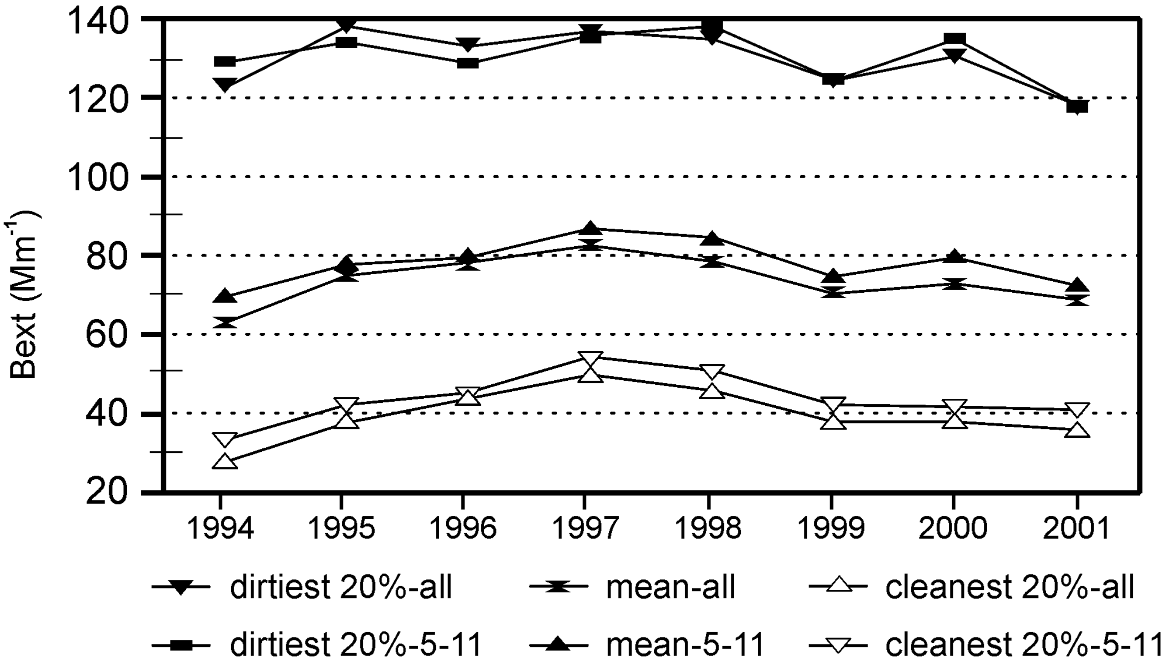


Figure 4-41b. Light extinction trends in Phoenix, Arizona from 1994 to 2001.

Source: Arizona Department of Environmental Quality (2002).

The State of Virginia compared visibility trends at five locations both with and without pre-1948 airport visual range data. Average annual airport visual-range-data from Roanoke (1936 to 1998), DC Reagan National (1930 to 1998), Richmond (1942 to 1998), Lynchburg (1935 to 1998), and Elkins, WV (1936 to 1994) were used in the analysis. Their findings indicate that trends in visibility conditions were dependent on the baseline year used for visibility measurements. When airport visual range data from 1948 are used as the baseline data for visibility conditions, the trend in visual range shows declining conditions for all sites. When pre-1948 data are included in the analysis, visibility conditions basically are unchanged or improved (except for Elkins). When 1948 data are used as the baseline for visibility trends measurements, visual range decreases at all locations. Average annual visual ranged varied between 7+ miles and 8+ miles for all sites (Virginia Climate Advisory, 2000).

4.4.6.2 Current Conditions

Current visibility conditions have been well-characterized for Class I areas using updated data from the IMPROVE network (U.S. Environmental Protection Agency, 2001; Malm et al., 2000; IMPROVE, 1998). During recent decades, daytime visibility conditions at all major airports throughout the United States were recorded hourly by human observation. These data were used to determine current visibility conditions and visibility trends in the United States, as well as the spatial distribution of visibility conditions (Trijonis et al., 1991). The use of human observation is being replaced by an automated observing system, the Automated Surface Observing System (ASOS). More than 900 airports are currently commissioned. In addition, the U.S. Environmental Protection Agency has deployed a new national monitoring network to assess $PM_{2.5}$ concentrations and composition.

More detailed information on visibility conditions for urban and suburban areas will become more widely available as data from the national $PM_{2.5}$ speciation monitoring network and the ASOS airport visibility network are further analyzed. Efforts are currently underway to develop a web-based system to allow the use of the high resolution ASOS data in air quality monitoring and assessment programs. The objectives are to collect and quality control an archive of the ASOS visibility data, to deliver processed hourly visibility data to public and air quality communities, and to use the web-based system to support the acquisition and dissemination of visibility data (Falke, 2001).

4.3.7 Economics of Particulate Matter Visibility Effects

Society recognizes the need to impose remedies for repairing and preventing further anthropogenic pollutant-related effects on visibility conditions. Various methods have been utilized to help determine the economic valuation of changes in visibility. Where possible, direct economic valuation can be determined using marketplace cost estimates. Avoided-cost methods estimate the costs of pollution by using the expenditures that are made necessary by pollution damage. As an example, if ambient levels of PM result in increased frequency of building cleaning or repainting, the appropriately calculated increase in these costs is a reasonable estimate of true economic damage. Benefits associated with reductions in the pollution levels are then represented by the avoided costs of these damages.

Estimating the benefits of clear skies is a more difficult and less precise exercise because, although the public values aesthetic views, they are not directly bought and sold in the marketplace. However, there are several methods available to economists to estimate the economic impact of these kinds of changes in environmental conditions (Freeman, 1993). These methods include hedonic valuation or pricing, contingent valuation and contingent choice, and travel cost (Johnson and Desvousges, 1997; Hanley and Spash, 1993). The primary methods used to date for valuation of visibility have been the hedonic price and contingent valuation methods (Hanley and Spash, 1993); but this is not an exact science, and there are still issues and limitations associated with each of these methods.

Hedonic pricing can be used to estimate economic valuations for environmental effects that have a direct effect on market values. It relies on the measurement of differentials in property values under various environmental quality conditions including air pollution and environmental amenities, such as aesthetic views. The hedonic method works by analyzing the way that market prices change with changes in environmental quality. Part of the economic costs imposed by PM-related reductions in visibility can be estimated by looking at the differences in sales price between otherwise identical houses that have different degrees of visibility impairment.

The contingent valuation method (CVM) is the most widely used method for estimating value changes in both visibility and ecosystem functions (Hanley and Spash, 1993; Chestnut, 1997; Watson and Chow, 1993). The CVM creates hypothetical markets for goods and services that have no market-determined price. For determination of visibility evaluation, individuals are shown photographs with perceivable differences in visibility levels. Carefully structured surveys are administered to estimate the amount of compensation equivalent to a given change in environmental quality or, equivalently, how much an individual would be willing to pay (WTP) for improvements in environmental quality or willing to accept (WTA) existing conditions without further deterioration. There is an extensive scientific literature and body of practice on both this theory and technique; however, there are still concerns about the use of this technique for quantitative purposes.

The travel-cost method estimates can be used to estimate the value of recreational benefits of an ecosystem based on the environmental quality at the site. The travel-cost method uses information on actual behavior rather than responses to hypothetical scenarios. The time and travel expenses incurred to visit a site represents the price of access to the site. The willingness to pay to maintain the site is determined by the number of times the individual visits the site at different travel costs.

The effects of PM on visibility may differ widely between urban residential and recreational areas. Therefore, separate estimates are needed to account for impact associated with changes in visibility in residential and recreational (Class I) areas. Chestnut and Dennis (1997) compared the findings of the more recent studies on the economic impact of changes in regional haze using the contingent valuation method in residential areas in several eastern cities and in Los Angeles and San Francisco and using the hedonic value method in Los Angeles and San Francisco. The findings of the contingent valuation studies are discussed in Table 4-16. Findings using the contingent and hedonic methods of valuation for Los Angeles and San Francisco are compared in Table 4-17.

Using the contingent valuation method, Chestnut and Rowe (1990) found that 83% of those individuals responding to a survey on visibility were willing to pay to improve visibility in the National Parks. Survey participants were selected from California, Arizona, Missouri, New York, and Virginia. The National Parks from three regions (California, southwestern United States, and southeastern United States) were considered in different versions of the survey. The survey included questions on past and future visitations to national parks, potential pollution effects from human activities outside of the park, three hypothetical visibility scenarios, socioeconomic characteristics, and various photographic presentations of visibility conditions within the parks. Higher responses were noted for residents residing in the state or region where the national park was located; responses for males and the elderly were generally lower and there was a direct correlation between household income and the response.

Using the results from the Chestnut and Rowe (1990) study, Chestnut and Dennis (1997) calculated an extinction coefficient of 85 for in-state residents and 50 for out-of-state residents. These extinction coefficients were suggested to represent an annual willingness to pay per household of $15 and $9 for a 20% improvement in visual range.

TABLE 4-16. RESIDENTIAL VISIBILITY CONTINGENT VALUATION STUDY RESULTS

City	Mean WTP ($1994)	Starting-Ending Visual Range (VR) (miles)	Extinction Coefficient	WTP for 20% Change in VR ($)	Reference
Atlanta	Unadj. $44	17.6 - 20	346	$63	McClelland et al. (1993)
Chicago	Partial $28		222		
	Full $20		159		
Chicago	−$361	9 - 4	416	$76	Tolley et al. (1986)
	$346	9 - 18			
	$430	9 - 30			
Atlanta	−$301	12 - 7	469	$86	
	$289	12 - 22			
	$432	12 -32			
Boston	−$222	18 - 13	422	$77	
	$212	18 - 28			
	$262	18 - 38			
Mobile	−$240	10 - 5	312	$57	
	$257	10 - 20			
	$302	10 - 30			
Washington, DC	−$356	15 - 10	635	$116	
	$366	15 - 25			
	$465	15 - 35			
Cincinnati	−$88	9 - 4	120	$22	
	$87	9 - 19			
	$98	9 - 29			
Miami	−$152	13 - 8	256	$47	
	$136	13 - 19			
	$160	13 - 29			
Cincinnati	$198	11.4 - 16.4	602	$110	Rae (1983)

Source: Chestnut and Dennis (1997).

TABLE 4-17. RESIDENTIAL VISIBILITY VALUATION STUDY RESULTS FOR LOS ANGELES AND SAN FRANCISCO

City	Method	Mean WTP	Starting-Ending Visual Range (VR) (miles)	Extinction Coefficient	WTP for 20% Change in VR	Reference
Los Angeles	CVM	$130	2 - 12	119	$22	Brookshire et al. (1979)
		$333	2 - 28			
		$183	12 - 28	1328	$242	
	Property Value				$245-647	Trijonis et al. (1984)
San Francisco	CVM	$211	18.6 - 16.3			Loehman et al. (1985)
		$124	16.3 - 18.3			
	Property Value				$496 - 552	Trijonis et al. (1984)

Adapted from: Chestnut and Dennis (1997).

4.4 PARTICULATE MATTER EFFECTS ON MATERIALS

Effects of air pollution on materials are related to both aesthetic appeal and physical damage. Studies have demonstrated that particles, primarily consisting of carbonaceous compounds, cause soiling of commonly used building materials and culturally important items, such as statutes and works of art. Physical damage from the dry deposition of air pollutants, such as PM (especially sulfates and nitrates) and SO_2, and the absorption or adsorption of corrosive agents on deposited particles also can result in the acceleration of naturally occurring weathering processes of man-made building and cultural materials.

In the atmosphere, PM may be “primary,” existing in the same form in which it was emitted, or “secondary,” formed by the chemical reactions of free, absorbed, or dissolved gases. The major constituents of atmospheric PM are sulfate, nitrate, ammonium, and hydrogen ions; particle-bound water; elemental carbon; a great variety of organic compounds; and crustal material. A substantial fraction of the fine particle mass, particularly during the warmer months, is secondary sulfate and nitrate. Sulfates may be formed by the gas-phase conversion of SO_2 to H_2SO_4 by OH radicals and aqueous-phase reactions of SO_2 with H_2O_2, O_3, or O_2. During the day, NO_2 may be converted to nitric acid (HNO_3) by reacting with OH radicals. Nitrogen dioxide also can be oxidized to HNO_3 by a sequence of reactions initiated by O_3. A more detailed discussion of the atmospheric chemistry of PM appears in Chapter 2 of this document.

4.4.1 Corrosive Effects of Particles and Sulfur Dioxide on Man-Made Surfaces

Limited new studies have been published that better define the role of air pollution in materials damage. This section briefly summarizes information on exposure-related effects on materials and sulfur-containing pollutants (formed by the chemical reactions of SO_2 with other atmospheric pollutants) addressed in the 1996 PM AQCD (U.S. Environmental Protection Agency, 1996a) and presents relevant information published since completion of that document. The effects of nitrates on man-made building materials and naturally occurring cultural materials were discussed in the earlier EPA Nitrogen Oxides Criteria Document (U.S. Environmental Protection Agency, 1993).

4.4.1.1 Metals

Metals undergo natural weathering processes in the absence of environmental pollutants. The additive effect of pollutants on the natural weathering processes depend on the nature of the pollutant, the deposition rate (the uptake of a pollutant by the material's surface), and the presence of moisture. The influence of the metal-protective corrosion film, the presence of other surface electrolytes, the orientation of the metal surface, the presence of surface moisture, and the variability in the electrochemical reactions will also contribute to the effect of pollutant exposure on metal surfaces.

Several studies demonstrate the importance of the duration of surface wetness (caused by dew and fog condensation and rain) on metals. Surface moisture facilitates the deposition of pollutants, especially SO_2, and promotes corrosive electrochemical reactions on metals (Haynie and Upham, 1974; Sydberger and Ericsson, 1977). Of critical importance is the formation of hygroscopic salts on the metal that increases the duration of surface wetness and, thereby, enhances the corrosion process.

Pitchford and McMurry (1994) and Zhang et al. (1993) demonstrated particle-size-related effects of relative humidity. The effect of temperature on the rate of corrosion is complex. Under normal temperature conditions, temperature would not have an effect on the rate of corrosion; but when the temperature decreases, the relative humidity increases and the diffusivity decreases. The corrosion rate decreases as the temperature approaches freezing because ice prohibits the diffusion of SO_2 to the metal surface and minimizes electrochemical processes (Haynie, 1980; Biefer, 1981; Sereda, 1974).

The metal protective corrosion film (i.e., the rust layer on metal surfaces) provides some protection against further corrosion. The effectiveness of the corrosion film in slowing down the corrosion process is affected by the solubility of the corrosion layer and the concentration and deposition rate of pollutants. If the metal-protective corrosion film is insoluble, it may add some protection against acidic pollutants. An atmospheric corrosion model that considers the formation and dissolution of the corrosion film on galvanized steel was proposed by Spence et al. (1992). The model considers the effects of SO_2, rain acidity, and duration of wetness on the rate of corrosion. Although the model does not specifically characterize particle effects, the contribution of particulate sulfate was considered in model development.

Whether suspended particles actually enhance the corrosion of metals is not clear. Several studies suggest that suspended particles will promote the corrosion of metals (Goodwin et al., 1969; Barton, 1958; Sanyal and Singhania, 1956; Baedecker et al., 1991); however, other studies have not demonstrated a correlation between particle exposure and metal corrosion (Mansfeld, 1980; Edney et al., 1989). Walton et al. (1982) suggested that catalytic species within several species in fly ash promote the oxidation of SO_x to a corrosive state. Still other researchers indicate that the catalytic effect of particles is not significant and that the corrosion rate is dependent on the conductance of the thin-film surface electrolytes during periods of wetness. Soluble particles likely increase the solution conductance (Skerry et al., 1988; Askey et al., 1993). The corrosion of most ferrous metals (iron, steel, and steel alloys) is increased by increasing SO_2 exposure. Steels are susceptible to corrosion when exposed to SO_2 in the absence of protective organic or metallic coatings. Studies on the corrosive effects of SO_2 on steel indicate that the rate of corrosion increases with increasing SO_2 and is dependent on the deposition rate of the SO_2 (Baedecker et al., 1991; Butlin et al., 1992a). The corrosive effects of SO_2 on aluminum is exposure-dependent, but appears to be insignificant (Haynie, 1976; Fink et al., 1971; Butlin et al., 1992a). The rate of formation of the patina (protective covering) on copper can take as long as five years and is dependent on the SO_2 concentration, deposition rate, temperature, and relative humidity (Simpson and Horrobin, 1970). Further corrosion is controlled by the availability of copper to react with deposited pollutants (Graedel et al., 1987).

Butlin et al. (1992a), Baedecker et al. (1991), and Cramer et al. (1989) reported an average corrosion rate of 1 µm/year for copper; however, less than a third of the corrosion was attributed to SO_2 exposure, suggesting that the rate of patina formation was more dependent on factors other than SO_2. A report by Strandberg and Johansson (1997) showed relative humidity to be the primary factor in copper corrosion and patina formation. The results of the studies on particles and SO_2 corrosion of metals are summarized in Table 4-18.

4.4.1.2 Painted Finishes

Exposure to air pollutants affects the durability of paint finishes by promoting discoloration, chalking, loss of gloss, erosion, blistering, and peeling. Evidence exists that indicates particles can damage painted finishes by serving as carriers for corrosive pollutants (Cowling and Roberts, 1954) or by staining and pitting of the painted surfaces (Fochtman and Langer, 1957; Wolff et al., 1990).

The erosion rate of oil-based house paint has been reported to be enhanced by exposure to SO_2 and high humidity. In a study by Spence et al. (1975), an erosion rate of 36.71 ± 8.03 µm/year was noted for oil-based house paint samples exposed to SO_2 (78.6 $\mu g/m^3$), O_3 (156.8 $\mu g/m^3$), and NO_2 (94 $\mu g/m^3$), and low humidity (50%). The erosion rate increased with increased SO_2 and humidity. The authors concluded that SO_2 and humidity accounted for 61% of the erosion. Acrylic coil coating and vinyl coil coating shows less pollutant-related erosion. Erosion rates range from 0.7 to 1.3 µm/year and 1.4 to 5.3 µm/year, respectively. Similar findings on SO_2-related erosion of oil-based house paints and coil coatings have been reported by other researchers (Davis et al., 1990; Yocom and Grappone, 1976; Yocom and Upham, 1977; Campbell et al., 1974). Several studies suggest that the effect of SO_2 is caused by its reaction with extender pigments such as calcium carbonate and zinc oxide (Campbell et al., 1974; Xu and Balik, 1989; Edney, 1989; Edney et al., 1988, 1989). However, Miller et al. (1992) suggested that calcium carbonate acts to protect paint substrates. Another study indicated that exposure to SO_2 can increase the drying time of some paints by reacting with certain drying oils and will compete with the auto-oxidative curing mechanism responsible for crosslinking the binder (Holbrow, 1962).

TABLE 4-18. CORROSIVE EFFECTS OF PARTICULATE MATTER AND SULFUR DIOXIDE ON METALS

Metal	Exposure Conditions	Comments	Source
Mild Steel Galvanized Steel	Specimens exposed to SO_2 and O_3 under natural and artificial conditions, and to NO_2 under natural conditions. SO_2 concentrations ranged from 2.1 to 60 µg/m^3. Annual average concentrations were about 20 µg/m^3. Meteorological conditions were unaltered. Specimens exposed at 29 sites for 2 years for mild steel and 1 y for galvanized steel.	Steel corrosion was dependent on long-term SO_2 exposure. The corrosion rate was about 50 µm/year for mild steel specimens for most industrial sites, but ranged from 21 to 71 µm/year. The corrosion rate ranged from 1.45 to 4.25 µm/year for galvanized steel. The authors concluded that rainfall also may have a significant effect on galvanized steel based on a corrosion rate of 3.4 µm/year seen at a very wet site.	Butlin et al. (1992a)
Zinc	Rolled zinc specimens exposed at various sites around the country (rural, industrialized, marine) for up to 20 years. Actual pollutant exposures not reported.	The highest corrosion rates were associated with industrialized environments and marine environments in direct contact with salt spray.	Showak and Dunbar (1982)
Zinc	Specimens exposed at 5 sites for 1 to 5 years. Average SO_2 concentrations ranged from 2 ± 4 to 15 ± 17 ppb (5.2 ± 10.4 to 39.3 ± 44.5 µg/m^3). PM concentrations ranged from 14 to 60 µg/m^3. Highest pollutant concentrations recorded at 1 year exposure site.	Average corrosion rate ranged from 0.63 to 1.33 µm/y. The highest corrosion was noted in the most industrialized area. However, the corrosion rates did not differ significant regardless of the SO_2 concentration, suggesting that SO_2 exposure may not be the dominant factor in zinc corrosion.	Baedecker et al. (1991) Cramer et al. (1989)
Carbon Steel Weathering Steel	See Baedecker et al. (1991) above for exposure conditions.	Average corrosion rate for samples exposed for 5 years ranged from 6.6 to 12.8 µm/year for carbon steel and 3.7 to 5.0 µm/year for weathering steel. Highest corrosion rate noted for samples exposed for 1 year.	Baedecker et al. (1991) Cramer et al. (1989)
Aluminum	See Baedecker et al. (1991) above for exposure conditions.	Corrosion rate was very low at all sites and ranged from 0.036 to 0.106 µm/year.	Baedecker et al. (1991)
Aluminum	See Butlin et al. (1992a) above for exposure conditions.	Corrosion greater on the under side of specimens, possibly because of lack of washoff and increased PM in area. Maximum corrosion rate was 0.85 µm/year. Pit depths of up to 72 µm were noted after 2 years of exposure.	Butlin et al. (1992a)

TABLE 4-18 (cont'd). CORROSIVE EFFECTS OF PARTICULATE MATTER AND SULFUR DIOXIDE ON METALS

Metal	Exposure Conditions	Comments	Source
Copper	See Baedecker et al. (1991) above for exposure conditions.	Average corrosion rate for 3- and 5-year exposures was about 1 µm/year but the soluble portion was less than a third of that which could be contributed to SO_2 exposure. Dry deposition of SO_2 was not as important in patina formation as wet deposition of H_+.	Baedecker et al. (1991)
Copper	See Butlin et al. (1992a) above for exposure conditions.	Majority of test sites showed a corrosion rate of 1 ± 0.2 µm/year. The corrosion rate was 1.48 µm/year at the site receiving the most rainfall. The lowest corrosion rate, 0.66 µm/year, was associated with low rainfall, low SO_2.	Butlin et al. (1992a)
Copper	Specimens exposed to 4 to 69 ppb (10.4 to 180.7 µg/m^3) and 1.0 ppm (2,618.7 µg/m^3) SO_2 for 20h at various relative humidities.	SO_2 had no effect on copper when relative humidity was $<75\%$. Increasing relative humidity increases patina formation in presence of trace SO_2. No SO_2-related effects were noted on copper specimens exposed to high SO_2 regardless of the percent relative humidity.	Strandberg and Johansson (1997)
Copper	Specimens exposed artificially to 0.49 ± 0.01 ppm (187 ± 3.8 µg/m^3) SO_2 for 4 weeks at 70 and 90% relative humidity.	Corrosive effect of SO_2 on copper increased with increasing relative humidity.	Eriksson et al. (1993)
Iron	Specimens from restorations of Acropolis monuments over many years. The oldest specimens were 142 years old. Other specimens used for monument restoration after 1950.	Specimens used after 1950s had an oxidation rate 25% greater than those specimens before 1950. The accelerated oxidation had a negative impact on the structure, producing a quicker formation of cracks inside the marble.	Zuburtikudis and Triantafyllou (2001)

4.4.1.3 Stone and Concrete

Numerous studies suggest that air pollutants can enhance the natural weathering processes on building stone. The development of crusts on stone monuments has been attributed to the interaction of the stone's surface with sulfur-containing pollutants, wet or dry deposition of atmospheric particles, and dry deposition of gypsum particles from the atmosphere. Because of a greater porosity and specific surface, mortars have a greater potential for reacting with environmental pollutants (Zappia et al., 1998). Details on these studies are discussed in Table 4-19. The stones most susceptible to the deteriorating effects of sulfur-containing pollutants are the calcareous stones (limestone, marble, and carbonated cement). Exposure-related damage to building stones result from the formation of salts in the stone that are subsequently washed away during rain events, leaving the stone surface more susceptible to the effects of pollutants. Dry deposition of sulfur-containing pollutants promotes the formation of gypsum on the stone's surface. Gypsum is a gray to black crusty material comprised mainly of calcium sulfate dihydrate from the reaction of calcium carbonate (calcite) in the stone with atmospheric SO_2 and moisture (relative humidities exceeding 65%) according to the following reaction.

$$CaCO_3 \text{ (marble)} + SO_3 + 2H_2O \rightarrow CaCO_4{\cdot}2H_2O + CO_2 \qquad (4\text{-}13)$$

The sulfate anions formed in the moist air reacts with the Ca^{+2} through diffusion processes forming the gypsum (Zuburtikudis and Triantafyllou, 2001). Approximately 99% of the sulfur in gypsum is sulfate because of the sulfonation process caused by the deposition of SO_2 aerosol. Sulfites also are present in the gypsum layer as an intermediate product (Sabbioni et al., 1996; Ghedini et al., 2000; Gobbi et al., 1998; Zappia et al., 1998). Gypsum is more soluble than calcite and is known to form on limestone, sandstones, and marble when exposed to SO_2. Gypsum also has been reported to form on granite stone by replacing silicate minerals with calcite (Schiavon et al., 1995). Gypsum occupies a larger volume than the original stone, causing the stone's surface to become cracked and pitted. The rough surface serves as a site for deposition of airborne particles. As the gypsum grows, it becomes loose and falls apart (Zuburtikudis and Triantafyllou, 2001).

TABLE 4-19. CORROSIVE EFFECTS OF PARTICULATE MATTER AND SULFUR DIOXIDE ON STONE

Stone	Exposure Conditions	Comments	Source
Vermont marble	Runoff water was analyzed from seven summer storms. SO_2 concentration stated to be low.	Between 10 to 50% of calcium in runoff water estimated from gypsum formation from dry deposition of SO_2.	Schuster et al. (1994)
Marble sandstone	Analysis of runoff water for five slabs test exposed to ambient conditions at a angle of 30° to horizontal.	Pollutant exposure related erosion was primarily caused by dry deposition of SO_2 and nitric acid between rain events and wet deposition of hydrogen ion. Recession estimates ranged from 15 to 30 µm/year for marble and 25 to 45 µm/year for limestone. A large portion of the erosion results from the reaction of CO_2 with the calcium in the stone.	Baedecker et al. (1992)
Limestone	Ambient air conditions. Exposure ranged from 70 to 1065 days. Averaged pollutant exposure ranged from 1.4 to 20.4 ppb (3.7 to 53.4 µg/m^3) SO_2; 4.1 to 41.1 ppb NO_x; 2.4 to 17.4 ppb (4.5 to 32.7 µg/m^3) NO_2; 10.1 to 25.6 ppb (19.8 to 50.2 µg/m^3) O_3.	Increased stone weight loss with increased SO_2. Rainfall did not significantly affect stone degradation. Stone loss associated with SO_2 exposure estimated to be 24 µm/year. Slight trend in decreasing stone loss with increasing length of exposure.	Webb et al. (1992)
Portland limestone White Mansfield dolomitic sandstone Monk's Park limestone	Experimental tablets exposed under sheltered and unsheltered ambient air conditions. Exposure for l and 2 years.	Significant correlations existed between the mean annual SO_2 concentration, rainfall volume, and hydrogen ion loading and the weight changes.	Butlin et al. (1992b)
Sandstones (calcite and noncalcite stones)	Ambient air; low concentrations of sulfates, SO_2, and nitrates; RH sufficient to produce condensation on stones rarely occurred.	Insignificant differences in erosion rate found between calcite and noncalcite sandstone. Moisture affected the rate of pollutant deposition and enhanced susceptibility to pollutant related erosion. Rain events given as primary factor affecting stone erosion. Pollutant related erosion judged to be insignificant.	Petuskey et al. (1995)
Limestones Sandstones Marble Granite Basalt	Ambient air; urban and rural locations in Mediterranean.	Crusts on stones were found to contain two layers; top layer, usually black in color, composed of gypsum between 40 and 400 µm thick. Innermost layer, ranging from brown to orange in color, primarily consisted of calcite, between 10 and 600 µm thick. Gypsum-rich layer thought to be the result of sulfation of the calcitic layer by atmospheric pollutants or dry or wet deposition of atmospheric dust.	Garcia-Vallès et al. (1998)
Portland limestone Massangis Jaune Roche limestone White Mansfield dolomitic	Samples exposed to SO_2, NO_2, and NO at 10 ppmv, both with and without O_3 and under dry (coming to equilibrium with the 84% RH) or wetted with CO_2-equilibrated deionized water conditions. Exposure was for 30 days.	In the absence of moisture, little reaction is seen. SO_2 is oxidized to sulfates in the presence of moisture. The effect is enhanced in the presence of O_3. Massangis Jaune Roche limestone was the least affected by the pollutant exposure. Crust lined pores of specimens exposed to SO_2.	Haneef et al. (1993)

TABLE 4-19 (cont'd). CORROSIVE EFFECTS OF PARTICULATE MATTER AND SULFUR DIOXIDE ON STONE

Stone	Exposure Conditions	Comments	Source
Monk's Park Portland limestone	Samples exposed for 2 mo under both sheltered and unsheltered conditions. Mean daily atmospheric SO_2 concentration was 68.7 µg/m^3 and several heavy rainfalls.	Significant amounts of gypsum were noted on the Portland stone. Sheltered stones also showed soiling by carbonaceous particles and other combustion products. Etch holes and deep etching was noted in some of the exposed unsheltered samples.	Viles (1990)
Carrara marble Travertine Tranistone	Sample exposed in laboratory to 3 ppm SO_2 and 95% RH at 25 °C for 150 days. Samples were coated with three carbonaceous particle samples from combustion sources, and with activated carbon and graphite.	Exposure to particles from combustion processes enhanced sulfation of calcareous materials by SO_2 because of metal content of particles.	Sabbioni et al. (1996)
Carrara marble Georgia marble	Samples exposed in sheltered ambient environment for 6, 12, or 20 mo.	Carrara marble found to be more reactive with SO_2 than Georgia marble possibly because of the compactness of the Georgia marble. Greater effects noted when samples were also exposed to NO_2.	Yerrapragada et al. (1994)
Carrara marble	Samples exposed for 6 mo (cold and hot conditions) in ambient environment. PM concentrations ranged from 57.3 to 116.7 µg/m^3 (site 1) and 88 to 189.8 µg/m^3 (site 2). Some exposures also were associated with high SO_2, NO, and NO_2.	Pollutant exposed samples showed increased weight gain over that expected from natural weathering processes. There was a blackening of stone samples exposed to carbonaceous rich particulate matter.	Realini et al. (1995)
Monk's Park limestone Portland limestone	Samples artificially exposed to fly-ash containing 1309.3 µg/m^3 SO_2 (0.5 ppm) at 95% RH and 25 °C for 81 or 140 days. Fly-ash samples from five different sources were used in the study.	Exposure to fly-ash did not enhance oxidation of SO_2 to sulfates. Mineral oxides in fly ash contributed to sulphation of $CaCO_3$.	Hutchinson et al. (1992)
Lime mortar Pozzolan mortar Cement mortar	Samples exposed to 7,856 µg/m^3 (3 ppm) SO_2 at 100% RH and 25 °C for 30, 60, or 90 days; samples sprayed with bidistilled water every 7 days to simulate rainfall.	Exposure to SO_2 produced significant quantities of calcium sulfite and calcium sulfate on specimens; however, the amount produced was dependent of the porosity, specific surface, and alkalinity of the sample.	Zappia et al. (1994)
Limestone Travertine marble	Samples exposed under actual ambient air conditions at two locations in Rome. Monitoring data obtained for SO_2, NO, NO_2, and total suspended particulates (TSP) but not reported. Exposure was for four seasons.	TSP exposure increased the cleaning frequency for stone monuments. Monuments are soiled proportionately overtime, based on brightness values. Horizontal surfaces showed higher graying values because of particle sediment.	Lorusso et al. (1997)

TABLE 4-19 (cont'd). CORROSIVE EFFECTS OF PARTICULATE MATTER AND SULFUR DIOXIDE ON STONE

Stone	Exposure Conditions	Comments	Source
Limestone Quartz-cemented sandstone Calcite-cemented sandstone Granite Brick	Samples from structures exposed for varying periods of time under ambient air conditions. Samples selected because of black layer on surface.	Black layers were found to be primarily comprised of iron compounds, quartz, silicate, soot, and dirt.	Nord and Ericsson (1993)
Carrara marble	Samples from structures taken from monuments in Venice Italy. Samples included those shielded from running water (unwashed), areas at the interface of the washed and unwashed areas, and washed areas. Samples of fog and rain near the monument were also taken for analysis.	Sulfate was higher in fog compared to other ions. The average concentration of chlorides and sulfates were 7 to 16 times higher in fog than rain. The degree of sulphonation on stone samples from areas shielded from running water was < 40%. At the interface between washed and unwashed surfaces and the washed surfaces, sulphonation is > 40%. Dendrite shaped crust from the transformation of calcium carbonate into gypsum was found on samples shielded from rain. Samples from the washed areas displayed superficial granular disaggregation, a natural process of deterioration ascribed to natural agents; however, the process was accelerated due to the ambient air sulfates.	Fassina et al. (2001)
Limestone Sandstone	Samples of ancient grey crust formed between 1180 and 1636 on the Church of Saint Trophime in Arks and formed between 1530 and 1187 on the Palazz d'Accursio in Bolonga.	Crust samples contained calcite, soil dust, carbonaceous particles, and gypsum crystals.	Ausset et al. (1998)
Carrara marble Travertine marble Trani limestone Portland limestone Lime mortar Pozzolan mortar Cement mortar	Samples of the stones and mortars were representative of those used in the past and currently for new construction and restorations. Samples were exposed for 6, 12, and 24 mo under ambient conditions in Milan.	Mortars were more reactive than the stones. Of the mortars, cement and pozzolan mortar were more reactive than the lime mortar. Carrara marble was the least reactive of the stones. The maximum amount of degradation was found in areas sheltered from rain.	Zappia et al. (1998)
Lime mortar	Sample of black crust taken from Zamboni Tower Gate.	Exposure to environmental pollutants caused the formation of two separate layers on the mortar: An outer thin surface black crust composed of gypsum and carbonaceous particles and the inner composed of products from the dissolution and sulphation of the carbonate matrix in the mortar.	Sabbioni et al. (1998)
Carrara marble	Samples of crust removed from Milan General Hospital, built around 1937.	Gypsum main component of crust followed by carbonaceous particles and iron oxides. Estimated rate of crust formation was 2-5 µm/year. Total amount of gypsum formed over the lifetime of exposure was 5 to 13 mg/cm^2, an estimated 0.2 mg/cm^2/year.	Bugini et al. (2000)

The dark colored gypsum is caused by surface deposition of carbonaceous particles (noncarbonate carbon) from combustion processes occurring in the area (Sabbioni, 1995; Saiz-Jimenez, 1993; Ausset et al., 1998; Hermosin and Saiz-Jimenez, 2000), trace metals contained in the stone, dust, and numerous other anthropogenic pollutants. After analyzing damaged layers of several stone monuments, Zappia et al. (1993) found that the dark-colored damaged surfaces contained 70% gypsum and 20% noncarbonate carbon. The lighter colored, damaged layers were exposed to rain and contained 1% gypsum and 4% noncarbonate carbon. It is assumed that rain removes reaction products, permitting further pollutant attack of the stone monument and likely redeposits some of the reaction products at rain runoff sites on the stone. Following sulfur compounds, carbon was reported to be the next highest element in dark crust on historical monuments in Rome. Elemental carbon and organic carbon accounted for 8 and 39% of the total carbon in the black crust samples. The highest percentage of carbon, carbonate carbon, was caused by the carbonate matrix in the stones. The high ratio of organic carbon to elemental carbon indicates the presence of a carbon source other than combustion processes (Ghedini et al., 2000). Cooke and Gibbs (1994) suggested that stones damaged during times of higher ambient pollution exposure likely would continue to exhibit a higher rate of decay, termed the “memory effect,” than newer stones exposed under lower pollution conditions. Increased stone damage also has been associated with the presence of sulfur-oxidizing bacteria and fungi on stone surfaces (Garcia-Vallès et al., 1998; Young, 1996; Saiz-Jimenez, 1993; Diakumaku et al., 1995).

Dissolution of gypsum on the stone’s surface initiates structural changes in the crust layer. Garica-Vallès et al. (1998) proposed a double mechanism: the dissolution of the gypsum, in the presence of sufficient moisture, followed by recrystallization inside fissures or pores. In the event of limited moisture, the gypsum is dissolved and recrystallizes at its original location. According to the authors, this would explain the gypsum-rich crustal materials on stone surfaces sheltered from precipitation.

Moisture was found to be the dominant factor in stone deterioration for several sandstones (Petuskey et al., 1995). Dolske (1995) reported that the deteriorative effects of sulfur-containing rain events, sulfates, and SO_2 on marble were largely dependent on the shape of the monument or structure rather than the type of marble. The author attributed the increased fluid turbulence over a non-flat vertical surface versus a flat surface to the increased erosion. Sulfur-containing particles also have been reported to enhance the reactivity of Carrara marble and Travertine and Trani stone to SO_2 (Sabbioni et al., 1992). Particles with the highest carbon content had the lowest reactivity.

The rate of stone deterioration is determined by the pollutant and the pollutant concentration, the stone's permeability and moisture content, and the pollutant deposition velocity. Dry deposition of SO_2 between rain events has also been reported to be a major causative factor in pollutant-related erosion of calcareous stones (Baedecker et al., 1991; Dolske, 1995; Cooke and Gibbs, 1994; Schuster et al., 1994; Hamilton et al., 1995; Webb et al., 1992). Sulfur dioxide deposition increases with increasing relative humidity (Spiker et al., 1992), but the pollutant deposition velocity is dependent on the stone type (Wittenburg and Dannecker, 1992), the porosity of the stone, and the presence of hygroscopic contaminants.

Although it is clear from the available information that gaseous pollutants (dry deposition of SO_2 in particular) will promote the decay of some types of stones under the specific conditions, carboneous particles (noncarbonate carbon) may help to promote the decay process by aiding in SO_2 transformation to a more acidic species (Del Monte and Vittori, 1985). Several authors have reported enhanced sulfation of calcareous material by SO_2 in the presence of particles containing metal oxides (Sabbioni et al., 1996; Hutchinson et al., 1992).

4.4.2 Soiling and Discoloration of Man-Made Surfaces

Ambient particles can cause soiling of man-made surfaces. Soiling has been defined as the deposition of particles of less than 10 μm on surfaces by impingement. Soiling generally is considered an optical effect, that is, soiling changes the reflectance from opaque materials and reduces the transmission of light through transparent materials. Soiling can represent a significant detrimental effect requiring increased frequency of cleaning of glass windows and concrete structures, washing and repainting of structures, and, in some cases, reduction in the useful life of the object. Particles, in particular carbon, also may help catalyze chemical reactions that result in the deterioration of materials during exposure.

It is difficult to determine the accumulated particle levels that cause an increase in soiling. Soiling is dependent on the particle concentration in the ambient environment, particle size distribution, the deposition rate, and the horizontal or vertical orientation and texture of the surface being exposed (Haynie, 1986). The chemical composition and morphology of the particles and the optical properties of the surface being soiled will determine the time at which soiling is perceived (Nazaroff and Cass, 1991). Carey (1959) reported that the average observer could observe a 0.2% surface coverage of black particles on a white background. Work by Bellan et al. (2000) indicates that it would take a 12% surface coverage by black particles before there is 100% accuracy in identifying soiling. Sharples et al. (2001) studied the effect of air pollution, moisture, and the function of the room/building on glazing daylight transmittance for a number of building windows. They found that the direct soiling load to a window was dependent on the immediate external and internal environment. For instance, there was only a 10% reduction in daylight transmittance for windows from an office building that had not been cleaned for 5 years compared to clean windows. The reduction in transmittance for windows in a swimming pool complex was in excess of 20% due to soiling of the interior surface. For most office buildings, there was a reduction of glazing transmittance ranging from 3 to 10%, with most windows showing about a 3% reduction. The rate at which an object is soiled increases linearly with time; however, as the soiling level increases, the rate of soiling decreases. The buildup of particles on a horizontal surface is counterbalanced by an equal and opposite depletion process. The depletion process is based on the scouring and washing effect of wind and rain (Schwar, 1998).

4.4.2.1 Stones and Concrete

Most of the research evaluating the effects of air pollutants on stone structures has concentrated on gaseous pollutants. The deposition of the sulfur-containing pollutants is associated with the formation of gypsum on the stone (see Section 4.5.1.3). The dark color of gypsum is attributed to soiling by carbonaceous particles from nearby combustion processes. A lighter gray colored crust is attributed to soil dust and metal deposits (Ausset et al., 1998; Camuffo, 1995; Moropoulou et al., 1998). Realini et al. (1995) recorded the formation of a dark gypsum layer and a loss of luminous reflection in Carrara marble structures exposed for 1 year under ambient air conditions. Dark areas of gypsum were found by McGee and Mossitti (1992) on limestone and marble specimens exposed under ambient air conditions for several years. The black layers of gypsum were located in areas shielded from rainfall; whereas particles of dirt were concentrated around the edges of the gypsum formations. Lorusso et al. (1997) attributed the need for frequent cleaning and restoration of historic monuments in Rome to exposure to total suspended particulates. They also concluded that, based on a decrease in brightness (graying), surfaces are soiled proportionately over time; however, graying is higher on horizontal surfaces because of sedimented particles. Davidson et al. (2000) evaluated the effects of air pollution exposure on a limestone structure on the University of Pittsburgh campus using estimated average TSP levels in the 1930s and 1940s and actual values for the years 1957 to 1997. Monitored levels of SO_2 were available for the years 1980 to 1998. Based on the available data concerning pollutant levels and photographs, it was thought that soiling began while the structure was under construction. With decreasing levels of pollution, the soiled areas have been slowly washed away, the process taking several decades, leaving a white, eroded surface.

4.4.2.2 Household and Industrial Paints

Few studies are available that evaluate the soiling effects of particles on painted surfaces. Particles composed of elemental carbon, tarry acids, and various other constituents are responsible for soiling of structural painted surfaces. Coarse-mode particles (> 2.5 μm) initially contribute more soiling of horizontal and vertical painted surfaces than do fine-mode particles (< 2.5 μm), but are more easily removed by rain (Haynie and Lemmons, 1990). The accumulation of fine particles likely promotes remedial action (i.e., cleaning of the painted surfaces); whereas coarse-mode particles are primarily responsible for soiling of horizontal surfaces. Rain interacts with coarse particles, dissolving the particle and leaving stains on the painted surface (Creighton et al., 1990; Haynie and Lemmons, 1990). Haynie and Lemmons (1990) proposed empirical predictive equations for changes in surface reflectance of gloss-painted surfaces that were exposed protected and unprotected from rain while oriented horizontally or vertically.

Early studies by Parker (1955) and Spence and Haynie (1972) demonstrated an association between particle exposure and increased frequency of cleaning of painted surfaces. Particle exposures also caused physical damage to the painted surface (Parker, 1955). Unsheltered painted surfaces are initially more soiled by particles than sheltered surfaces but the effect is reduced by rain washing. Reflectivity is decreased more rapidly on glossy paint than on flat paint (Haynie and Lemmons, 1990). However, surface chalking of the flat paint was reported during the exposure. The chalking interfered with the reflectance measurements for particle soiling. Particle composition measurements that were taken during exposure of the painted surfaces indicated sulfates to be a large fraction of the fine mode and only a small fraction of the coarse mode. Although no direct measurements were taken, fine mode particles likely also contained large amounts of carbon and possibly nitrogen or hydrogen (Haynie and Lemmons, 1990).

4.5 ATMOSPHERIC PARTICULATE MATTER, CLIMATE CHANGE, AND EFFECTS ON SOLAR UVB RADIATION TRANSMISSION

Atmospheric particles alter the amount of solar radiation transmitted through the Earth's atmosphere. The absorption of solar radiation by atmospheric particles, together with trapping of infrared radiation emitted by the Earth's surface by certain gases, enhances heating of the Earth's surface and lower atmosphere (i.e., the widely-known "greenhouse effect") potentially leading to "global warming" impacts on human health and the environment. Lesser impacts of airborne particles include alterations in the amount of ultraviolet solar radiation (especially UV-B) penetrating through the Earth's atmosphere and reaching its surface where UV radiation can exert various effects on human health, plant and animal biota, and other environmental components.

The effects of atmospheric PM on the transmission of electromagnetic radiation emitted by the sun at ultraviolet and visible wavelengths and by the Earth at infrared wavelengths depend on radiative properties (extinction efficiency, single scattering albedo, and asymmetry parameter) of the particles, which depend, in turn, on the size and shape of the particles, the composition of the particles, and the distribution of components within individual particles. In general, the radiative properties of particles are size- and wavelength-dependent. In addition, the extinction cross-section tends to be at a maximum when the particle radius is similar to the wavelength of the incident radiation. Thus, fine particles present mainly in the accumulation mode would be expected to exert a greater influence on the transmission of electromagnetic radiation than would coarse particles. The composition of particles can be crudely summarized in terms of the broad classes identified in Chapter 2 of this document. These include fine particles consisting mainly of (a) nitrate, sulfate, mineral dust, elemental carbon, organic carbon compounds (e.g., PAHs), and (b) metals derived from high temperature combustion or smelting processes. The major sources of these components are shown in Table 3-9 of Chapter 3 in this document.

Knowledge of the effects of PM on the transfer of radiation in the visible and infrared spectral regions is needed for assessing relationships between particles and global warming processes and associated environmental and biological changes. Knowledge of the factors controlling the transfer of solar radiation in the ultraviolet spectral range is needed to assess potential the biological and environmental effects associated with exposure to UV-B radiation (290 to 315 nm). Climate change processes, their potential to affect human and environmental health, and their potential relationships to atmospheric PM are discussed below. Subsequently, aspects related to solar ultraviolet radiation processes and effects are summarized and the roles of atmospheric PM are discussed.

4.5.1 Atmospheric Particle Interactions with Solar and Terrestrial Radiation Related to Climate Change

4.5.1.1 The Projected Impacts of Global Climate Change

The study of atmospheric processes involved in mediating global climate change and its potential consequences for human health and global ecosystems is an area of active research. The most thorough evaluation of current scientific understanding of climate change available at this time is the Third Assessment Report (TAR) of the Intergovernmental Panel on Climate Change (IPCC, 2001a). Earlier assessments include those conducted by the United Nations Environment Program (UNEP, 1986), the World Meteorological Organization (WHO1988), the U.S. Environmental Protection Agency (U.S. Environmental Protection Agency, 1987), and others (e.g., Patz et al., 2000a,b). The reader is referred to these documents for a complete discussion of climate change science. An abbreviated list of the IPCC conclusions, to date, and a short discussion of the potential impacts of climate change on human health and welfare is provided here to serve as the context for the discussion of the role of particulate matter in climate.

The IPCC TAR (2001a) notes that the increasing body of observations indicates that the Earth is warming and that other climate changes are underway. These observations include the global surface temperature record assembled since the year 1860, the satellite temperature record begun in 1979, recorded changes in snow and ice cover since the 1950's, sea level measurements taken throughout the 20th century, and sea surface temperature observations since the 1950's. Other evidence includes a marked increase over the past 100 years in the frequency, intensity and persistence of the zonal atmospheric circulation shifts known as the El Nino-Southern

Oscillation (ENSO). ENSO events occur when the tropical ocean has accumulated a large, localized mass of warm water which interrupts cold surface currents along South America, altering precipitation and temperature patterns in the tropics, sub-tropics and the mid-latitudes.

Atmospheric concentrations of greenhouse gases (GHGs) which trap solar energy within the climate system, are continuing to increase due to human activities. These activities will continue to result changes in the composition of the atmosphere throughout the 21st century. The IPCC TAR describes the scientific evidence that ties this increase in GHGs over the past 50 years to human activities (IPCC 2001b).

The IPCC (1998, 2001b) reports also describe the results of general circulation model (GCM) studies that indicate that human activities will alter the climate system in a manner that will likely to lead to marked global and regional changes in temperature, precipitation and other climate properties. This is expected to increase global mean sea level; increase the number of extreme weather events including floods, and droughts; and induce changes in soil moisture. These changes will directly impact human health, ecosystems, and global economic sectors, e.g., hydrology and water resources, food and fiber production, etc., (IPCC 1998, 2001b). Table 4-20 summarizes these projected impacts. Wide variations in the course and net impacts of climate change in different geographic areas can be expected. In general, projected climate change impacts can be expected to represent additional stresses on those natural ecosystems and human societal systems already impacted by increasing resource demands, unsustainable resource management practices, and pollution — with wide variation likely across regions and nations in their ability to cope with consequent alterations in ecological balances, in availability of adequate food, water, and clean air, and in human health and safety. However, although many regions are likely to experience severe adverse impacts (some possibly irreversible) of climate change, some climate change impacts may be locally beneficial in some regions. For example, sectors or subregions may benefit from warmer temperatures or increased CO_2 fertilization (e.g., west coast coniferous forests; some western rangelands; reduced energy costs for heating in northern latitudes; reduced road salting and snow-clearance costs; longer open-water seasons in northern channels and ports; and agriculture in the northern latitudes, the interior West, and the west coast). The IPCC report, "The Regional Impacts of Climate Change" (IPCC, 1998), describes the projected effects of human-induced climate change on the different regions of the globe, including Africa, the Arctic and Antarctic, the Middle East and arid Asia, Australasia,

TABLE 4-20. EXAMPLES OF IMPACTS RESULTING FROM PROJECTED CHANGES IN EXTREME CLIMATE EVENTS

Projected changes during the 21st Century in Extreme Climate Phenomena and their Likelihood[a]	Representative Examples of Projected Impacts[b] *(all high confidence of occurrence in some areas[c])*
Simple Extremes	
Higher maximum temperatures; more hot days and heat waves[d] over nearly all land areas (*very likely*[a])	• Increased incidence of death and serious illness in older age groups and urban poor • Increased heat stress in livestock and wildlife • Shift in tourist destinations • Increased risk of damage to a number of crops • Increased electric cooling demand and reduced energy supply reliability
Higher (increasing) minimum temperatures; fewer cold days, frost days, and cold waves[d] over nearly all land areas (*very likely*[a])	• Decreased cold-related human morbidity and mortality • Decreased risk of damage to a number of crops, and increased risk to others • Extended range and activity of some pest and disease vectors • Reduced heating energy demand
More intense precipitation events (*very likely*[a] over many years)	• Increased flood, landslide, avalance, and mudslide damage • Increased soil erosion • Increased flood runoff could increase recharge of some floodplain aquifers • Increased pressure on government and private flood insurance systems and disaster relief
Complex Extremes	
Increased summer drying over most mid-latitude continental interiors and associated risk of drought (*likely*[a])	• Decreased crop yields • Increased damage to building foundations caused by ground shrinkage • Decreased water resource quantity and quality • Increased risk of forest fire
Increase in tropical cyclone peak wind intensities, mean and peak precipitation intensities (*likely*[a] over some areas)[e]	• Increased risk to human life, risk of infections, disease epidemics, and many other risks • Increased coastal erosion and damage to coastal buildings and infrastructure • Increased damage to coastal ecosystems such as coral reefs and mangroves
Intensified droughts and floods associated with El Niño events in many different regions (*likely*[a]) (see also under droughts and intense precipitation events)	• Decreased agricultural and rangeland productivity in drought- and flood-prone regions • Decreased hydro-power potential in drought-prone regions
Increased Asian summer monsoon precipitation variability (*likely*[a])	• Increased flood and drought magnitude and damages in temperate and tropical Asia
Increased intensity of mid-latitude storms (little agreement between current models)[d]	• Increased risks to human life and health • Increased property and infrastructure losses • Increased damage to coastal ecosystems

[a] Likelihood refers to judgmental estimates of confidence used by TAR WGI: *very likely* (90-99% chance); *likely* (66-90% chance). Unless otherwise stated, information on climate phenomena is taken from the Summary for Policymakers, TAR WGI. TAR WGI = Third Assessment Report of Working Group 1 (IPCC, 2001a).
[b] These impacts can be lessened by appropriate response measures.
[c] High confidence refers to probabilities between 67 and 95%.
[d] Information from TAR WGI, Technical Summary.
[e] Changes in regional distribution of tropical cyclones are possible but have not been established.

Source: IPCC (2001b).

Europe, Latin America, North America, the small island nations, temperate Asia, and tropical Asia. For further details about the projected effects of climate change on a US-regional scale, the reader is also referred to several regionally-focused reports (MARAT, 2000; Yarnal et al., 2000; NERAG, 2001; GLRAG, 2000), as well as a report on potential impacts upon human health due to climate change (Bernard et al., 2001).

It must be borne in mind that while current climate models are successful in simulating present annual mean climate and the seasonal cycle on continental scales, they are less successful at regional scales. Clouds and humidity, essential factors in defining local and regional ("sub-grid") climate, are significantly uncertain (IPCC 2001a). Due to modeling uncertainties, both in reproducing regional climate and in predicting future economic activity, the projected impacts discussed above are also uncertain.

Findings from the IPCC TAR (2001a), Regional Impacts Assessment (1998) and other regional assessments cited above illustrate well the considerable uncertainties and difficulties in projecting likely climate change impacts on regional or local scales. The findings also reflect the mixed nature of projected potential climate change impacts (combinations of mostly deleterious, but other possible beneficial effects) for U.S. regions and their variation across the different regions. Difficulties in projecting region-specific climate change impacts are complicated by the need to evaluate potential effects of local- or regional-scale changes in key air pollutants not only on global scale temperature trends but also in terms of potentially more local- or regional-scale impacts on temperature and precipitation patterns.

4.5.1.2 Airborne Particle Relationships to Global Warming and Climate Change

Atmospheric particles both scatter and absorb incoming solar radiation. Visibility reduction is caused by particle scattering in all directions; whereas climate effects result mainly from scattering in the upward direction. Upward scattering of solar radiation reduces the total amount of energy received by the Earth system, leading to surface cooling. The effect on climate due to upward scattering and to absorption of radiation by aerosol can be roughly quantified as a "radiative forcing" (Houghton et al., 1990). Global and regional climate (at equilibrium) is defined by the balance between a large number of "positive" and "negative" forcings induced by different components of the Earth system. The Earth system responds to these forcings in a potentially complex way due to feedback mechanisms that are theorized but very difficult to define. In the absence of information about climate feedbacks, radiative forcing values for the many components of the climate system are estimated as a tool for comparing, to first order, their relative importance in climate change. Forcing estimates for various classes of atmospheric particles are derived on the basis of climate modeling studies and reported by the IPCC (IPCC 2001b).

Particulate matter appears to play a significant role in defining climate on both a global and regional scale. Haywood et al. (1999) found that the inclusion of anthropogenic aerosols results in a significant improvement between calculations of reflected sunlight at the top of the atmosphere and satellite observations in oceanic regions close to sources of anthropogenic PM. Significant reductions over the past 50 years in solar radiation received at the Earth's surface on a globally averaged basis correlate with increases in atmospheric aerosol (Stanhill and Cohen, 2001). While this correlation seems clear, quantifying the cooling and warming effects of aerosol in relation to greenhouse gas-related warming is difficult. Aerosol complicates the interpretation of climate change due to its spatial and temporal inhomogeneities and uncertain radiative properties. However, to first order, inclusion of modeled atmospheric sulfate concentrations substantially improved the agreement between modeled and observed surface temperatures (Kiehl and Briegleb, 1993). On a regional scale, the suspected influence of aerosols upon climate relates to regional hydrological cycles. Evidence is accumulating that pollution aerosols reduce precipitation frequency by clouds, potentially leading to drought in some parts of the world (Ramanathan et al, 2001).

Greenhouse Gases, Particulate Matter and the Earth's Radiative Equilibrium

According to simple radiative transfer theory, at thermal equilibrium, the Earth's surface should be near -15 °C. This is the temperature of a theoretical "black body" that is receiving and then re-emitting 342.5 Wm^{-2} (i.e., the globally averaged amount of solar radiation absorbed and then re-emitted by the Earth as infrared terrestrial radiation). In fact, satellite observations indicate that the Earth's average planetary temperature is remarkably close to the theoretical black body value at -18 °C, a temperature at which liquid water ordinarily does not exist.

At its surface, however, the Earth's average temperature is + 15 °C. The 33 °C temperature differential between Earth's planetary temperature and its surface temperature is due to the existence of infrared radiation-absorbing components in the atmosphere, i.e. GHGs, including carbon dioxide, methane, several other trace gases and some types of particles and clouds. The phenomenon of planetary surface warming due to atmospheric absorption and re-emission of infrared radiation is popularly known as the "greenhouse effect" (Arrhenius, 1896; Schneider, 1992). Radiation trapped by the Earth's atmosphere is reflected back to its surface, with some small fraction absorbed by dark atmospheric particles. The fraction of this radiation that is not directly re-emitted as long-wave terrestrial radiation transforms into heat energy that drives the atmospheric processes that form the basis of weather and climate. Eventually this energy is transformed a second time, to terrestrial radiation, and is re-emitted as part of the process that maintains Earth's radiative equilibrium.

Satellite measurements of the Earth's radiation budget suggest that the Earth is, however, out of equilibrium. These measurements indicate that from 1985 through 1990, the Earth absorbed 238 W/m^2 and emitted 235 Wm^{-2} – an imbalance of 3 Wm^{-2}. If these measurements are correct, they suggest that continuously changing atmospheric concentrations of radiatively active species along with other alterations to the climate system due to human activities may be responsible for preventing the re-establishment of the Earth's radiative equilibrium.

Radiatively active gases in the atmosphere are largely responsible for the greenhouse effect, although some light absorbing particles and clouds contribute to atmospheric and surface warming (IPCC 2001a). The majority of clouds and particles play a role in counteracting the greenhouse effect by increasing the degree to which the Earth is able to reflect solar radiation, i.e., its "albedo." Successful modeling of the Earth's climate and, therefore, assessment of the degree of human-induced climate change and development of appropriate policy depends on the high quality information on the relative efficiencies, amounts, spatial and temporal distributions of the various radiatively active components of the atmosphere at absorbing and/or reflecting solar and terrestrial radiation.

"Forcing" and the Earth's Radiative Balance

A measure of the relative influence of a given component of the climate system on the Earth's radiative balance is its "radiative forcing." Radiative forcing, in Wm^{-2}, is a quantity that was developed by the climate modeling community as a first order-only means of estimating relative effects of anthropogenic and natural processes on the surface-troposphere system. No more precise metric has yet been found to replace radiative forcing as a measure of impact of upon climate (IPCC, 2001). The convention for this quantity assigns a negative forcing to climate system components that reflect solar radiation back into space and positive forcing for those which enhance the greenhouse effect, or otherwise act to enhance the heating absorbing capacity of the Earth system. Purely reflective atmospheric aerosol, snow-covered land surfaces and dense sea ice provide a negative forcing, while highly absorbing atmospheric aerosol, greenhouse gases and dark ocean surfaces positively force the climate system.

The IPCC reports estimated values for forcing by the individual radiatively active gas and particle-phase components of the atmosphere. These estimates are derived primarily through expert judgment incorporating the results of peer-reviewed modeling studies. Uncertainty ranges are assigned that reflect the range of modeled values reported in these studies. According to the available research on climate forcing by aerosol, the panel has provided estimates for sulfate, organic, black carbon, biomass burning, and mineral dust aerosol. The current estimate of forcing due to long-lived, well-mixed, greenhouse gases accumulated in the atmosphere from the pre-industrial era (ca., 1750) through the year 2000 is + 2.4 Wm^{-2} (IPCC, 2001). In contrast, forcing due to a sulfate aerosol-related increase in planetary albedo has been assigned a value of – 0.4 Wm^{-2}. Biomass burning and fossil-fuel-related organic aerosol also increase the Earth's reflectivity and are estimated to contribute a –0.2 Wm^{-2} and –0.1 Wm^{-2} forcing, respectively. Fossil-fuel black carbon is expected to warm the atmosphere, resulting in an estimated + 0.2 Wm^{-2} forcing. No estimate for forcing by nitrate aerosol has been proposed due to wide discrepancies in current global modeling results and the difficulties associated with obtaining accurate ambient samples of nitrate concentrations and size distributions. Likewise, no specific estimate has been offered for forcing by mineral dust aerosol introduced into the atmosphere due to human activities beyond the assignment of a tentative range of – 0.6 to + 0.4 Wm^{-2}. The estimated forcing and associated uncertainty for each aerosol type is shown in relation to forcing estimates for the known greenhouse gases along with an indication of the level of confidence in each of these estimates in Figure 4-42.

The relationship between perturbations to the Earth's radiative balance and climate is complicated by various feedbacks within the climate system. An example would be the positive feedback associated with melting sea ice. As sea ice melts with increasing surface temperatures, the dark ocean surface is revealed which absorbs, rather than reflects, solar radiation. Such a feedback increases the rate of surface warming. The role of feedbacks in determining the

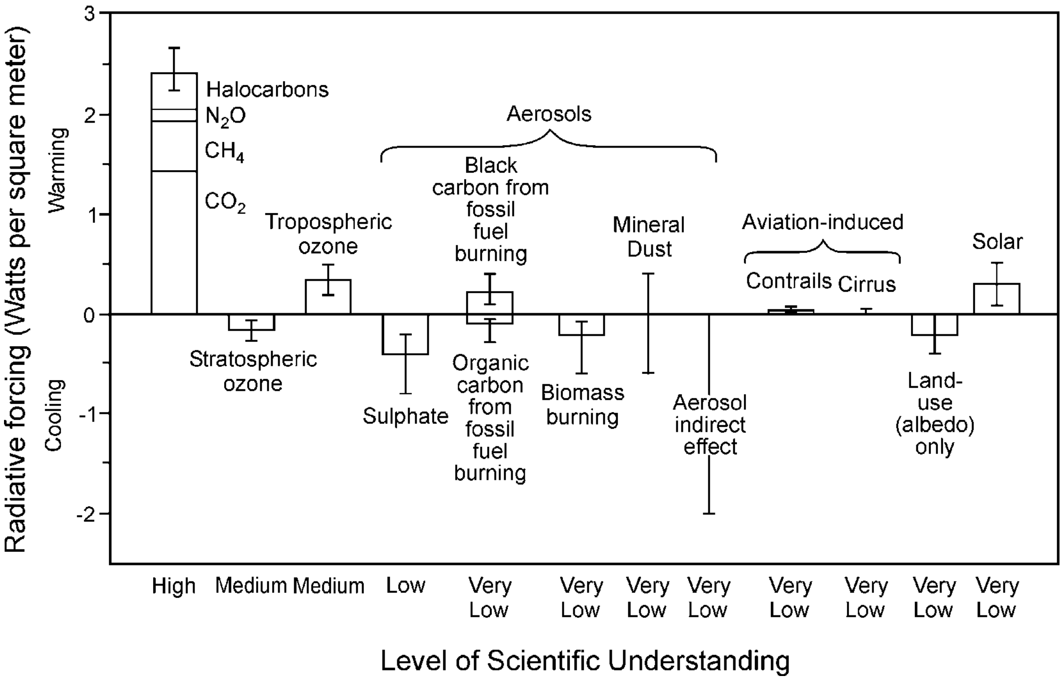


Figure 4-42. Estimated global mean radiative forcing exerted by gas and various particle phase species for the year 2000, relative to 1750.

Source: IPCC (2001a).

sensitivity of climate to changes in radiative forcing is described in detail by the IPCC in its third assessment report (IPCC, 2001a).

One possible feedback of interest in the discussion of the role of aerosols in determining climate may result from the possible sensitivity of aerosol number and mass to atmospheric temperature (Hemming and Seinfeld, 2001). Increasing atmospheric temperatures may result in a reduction of aerosol as semivolatile organic and inorganic aerosol constituents evaporate, leading to a change in aerosol forcing. As described in Chapter 2 of this document, and further discussed below, ambient aerosols are known to contain complex chemical mixtures of both scattering and absorbing materials. The feedback that may result from this phenomenon will depend upon whether the aerosols become more absorbing or more reflective upon the loss of semivolatile material. Research is presently underway to evaluate both the role of temperature in determining aerosol mass and in defining the link between air quality and climate, but no literature presently exists to support an assessment of these effects. The following discussion, therefore, will focus solely on the relative forcing properties of aerosols, for which a body of scientific research is available for consideration.

The physical and chemical properties of atmospheric aerosols, and their regional distribution and temporal nature, all play a role in determining the degree to which they force climate. These details are described, below, followed by a description of the "indirect" effect of aerosols due to changes in cloud properties; and brief discussions of the sources of uncertainty in determining aerosol-related climate forcing and of the link to human health and the environment then follow.

The Physics of PM and Its Climate Effects

Four wavelength-dependent physical properties of ambient aerosols are needed to calculate optical depth and thus their radiative properties: the mass light-scattering efficiency (a_{sp}), the functional dependence of light-scattering on relative humidity f(RH), the single-scattering albedo (ω_0), and the scattering asymmetry parameter (g); (Charlson et al., 1992; Penner et al., 1994a). Direct forcing by aerosols is especially sensitive to single scattering albedo. Depending on the color of the underlying surface, small changes in ω_0 can change the sign of the calculated aerosol forcing (Hansen et al., 1997).

The wavelength-dependent phase function and scattering and absorption coefficients are calculated using Mie scattering theory. These values are then used to calculate mass light-scattering efficiency, single-scattering albedo, and the asymmetry factor. Mie calculations require the ratio of particle size versus wavelength and the complex refractive index of the particle – a composition-dependent property (Salby, 1996). The relationship between light-scattering and relative humidity likewise depends upon composition as water absorption depends upon the presence of hygroscopic material within the particle. Therefore, according to the current understanding of aerosol optics, good information about composition and size distribution is needed to successfully predict aerosol-related forcing.

The Chemistry of PM and Its Climate Effects

Although forcing estimates are reported for specific aerosol classes (i.e., sulfate, black carbon, dust, etc.) it is understood that shortly after emission, primary aerosols undergo chemical transformation in the atmosphere. These transformations occur through partitioning of gas phase compounds, by coagulation with other aerosol or a combination of both processes (Pandis and Seinfeld, 1998). While the radiative properties of non-absorbing aerosol, such as sulfates or nitrates, are primarily sensitive to particle size, the radiative properties of aerosols containing absorbing constituents (i.e., black carbon and mineral aerosols) are also sensitive to chemical composition and mixing state. Studies of refractive index changes as a function of composition have shown that the type of mixing present both in the population of aerosols (i.e., "internal" versus "external" mixtures) and the extent of mixing within individual aerosols influence aerosol optical properties when absorbing material is present (Fuller et al., 1999). Modeled estimates for radiative forcing by black-carbon-containing aerosols do, in fact, range widely depending on whether the aerosol population is assumed to be internally or externally mixed and whether the absorbing carbon is uniformly distributed in the particle or whether it exists as a core surrounded by non-absorbing material. The IPCC Third Assessment report (2001) provides a tabulation of studies and their forcing estimates for black carbon existing in different mixing states. For example, Haywood and Shine (1997) calculated that externally mixed fossil-fuel black carbon forces climate by + 0.2 W/m^2. Jacobson (2000) assumed that if black carbon exists as a solid core contained within an otherwise non-absorbing droplet, the global forcing will be + 0.54 W/m^2.

Chemically and physically detailed models at high spatial resolution are required to accurately represent the chemical transformation and size evolution of aerosol within the ambient atmosphere. Such models, however, are impractical for global scale climate modeling. Parameterizations are formulated to represent processes occurring at spatial and temporal scales that are too fine for climate models (i.e., "sub-grid" processes). Several important fundamental chemical and physical processes, however, are not yet well-enough defined to assure reasonable parameterization in large scale climate models. Prediction of the organic and black carbon content of ambient aerosols and their associated radiative properties, as described above, and the aerosol-induced changes in cloud properties, remain especially weak.

Modeling of the effect of black carbon aerosol on climate, to date, has been done on the basis of limited and poor quality data regarding total global emissions, aerosol composition, and the mixing state of ambient aerosols. Appendix 2B.2 of Chapter 2 in this document describes the many problems associated with the most commonly used organic carbon/elemental carbon measurement method (thermal optical reflectance and transmittance). For example, elemental carbon comprises a relatively small fraction of total carbon in biomass burning-related aerosol which is, nevertheless, an important source of black carbon in the atmosphere due to the extensive use of biofuels in developing countries and to the prevalence of natural and agriculture-related open biomass burning (Ludwig et al., 2003). The concentrations of elemental carbon in these aerosols are close to the detection limits of thermal optical measurement systems, adding a high degree of uncertainty to the reported values. Thermal optical measurements also do not provide information about the specific chemical composition of carbonaceous aerosol that is needed to calculate refractive indices. Furthermore, the technique is based on filter collection, which only provides an average concentration of organic and elemental carbon and no information about mixing states.

The magnitude of the errors introduced into estimates of black carbon-related radiative forcing due to the lack of detailed information about optical properties of ambient black carbon aerosol cannot, yet, be estimated. The forcing estimate of + 0.2 Wm^{-2} provided by the IPCC is based upon a summary of the available modeling estimates, some of which are founded on simplistic assumptions about the composition and mixing state of ambient BC aerosol.

New methods, such as photo-acoustic spectroscopy, hold promise for detecting quantities of light absorbing materials in streams of ambient aerosol (Arnott et al., 1999; Moosmuller et al., 2001). The photo-acoustic method is capable of identifying the absolute fraction of a given ambient aerosol sample that absorbs radiation at a given wavelength at high temporal resolution. The method does not alter the composition of the aerosol sample through heating and oxidation, thus eliminating chemical artifacts. Present photo-acoustic instruments detect absorption at wavelengths of interest for visibility studies, but the measurement principle can be adapted to climate studies through the selection of climate-forcing relevant wavelengths. Specific chemical speciation at the organic and inorganic compound level coupled with photo-acoustic measurements of the light absorbing properties of ambient aerosol would provide the best available test of atmospheric chemistry models attempting to simulate the evolution in aerosol radiative properties between emission and atmospheric removal.

The Regional and Temporal Dependence of Aerosol Forcing

In addition to information about the composition and size distributions of ambient aerosol, details regarding atmospheric concentrations on a spatial and temporal basis are needed for estimating climate forcing. Unlike the long-lived greenhouse gases, aerosols have lifetimes averaging only a week or less, leading to inhomogeneity in regional and global scale concentrations. Industrial processes and other human activities that produce air pollution aerosols also vary on a seasonal, monthly, weekly and diurnal basis, introducing other complications into forcing estimates (IPCC, 2001). Peak aerosol concentrations, along with the greatest temporal variation, exist near emissions sources.

Deviations from global mean forcing estimates can be very large on the regional scale. For instance, Tegen et al. (1996) found that local radiative forcing exerted by dust raised from disturbed lands ranges from -2.1 W m^{-2} to 5.5 W m^{-2} over desert areas and their adjacent seas. The largest regional values of radiative forcing caused by anthropogenic sulfate are about -3 W m^{-2} in the eastern United States, south central Europe, and eastern China (Kiehl and Briegleb, 1993). These regional maxima in aerosol forcing are at least a factor of 10 greater than their global mean values shown in Figure 4-41. By comparison, regional maxima in forcing by the well-mixed greenhouse gases are only about 50% greater than their global mean value (Kiehl and Briegleb, 1993). Thus, the estimates of local radiative forcing by particles also are large enough to completely cancel the effects of greenhouse gases in many regions and to cause a number of changes in the dynamic structure of the atmosphere that still need to be evaluated. A number of anthropogenic pollutants whose distributions are highly variable are also effective greenhouse absorbers. These gases include O_3 and, possibly, HNO_3 , C_2H_4 , NH_3, and SO_2, all of which are not commonly considered in radiative forcing calculations (Wang et al., 1976). High ozone values are found downwind of urban areas and areas where there is biomass burning. However, Van Dorland et al. (1997) found that there may not be much cancellation between the radiative effects for ozone and for sulfate because both species have different seasonal cycles and show significant differences in their spatial distribution.

“Indirect” Effects of PM on Climate

Aerosols directly affect climate by scattering and absorbing solar and terrestrial radiation. Depending on chemical composition, they can also nucleate new cloud droplets. For a given total liquid water content (LWC), increasing cloud droplet number means smaller droplets that both scatter solar radiation more effectively, reduce the amount of precipitation from the cloud, and consequently increase cloud lifetime – and the cloud’s ability to scatter solar radiation.

Observational evidence exists of this impact of hygroscopic aerosol on both warm and ice cloud properties. Increased albedo and increased cloud lifetime effects are treated separately by the climate modeling community. Particle-induced increases in cloud albedo are referred to as the "first" indirect effect, and changes to the cloud lifetime due to reduced precipitation are referred to as the "second" indirect effect. The highly uncertain estimated forcing due to the effects of particles on cloud albedo is given as a range from 0 to + 2.0 W m^{-2} (IPCC, 2001a). A further effect, referred to as the "semi-indirect effect" is the reduction in cloud reflectivity due to the inclusion of black carbon-containing aerosol within the cloud drops themselves or as interstitial aerosol (Hansen et al., 2000).

Sulfate aerosols, especially those larger than 50 nm in diameter, are believed to alter clouds to the largest extent due to their efficient nucleation of cloud drops and ice crystals (Twomey, 1974). Organic aerosols that contain highly oxidized carbon compounds may be similarly efficient in nucleating cloud droplets (Novakov and Penner, 1993). Both satellite and in-situ aircraft observations reinforce the hypothesis that pollutant aerosols increase cloud reflectivity and lifetime (Ramanathan et al., 2001).

An important consequence of this property of aerosols on regional climate includes suppression of rain over polluted regions. Satellite observations show that precipitation occurs only outside of pollution tracks, while clouds within pollution tracks show a reduction in effective cloud drop radius to below the precipitation threshold (D. Rosenfeld, 1999). Desert dust also appears to alter the microphysical properties of clouds, suppressing precipitation from warm clouds while nucleating ice crystals in cold clouds.

While climate models are not yet equipped for modeling the effect of aerosols on regional and global hydrological cycles, it has been proposed that aerosols will reduce precipitation efficiency over land where anthropogenic activities provide a major source of cloud condensation nuclei. Several studies using coupled ocean-atmosphere general circulation models support the possibility of a "spin down" effect upon hydrological cycles due only to a reduction in surface radiation receipts from sulfate aerosol scattering. When indirect effects are included, the reduction in precipitation rates from clouds was large enough to reverse the effect of greenhouse gas-related forcing (Ramanathan et al., 2001).

Sources of Uncertainty in Aerosol Forcing Estimates

Uncertainties in calculating the direct effect of airborne particles arise from a lack of knowledge of their vertical and horizontal variability, their size distribution, chemical composition, and the distribution of components within individual particles. For instance, gas-phase sulfur species may be oxidized to form a layer of sulfate around existing particles in continental environments or they may be incorporated in sea-salt particles (e.g., Li-Jones and Prospero, 1998). In either case, the radiative effects of a given mass of the sulfate will be much lower than if pure sulfate particles were formed. It also must be stressed that the overall radiative effect of particles at a given location is not simply determined by the sum of effects caused by individual classes of particles because of radiative interactions between particles with different radiative characteristics and with gases.

Calculations of the indirect effects of particles on climate are subject to much larger uncertainties than are calculations of their direct effects, reflecting uncertainties in a large number of chemical and microphysical processes that determine aerosol chemistry, size distribution, and the number of droplets within a cloud. A complete assessment of the radiative effects of PM will require computationally intensive calculations that incorporate the spatial and temporal behavior of particles of varying composition that have been emitted from (or formed from precursors emitted from) different sources. Refining values of model input parameters (such as improving emissions estimates) may be as important as improving the models per se in calculations of direct radiative forcing (Pan et al., 1997) and indirect radiative forcing (Pan et al., 1998). However, uncertainties associated with the calculation of radiative effects of particles will likely remain much larger than those associated with well-mixed greenhouse gases.

Aerosol-Related Climate Effects, Human Health and the Environment

Given the present difficulty in accurately modeling aerosol physical, chemical and temporal properties, its regionally-dependent atmospheric concentration levels, combined with difficulties in projecting location-specific increases or decreases in anthropogenic emissions of atmospheric particles (or their precursors), the specific impacts on human health and the environment due to aerosol effects on the climate system can not be calculated with confidence. However, substantial qualitative information, from observation and modeling, indicates that aerosol forces climate both positively and negatively, both globally and regionally, and may be negatively impacting hydrological cycles on a regional scale. The global and other regional scale impacts are suspected, on the basis of current, though uncertain, modeling studies suggest that climate change in general can have positive and negative effects on human health, human welfare and the environment.

4.5.2 Atmospheric Particulate Matter Effects on the Transmission of Solar Ultraviolet Radiation Transmission: Impacts on Human Health and the Environment

4.5.2.1 Potential Effects of Increased Ultraviolet Radiation Transmission

The transmission of solar UV-B radiation through the Earth's atmosphere is controlled by ozone, clouds, and particles. The depletion of stratospheric ozone caused by the release of anthropogenically produced chlorine (Cl)- and bromine (Br)-containing compounds has resulted in heightened concern about potentially serious increases in the amount of solar UV-B radiation (SUVB) reaching the Earth's surface. SUVB is also responsible for initiating the production of OH radicals that oxidize a wide variety of volatile organic compounds, some of which can deplete stratospheric ozone (e.g., CH_3Cl, CH_3Br), absorb terrestrial infrared radiation (e.g., CH_4), and contribute to photochemical smog formation (e.g., C_2H_4 , C_5H_8).

Increased penetration of SUVB to the Earth's surface as the result of stratospheric ozone depletion continues to be of much concern because of projections of consequent increased surface-level SUVB exposure and associated potential negative impacts on human health, plant and animal biota, and man-made materials. Several summary overviews (Kripke, 1989; Grant, 1989; Kodama and Lee, 1994; Van der Leun et al., 1995, 1998) of salient points related to stratospheric ozone depletion and bases for concern provide a concise introduction to the subject. Only a brief summary will be given here. Stratophospheric ozone depletion results from (a) anthropogenic emissions of certain trace gases having long atmospheric residence times, e.g., chlorofluorocarbons (CFCs), carbon tetrachloride (CCl_4), and Halon 1211 (CF_2Cl Br) and 1301 (CF_3Br) — which have atmospheric residence times of 75 to 100 years, 50 years, 25 years, and 110 years, respectively; (b) their tropospheric accumulation and gradual transport, over decades, up to the stratosphere, where (c) they photolyze to release Cl and Br that catalyze ozone destruction; leading to (d) stratospheric ozone depletion. Such ozone depletion is most marked over Antarctica during spring in the Southern Hemisphere, to a less marked but still significant extent over the Arctic Polar Region during late winter and spring in the Northern Hemisphere, and to a lesser extent, over mid-latitude regions during any season. Given the long time frame involved in transport of such gases to the stratosphere and their long residence times there, any effects already seen on stratospheric ozone are likely caused by the atmospheric loadings of trace gases from anthropogenic emissions over the past few decades. Ozone-depleting gases already in the atmosphere will continue to affect stratospheric ozone concentrations well into the 21st century. Shorter-lived gases, such as CH_3Br, also exert significant ozone depletion effects.

The main types of deleterious effects hypothesized as likely to result from stratospheric ozone depletion and consequent increased SUVB penetration through the Earth's atmosphere include the following:

(1) *Direct Human Health Effects*, such as skin damage (sunburn), leading to more rapid aging and increased incidence of skin cancer; ocular effects (retinal damage and increased cataract formation possibly leading to blindness); and suppression of some immune system components (contributing to skin cancer induction and spread to nonirradiated skin areas, as well as possibly increasing susceptibility to certain infectious diseases).

(2) *Agricultural/Ecological Effects*, mediated largely through altered biogeochemical cycling resulting in consequent damaging impacts on terrestrial plants (leading to possible reduced yields of rice, other food crops, and commercially important trees, as well as to biodiversity shifts in natural terrestrial ecosystems); and deleterious effects on aquatic life (including reduced ocean zooplankton and phytoplankton, as important base components of marine food-chains supporting the existence of commercially important, edible fish and other seafood, as well as to other aquatic ecosystem shifts).

(3) *Indirect Human Health and Ecological Effects*, mediated through increased tropospheric ozone formation (and consequent exacerbation of surface-level, ozone-related health and ecological impacts) and alterations in the concentrations of other important trace species, most notably the hydroxyl radical and acidic aerosols.

(4) *Other Types of Effects*, such as faster rates of polymer weathering because of increased UV-B radiation and other effects on man-made commercial materials and cultural artifacts, secondary to climate change or exacerbation of air pollution problems.

Extensive qualitative and quantitative characterizations of stratospheric ozone depletion processes and projections of their likely potential impacts on human health and the environment have been the subjects of periodic (1988, 1989, 1991, 1994, 1998) international assessments carried out under WMO and UNEP auspices since the 1987 signing of the Montreal Protocol on Substances that Deplete the Ozone Layer. For more detailed up-to-date information, the reader is referred to recent international assessments of (a) processes contributing to stratospheric ozone depletion and the status of progress towards ameliorating the problem (WMO, 1999) and (b) revised qualitative and quantitative projections of potential consequent human health and environmental effects (UNEP, 1998, 2000).

Of considerable importance is the growing recognition, as reflected in these newer assessments, of impacts of enhanced solar radiation on biogeochemical cycles (see, for example, Zepp et al., 1998). As noted in that paper, the effects of UV-B radiation (both in magnitude and direction) on trace gas (e.g., CO) emissions and mineral nutrient cycling are species specific and can affect a variety of processes. These include, for example, changes in the chemical composition of living plant tissue, photodegradation of dead plant matter (e.g., ground litter), release of CO from vegetation previously charred by fire, changes in microbial decomposer communities, and effects on nitrogen-fixing microorganisms and plants. In addition, changes in the amount and composition of organic matter, caused by enhanced UV-B penetration, affect the transmission of solar ultraviolet and visible radiation through the water column. These changes in light quality broadly impact the effects of UV-B on aquatic biogeochemical cycles. Enhanced UV-B levels cause both positive and negative effects on microbial activities in aquatic ecosystems that can affect nutrient cycling and the uptake or release of greenhouse gases. Thus, there are emerging complex issues regarding interactions and feedbacks between climate change and changes in terrestrial and marine biogeochemical cycles because of increased UV-B penetration to the Earth's surface.

In contrast to the above types of negative impacts projected as likely to be associated with increased UV-B penetration to Earth's surface, some research results are suggestive of possible beneficial effects of increased UV-B radiation. For example, a number of U.S. and international studies have focused on the protective effects of UV-B radiation with regard to non-skin cancer incidence. One of the first of these studies investigated potential relationships between sunlight, vitamin D, and colon cancer (Garland and Garland, 1980). More recent studies continue to provide suggestive evidence that UV-B radiation may be protective against several types of cancer and some other diseases. For example, Grant (2002) conducted a number of ecologic-type epidemiologic studies, which suggest that UV-B radiation, acting through the production of vitamin D, is a risk-reduction factor for mortality due to several types of cancer, including cancer of the breast, colon, ovary, and prostate, as well as non-Hodgkin lymphoma. Other related studies that provide evidence for protective effects of UV-B radiation include Gorham et al. (1989); Gorham et al. (1990); Garland et al. (1990); Hanchette and Schwartz (1992); Ainsleigh (1993); Lefkowitz and Garland (1994); Hartge et al. (1996); and Freedman et al. (1997).

As noted in the above detailed international assessments, since the signing of the Montreal Protocol, much progress has been made in reducing emissions of ozone depleting gases, leading to estimates that the maximum extent of stratospheric ozone depletion has likely leveled off during recent years, and this is expected to be followed by gradual lessening of the problem and its impacts during the next half-century. However, the assessments also note that the modeled projections are subject to considerable uncertainty (see, for example, UNEP, 2000). Varying potential roles of atmospheric particles, discussed below, are among salient factors complicating predictive modeling efforts.

4.5.2.2 Airborne Particle Effects on Atmospheric Transmission of Solar Ultraviolet Radiation

A given amount of ozone in the lower troposphere has been shown to absorb more solar radiation than an equal amount of ozone in the stratosphere because of the increase in its effective optical path produced by Rayleigh scattering in the lower atmosphere (Brühl and Crutzen, 1988). The effects of particles are more complex. The impact of particles on the SUVB flux throughout the boundary layer are highly sensitive to the altitude of the particles and to their single scattering albedo. Even the sign of the effect can reverse as the composition of the particle mix changes from scattering to absorbing types (e.g., from sulfate to elemental carbon or PAHs; Dickerson et al., 1997). In addition, scattering by particles also may increase the effective optical path of absorbing molecules, such as ozone, in the lower atmosphere.

The effects of particles present in the lower troposphere on the transmission of SUVB have been examined both by field measurements and by radiative transfer model calculations. The presence of particles in urban areas modifies the spectral distribution of solar irradiance at the surface. Shorter wavelength radiation (i.e., in the ultraviolet) is attenuated more than visible radiation (e.g., Peterson et al., 1978; Jacobson, 1999). Wenny et al. (1998) also found greater attenuation of SUVB than SUVA (315 to 400 nm). However, this effect depends on the nature of the specific particles involved and, therefore, is expected to depend strongly on location. Lorente et al. (1994) observed an attenuation of SUVB ranging from 14 to 37%, for solar zenith angles ranging from about 30º to about 60º, in the total (direct and diffuse) SUVB reaching the surface in Barcelona during cloudless conditions on very polluted days (aerosol scattering optical depth at 500 nm, $0.46 \lesssim \tau_{500\text{ nm}} \lesssim 1.15$) compared to days on which the turbidity of urban air was similar to that for rural air ($\tau_{500\text{ nm}} \lesssim 0.23$).

Particle concentrations that can account for these observations can be estimated roughly by combining Koschmieder's relation for expressing visual range in terms of extinction coefficient with one for expressing the mass of $PM_{2.5}$ particles in terms of visual range (Stevens et al., 1984). By assuming a scale height (i.e., the height at which the concentration of a substance falls off to 1/e of its value at the surface) of 1 km for $PM_{2.5}$, an upper limit of 30 μg/ m^3 can be derived for the clear case and between 60 and 150 μg/m^3 for the polluted case. Estupiñán et al. (1996) found that summertime haze under clear sky conditions attenuates SUVB between 5 and 23% for a solar zenith angle of 34°compared to a clear sky day in autumn. Mims (1996) measured a decrease in SUVB by about 80% downwind of major biomass burning areas in Amazonia in 1995. This decrease in transmission corresponded to optical depths at 340 nm ranging from three to four. Justus and Murphey (1994) found that SUVB reaching the surface decreased by about 10% because of changes in aerosol loading in Atlanta, GA, from 1980 to 1984. In addition, higher particle levels in Germany (48 °N) may be responsible for greater attenuation of SUVB than in New Zealand (Seckmeyer and McKenzie, 1992).

In a study of the effects of nonurban haze on SUVB transmission, Wenny et al. (1998) derived a very simple regression relation between the measured aerosol optical depth at 312 nm,

$$\ln(\text{ SUVB transmission at solar noon}) = -\ 0.1422\ \tau_{312\text{ nm}} - 0.138,\ R^2 = 0.90, \qquad (4\text{-}14)$$

and the transmission of SUVB to the surface. In principle, values of $\tau_{312\text{ nm}}$ could be found from knowledge of the aerosol optical properties and visual range values. Wenny et al. (1998) also found that absorption by particles accounted for 7 to 25% of the total (scattering + absorption) extinction. Relations such as the above one are strongly dependent on local conditions and should not be used in other areas without knowledge of the differences in aerosol properties. Although all of the above studies reinforce the idea that particles play a major role in modulating the attenuation of SUVB, none included measurements of ambient PM concentrations, so direct relations between PM levels and SUVB transmission could not be determined.

Vuilleumier et al. (2001) concluded that variations in aerosol scattering and absorption were responsible for 97% of the variability in the optical depth measured at seven wavelengths from 300 to 360 nm at Riverside, CA, from 1 July to 1 November, 1997. Similar measurements made at nearby Mt. Wilson, located above the main surface haze layer, showed that 80% of the variations in optical depth were still driven by variations in aerosol scattering and absorption. The remainder of the variability in optical depth was attributed mainly to variability in ozone under clear-sky conditions. However, these results cannot be extrapolated to other locations because these effects are coupled and non-linear and are not straightforward. They depend on the concentrations of these species and on the physical and chemical characteristics of the particles. Hence, any quantitative statements regarding the relative importance of particles and ozone will be location-specific.

Liu et al. (1991) roughly estimated the overall effects on atmospheric transmission of SUVB of increases of anthropogenic airborne particles that have occurred since the beginning of the industrial revolution. Based on (a) estimates of the reduction in visibility from about 95 km to about 20 km over nonurban areas in the eastern United States and in Europe, (b) calculations of optical properties of airborne particles found in rural areas to extrapolate the increase in extinction at 550 to 310 nm, and (c) radiative transfer model calculations, Liu et al. concluded that the amount of SUVB reaching Earth's surface likely has decreased from 5 to 18% since the beginning of the industrial revolution. This was attributed mainly to scattering of SUVB back to space by sulfate-containing particles. Radiative transfer model calculations have not been done for urban particles.

Although aerosols are expected to decrease the flux of SUVB reaching the surface, scattering by particles is expected to result in an increase in the actinic flux within and above the aerosol layer. However, when the particles significantly absorb SUVB, a decrease in the actinic flux is expected. Actinic flux is the radiant energy integrated over all directions at a given wavelength incident on a point in the atmosphere and is the quantity needed to calculate rates of photolytic reactions in the atmosphere. Blackburn et al. (1992) measured attenuation of the photolysis rate of ozone and found that aerosol optical depths near unity at 500 nm reduced ozone photolysis rate by as much as a factor of two. Dickerson et al. (1997) showed that the photolysis rate for NO_2 , a key parameter for calculating the overall intensity of photochemical activity, could be increased within and above a scattering aerosol layer extending from the surface although it would be decreased at the surface. This effect is qualitatively similar to what is seen in clouds, where photolysis rates are increased in the upper layers of a cloud and above the cloud (Madronich, 1987). For a simulation of an ozone episode that occurred during July 1995 in the Mid-Atlantic region, Dickerson et al. (1997) calculated ozone increases of up to 20 ppb compared to cases that did not include the radiative effects of particles in urban airshed model (UAM-IV) simulations. In contrast, Jacobson (1998) found that particles may have caused a 5 to 8% decrease in O_3 levels during the Southern California Air Quality Study in 1987. Absorption by organic compounds and nitrated inorganic compounds was hypothesized to account for the reductions in UV radiation intensity.

The photolysis of ozone in the Hartley bands also leads to production of electronically excited oxygen atoms, $O(^1D)$ that then react with water vapor to form OH radicals. Thus, enhanced photochemical production of ozone is accompanied by the scavenging of species involved in greenhouse warming and stratospheric depletion. However, these effects may be neutralized or even reversed by the presence of absorbing material in the particles. Any evaluation of the effects of particles on photochemical activity therefore will depend on the composition of the particles and will also be location-specific.

Further complicating any straightforward evaluation of UV-B penetration to specific areas of the Earth’s surface are the influences of clouds, as discussed by Erlick et al. (1998), Frederick et al. (1998), and Soulen and Fredrick (1999). The transmission of solar UV and visible radiation is highly sensitive to cloud type, cloud amount, and the extent of their external or internal mixing with cloud droplets. Even in situations of very low atmospheric PM (e.g., over Antarctica), interannual variations in cloudiness over specific areas can be as important as ozone levels in determining UV surface irradiation, with net impacts varying from a month or season to another (Soulen and Fredrick, 1999). Evaluations of the effects of changes in the transmission of solar UV-B radiation to the surface have been performed usually for cloud-free or constant cloudiness conditions.

Given the above considerations, quantification of projected effects of variations in atmospheric PM on human health or the environment because of the effects of particles on the transmission of solar UV-B radiation would require location-specific evaluations, that take into account (a) composition, concentration, and internal structure of the particles; (b) temporal variations in atmospheric mixing height and depths of layers containing the particles; and (c) the abundance of ozone and other absorbers within the planetary boundary layer and the free troposphere. The outcome of such modeling effects would likely vary from location to location in terms of increased or decreased surface level UV-B exposures because of location-specific changes in atmospheric PM concentrations or composition. For example, to the extent that any location-specific scattering by airborne PM were to affect the directional characteristics of UV radiation at ground level, and thereby enhance radiation incident from low angles (Dickerson, 1997), the biological effectiveness (whether deleterious or beneficial) of resulting ground-level UV-B exposures could be enhanced. Airborne PM also can reduce the ground-level ratio of photorepairing radiation (UV-A and short-wavelength visible) to damaging UV-B radiation. Lastly, PM deposition is a major source of PAHs in certain freshwater lakes and coastal areas, and the adverse effects of solar UV are enhanced by the uptake of PAHs by aquatic organisms. Thus, although airborne PM may, in general, tend to reduce ground-level UV-B, its net effect in some locations may be to increase UV damage to certain aquatic and terrestrial organisms, as discussed by Cullen and Neale (1997).

4.6 SUMMARY AND KEY CONCLUSIONS

4.6.1 Particulate Matter Effects on Vegetation and Ecosystems

The first section of this chapter assesses and characterizes the overall ecological integrity and indicate the status of ecosystems within the United States affected by the deposition of the anthropogenic stressors associated with PM. There are six Essential Ecological Attributes (EEAs) — Landscape Condition, Biotic Condition, and Chemical/ Physical Characteristics, and Ecological Processes, Hydrology/Geomorphology, and Natural Disturbance Regimes that can be used to provide a hierarchical framework for determining ecosystem status. The first three can be separated into "patterns" and the last three into "processes." The ecological processes create and maintain the ecosystem elements in patterns. The patterns in turn affect how the ecosystem processes are expressed. Patterns at the higher level of biological organization emerge from the interactions and selection processes at localized levels. Changes in patterns or processes result in changes in the status and functioning of an ecosystem. The relationships among the EEAs are complex because all are interrelated (i.e., changes in one EEA may affect, directly or indirectly, every other EEA).

Human existence on Earth depends on the life-support services provided by the interaction of the different EEAs. Ecosystem processes and patterns provide the functions that maintain clean water, clean air, a vegetated earth, and a balance of organisms that enable humans to survive. The benefits they impart include the absorption and breakdown of pollutants, cycling of nutrients, binding of soil, degradation of organic waste, maintenance of a balance of gases in the air, regulation of radiation balance, climate, and fixation of solar energy. Concern has arisen in recent years regarding biodiversity and the integrity of ecosystems. There are few ecosystems on Earth today whose activities are not influenced by humans. For this reason, understanding the changes in biodiversity and nutrient cycling resulting from PM deposition are of great importance.

The PM whose effects on vegetation and ecosystems is discussed in this section is not a single pollutant but represents a heterogeneous mixture of particles differing in origin, size and chemical constituents. The effects of exposure to a given mass concentration of PM of particular size may, depending on the particular mix of deposited particles, lead to widely differing phytotoxic responses.

The deposition of PM onto vegetation and soil, depending on its chemical composition (acid/base, trace metal, or nutrients, e.g., nitrates or sulfates), can produce direct or indirect responses within an ecosystem. Ecosystem response to pollutant deposition is a direct function of the level of sensitivity of the ecosystem and its ability to ameliorate resulting change. Changes in ecosystem structural patterns and the functioning of ecological processes, must be scaled in both time and space and propagated to the more complex levels of community interaction to produce observable ecosystem changes.

The nitrates and sulfates deposited in PM whose indirect effects occur via the soil are the stressors of greatest environmental significance. Upon entering the soil environment, they can alter the ecological processes of energy flow and nutrient cycling, inhibit nutrient uptake, change ecosystem structure, and affect ecosystem biodiversity. The soil environment is one of the most dynamic sites of biological interaction in nature. It is inhabited by microbial communities of bacteria, fungi and actinomycetes. Bacteria are essential participants in the nitrogen and sulfur cycles that make these elements available for plant uptake. Fungi in association with plant roots form mycorrhizae, a mutualistic symbiotic relationship that is integral in mediating plant uptake of mineral nutrients. Changes in the soil environment that influence the role of the bacteria in nutrient cycling and fungi in making minerals available for plant utilization, determine plant and ultimately ecosystem response.

The affects on the growth of plants resulting from the deposition of nitrates and sulfates and the acidifying effect of the associated H^+ ion in wet and dry deposition in PM are the most important environmentally. Nitrogen is of overriding importance in plant metabolism and, to a large extent governs the utilization of phosphorus, potassium, and other nutrients. Typically, the availability of nitrogen via nitrogen cycle controls net primary productivity, and possibly, the decomposition rate of plant litter. Plants usually obtain nitrogen directly from the soil by absorbing NH_4^+ or NO_3^- through their roots, or it is formed by symbiotic organisms in their roots. Plants vary in their ability to absorb ammonium and nitrate from the soil.

Although nitrogen as molecular nitrogen (N_2) is the most abundant element in the atmosphere, it only becomes available to support the growth of plants after it is converted into reactive forms. In nature, nitrogen may be divided into two groups: reactive (Nr) and nonreactive (N_2). Reactive Nr includes the inorganic reduced forms of nitrogen (e.g., ammonia [NH_3] and ammonium [NH_4^+]), inorganic oxidized forms (e.g., nitrogen oxides [NO_x], nitric acid [HNO_3], nitrous oxide [N_2O], and nitrate [NO_3^-]), and organic compounds (e.g., urea, amine, proteins, and nucleic acids).

Reactive nitrogen is now accumulating in the environment on all spatial scales – local, regional and global. The three main causes of the increase in global Nr is the result of the (1) widespread cultivation of legumes, rice and other crops that promote conversion of N_2 to organic nitrogen through biological nitrogen fixation; (2) combustion of fossil fuels, which converts both atmospheric N_2 and fossil nitrogen to reactive NO_x; and the (3) Haber-Bosch process, which converts nonreactive NH_3 to sustain food production and some industrial activities. The major changes in the nitrogen cycle due to the cited causes can be both beneficial and detrimental to the health and welfare of humans and ecosystems.

Reactive nitrogen can be widely dispersed and accumulate in the environment when the rates of its formation exceed the rates of removal via denitrification. Nr creation and accumulation is projected to increase as per capita use of resources by human populations increases. The cascade of environmental effects of increases in Nr include the following: (1) production of tropospheric ozone and aerosols that induce human health problems; (2) increases in the productivity in forests and grasslands followed by decreases wherever deposition increases significantly and exceeds critical thresholds; Nr additions probably also decrease biodiversity in many natural habitats; (3) in association with sulfur is responsible for acidification and loss of biodiversity in lakes and streams in many regions of the world; (4) eutrophication, hypoxia, loss of biodiversity, and habitat degradation in coastal ecosystems. [Eutrophication is now considered the biggest pollution problem in coastal waters.] (5) contributes to global climate change and stratospheric ozone depletion, which can in turn affect ecosystems and human health (See Table 4-21).

Changes in nitrogen supply can have a considerable effect on an ecosystem's nutrient balance. Large chronic additions of nitrogen influence normal nutrient cycling and alter many plant and soil processes involved in nitrogen cycling. "Nitrogen saturation" results when Nr concentrations exceed the capacity of a system to utilize it. Saturation implies that some resource other than nitrogen is limiting biotic function. Water and phosphorus for plants and carbon for microorganisms are most likely to be the secondary limiting factors. The appearance of nitrogen in soil solution is an early symptom of excess nitrogen. In the final stage, disruption of ecosystem structure becomes visible.

Possible ecosystem responses to nitrogen saturation include (1) a permanent increase in foliar nitrogen and reduced foliar phosphorus and lignin caused by the lower availability of carbon, phosphorus, and water; (2) reduced productivity in conifer stands because of disruptions of physiological function; (3) decreased root biomass and increased nitrification and nitrate leaching; and (4) reduced soil fertility, resulting from increased cation leaching, increased nitrate and aluminum concentrations in streams, (5) decreased water quality and (6) changes in soil microbial communities from predominantly fungal (mycorrhizal) communities to those dominated by bacteria during saturation.

Although soils of most North American forest ecosystems are nitrogen limited, there are some that exhibit severe symptoms of nitrogen saturation (See Table 4-14). They include the

TABLE 4-21. EFFECTS OF REACTIVE NITROGEN

Direct effects of Nr on ecosystems include:
Increased productivity of Nr-limited natural ecosystems. Ozone-induced injury to crop, forest, and natural ecosystems and predisposition to attack by pathogens and insects. Acidification and eutrophication effects on forests, soils, and freshwater aquatic ecosystems. Eutrophication and hypoxia in coastal ecosystems. N saturation of soils in forests and other natural ecosystems. Biodiversity losses in terrestrial and aquatic ecosystems and invasions by N-loving weeds. Changes in abundance of beneficial soil organisms that alter ecosystem functions.
Indirect effects of Nr on other societal values include:
Increased wealth and well being of human populations in many parts of the world. Significant changes in patterns of land use. Regional hazes that decrease visibility at scenic vistas and airports. Depletion of stratospheric ozone by N_2O emissions. Global climate change induced by emissions of N_2O and formation of tropospheric ozone. Damage to useful materials and cultural artifacts by ozone, other oxidants, and acid deposition. Long-distance transport of Nr which causes harmful effects in countries distant from emission sources and/or increased background concentrations of zone and fine particulate matter.
In addition to these effects, it is important to recognize that:
The magnitude of Nr flux often determines whether effects are beneficial or detrimental. All of these effects are linked by biogeochemical circulation pathways of Nr. Nr is easily transformed among reduced and oxidized forms in many systems. Nr is easily distributed by hydrologic and atmospheric transport processes.

high-elevation, non-aggrading spruce-fir ecosystems in the Appalachian Mountains; the eastern hardwood watersheds at the Fernow Experimental Forest near Parsons, WV; forests in southern California, the southwestern Sierra Nevada in Central California; and the Front Range in northern Colorado. The mixed conifer forest and chaparral watershed with high smog exposure in the Los Angeles Air Basin exhibit the highest stream water NO_3^- concentrations for wild-lands in North America;

Increases in soil nitrogen play a selective role in ecosystems. Plants adapted to living in an environment of low nitrogen availability will be replaced by nitrophilic plants capable of using increased nitrogen because they have a competitive advantage when nitrogen becomes more readily available. Plant succession patterns and biodiversity are affected significantly by chronic nitrogen additions in some North American ecosystems. Long-term nitrogen fertilization studies in both New England and Europe suggest that some forests receiving chronic inputs of nitrogen may decline in productivity and experience greater mortality. Declining coniferous forest stands with slow nitrogen cycling may be replaced by deciduous fast-growing forests that cycle nitrogen.

Linked to the nitrogen cascade is the deposition of Nr and sulfates and the associated hydrogen ion is acidic precipitation, a critical environmental stress that affects forest landscapes and aquatic ecosystems in North America, Europe, and Asia. Composed of ions, gases, and particles derived from gaseous emissions of sulfur dioxide (SO_2), nitrogen oxides (NO_x), ammonia (NH_3) and particulate emissions of acidifying and neutralizing compounds, acidic precipitation is highly variable across time and space. Its deposition and the resulting soil acidity can lead to nutrient deficiencies and to high aluminum-to-nutrient ratios that limit uptake of calcium and magnesium and create a nutrient deficiency. Aluminum accumulation in root tissue can reduce calcium uptake and causes Ca^{2+}deficiencies. Tree species can be adversely affected if altered Ca/Al ratios impair calcium or magnesiums uptake. Calcium is essential in the formation of wood and the maintenance of the primary plant tissues necessary for tree growth. Studies suggest that the decline of red spruce stands in Vermont may be related to the Ca/Al ratio (Johnson and Lindberg, 1992b).

The evidence of the effects of wet and dry particulate deposition SO_4^- and Nr species on nutrient cycling in forest ecosystems is provided by the Integrated Forest Study (IFS). The deposition data from the study illustrates several important aspects of the atmospheric exposure characteristics across a wide elevational gradient and over a wide spatial scale. Atmospheric deposition plays a significant role in the biogeochemical cycles at all IFS sites, but is most important in the east at high-elevation sites. The flux of the sulfate ion, Nr compounds, and H^+ ions in throughfall at all sites is dominated by atmospheric deposition. Atmospheric deposition may have significantly affected the nutrient status of some IFS sites through the mobilization of aluminum by impeding cation uptake. Nitrates and sulfate are the dominant anions in the Smokies and pulses of nitrates are the major causes of aluminum pulses in soil solutions. However, the connection between aluminum mobilization and forest decline is not clear, hence, aluminum mobilization presents a situation worthy of further study.

Notable impacts of excess nitrogen deposition also have been observed with regard to aquatic systems. For example, atmospheric nitrogen deposition into soils in watershed areas feeding into estuarine sound complexes (e.g., the Pamlico Sound of North Carolina) appear to contribute to excess nitrogen flows in runoff (especially during and after heavy rainfall events such as hurricanes) from agricultural practices or other uses (e.g., fertilization of lawns or gardens), massive influxes of such nitrogen into watersheds and sounds can lead to dramatic decreases in water oxygen and increases in algae blooms that can cause extensive fish kills and damage to commercial fish and sea food harvesting.

The critical loads concept is useful for estimating the amounts of pollutants (e.g., Nr and acidic precipitation) that sensitive ecosystems can absorb on a sustained basis without experiencing measurable degradation. The estimation of ecosystem critical loads requires an understanding of how an ecosystem will respond to different loading rates in the long term and can be of special value for ecosystems receiving chronic deposition of Nr and sulfur independently and as acidic deposition when in combination.

Changes in the soil can result from the deposition of heavy metals. Exposures to heavy metals are highly variable depending whether deposition is by wet or dry processes. Few (e.g., copper, nickel, zinc) have been documented to have direct phytoxicity under field conditions. Exposure to coarse particles of natural origin and elements such as iron and manganese are more likely to occur via dry deposition while fine particles of atmospheric origin and elements such as cadmium, chromium, lead nickel, and vanadium. Ecosystems immediately downwind of major emissions sources such as power generating, industrial, or urban complexes can receive locally heavy inputs. Heavy metal accumulation by affecting litter decomposition presents the greatest potential for influencing nutrient cycling. Microbial populations decreased and logarithmic rates of microbial increase were prolonged as a result of cadmium toxicity. Additionally, the presence of cadmium, copper and nickel were observed to affect the symbiotic activity of fungi, bacteria, and actinomycetes.

Phytochelatins produced by plants as a response to sublethal concentrations of heavy metals, are indicators of metal stress and can be used to indicate that heavy metals are involved in forest decline. Increasing concentrations of phytochelatins with increase in altitude and their increase across regions showing increased levels of forest injury implicated them in forest decline.

The ambient concentration of particles, the parameter for which there is most data (Chapter 3), is at best an indicator of exposure. The amount of PM entering the immediate plant environment, deposited onto the plant surfaces or soil in the vicinity of the roots, determines the biological effect. Three major routes are involved during the wet and dry deposition processes:

(1) precipitation scavenging in which particles are deposited in rain and snow; (2) occult (fog, cloud water, and mist interception); and (3) dry deposition, a much slower, yet more continuous removal to place surfaces.

Deposition of PM on above-ground plant parts can have either a physical and/or chemical effect. Particles transferred from the atmosphere to plant surfaces may cause direct effects if they (1) reside on the leaf, twig, or bark surface for an extended period; (2) are taken up through the leaf surface; or (3) are removed from the plant via resuspension to the atmosphere, washing by rainfall, or litter-fall with subsequent transfer to the soil. Ecosystem effects have been observed only in the neighborhood limestone quarries.

Secondary organics formed in the atmosphere have been variously subsumed under the following terms: toxic substances, pesticides, hazardous air pollutants (HAPS), air toxics, semivolatile organic compounds (SOCs), and persistent organic pollutants (POPS). The substances alluded to under the above headings are controlled under CAA Sect.112, Hazardous Air Pollutants not as criteria pollutants controlled by NAAQS under CAA Sections 108 and 109 (U.S. Code, 1991). Their possible effects on humans and ecosystems are discussed in many other government documents and publications. They are noted in this chapter because, in the atmosphere, many of the chemical compounds are partitioned between gas and particle phases and are deposited as particulate matter. As particles, they become airborne and can be distributed over a wide area and affect remote ecosystems. Some of the chemical compounds are of concern to humans because they may reach toxic levels in food chains of both animals and humans; whereas others tend to decrease or maintain the same toxicity as they move through the food chain.

An important characteristic of fine particles is their ability to affect flux of solar radiation passing through the atmosphere directly, by scattering and absorbing solar radiation, and indirectly, by acting as cloud condensation nuclei that, in turn, influence the optical properties of clouds. Regional haze has been estimated to diminish surface solar visible radiation by approximately 8%. Crop yield have been reported as being sensitive to the amount of sunlight receive, and crop losses have been attributed to increased airborne particle levels in some area of the world.

From among all of the various effects of PM on ecosystems discussed above, the effects of excess nitrogen added to the environment via emissions to the atmosphere and especially increases in Nr due to food production has resulted in the accumulation in the environmental at all spatial scales, local, regional and global. The results of the nitrogen cascade as Nr moves through the different environmental compartments has effects both beneficial and detrimental to humans and ecosystems. Table 4-21 summarizes a variety of effects (both and indirect) associated with the presence of Nr as it circulates through the various environmental compartments. These effects are associated with the long-term chronic deposition of Nr on the terrestrial and aquatic ecosystems.

4.6.2 Particulate Matter-Related Effects on Visibility

Visibility is defined as the degree to which the atmosphere is transparent to visible light and the clarity and color fidelity of the atmosphere. Visual range is the farthest distance a black object can be distinguished against the horizontal sky. Visibility impairment is any humanly perceptible change in visibility. For regulatory purposes, visibility impairment, characterized by light extinction, visual range, contrast, and coloration, is classified into two principal forms: (1) “reasonably attributable” impairment, attributable to a single source or small group of sources, and (2) regional haze, any perceivable change in visibility caused by a combination of many sources over a wide geographical area.

Visibility is measured by human observation, light scattering by particles, the light extinction-coefficient, and parameters related to the light-extinction coefficient (visual range and deciview scale), and fine PM mass concentrations.

The air quality within a sight path will affect the illumination of the sight path by scattering or absorbing solar radiation before it reaches the Earth’s surface. The rate of energy loss with distance from a beam of light is the light extinction coefficient. The light extinction coefficient is the sum of the coefficients for light absorption by gases (σ_{ag}), light scattering by gases (σ_{sg}), light absorption by particles (σ_{ap}), and light scattering by particles (σ_{sp}). Corresponding coefficients for light scattering and absorption by fine and coarse particles are σ_{sfp} and σ_{afp} and σ_{scp} and σ_{acp}, respectively. Visibility within a sight path longer than approximately 100 km (60 mi) is affected by the change in the optical properties of the atmosphere over the length of the sight path.

Visual range was developed for and continues to be used as an aid in military operations and to a lesser degree in transportation safety. Visual range is commonly taken to be the greatest distance a dark object can be seen against the background sky. The deciview is an index of haziness. A change of 1 or 2 deciviews is seen as a noticeable change in the appearance of a scene.

Under certain conditions, fine particle mass concentrations may be used as a visibility indicator. However, the relationship may differ between locations and for different times of the year. Also, measurement should be made under dry conditions.

Visibility impairment is associated with airborne particle properties, including size distributions (i.e., fine particles in the 0.1- to 1.0-µm size range) and aerosol chemical composition, and with relative humidity. With increasing relative humidity, the amount of moisture available for absorption by particles increases, thus causing the particles to increase in both size and volume. As the particles increase in size and volume, the light scattering potential of the particles also generally increases. Visibility impairment is greatest in the eastern United States and Southern California. In the eastern United States, visibility impairment is caused primarily by light scattering by sulfate aerosols and, to a lesser extent, by nitrate particles and organic aerosols, carbon soot, and crustal dust. Up to 86% of the haziness in the eastern United States is caused by atmospheric sulfate. Further West, scattering contributions to visibility impairment decrease to from 25 to 50%. Light scattering by nitrate aerosols is the major cause of visibility impairment in southern California. Nitrates contribute about 45% to the total light extinction in the West and up to 17% of the total extinction in the East. Organic particles are the second largest contributors to light extinction in most U.S. areas. Organic carbon is the greatest cause of light extinction in the West, accounting for up to 40% of the total extinction and up to 18% of the visibility impairment in the East. Coarse mass and soil, primarily considered "natural extinction," is responsible for some of the visibility impairment in the West, accounting for up to 25% of the light extinction.

4.6.3 Particulate Matter-Related Effects on Materials

Building materials (metals, stones, cements, and paints) undergo natural weathering processes from exposure to environmental elements (wind, moisture, temperature fluctuations, sun light, etc.). Metals form a protective film of oxidized metal (e.g., rust) that slows environmentally induced corrosion. On the other hand, the natural process of metal corrosion from exposure to natural environmental elements is enhanced by exposure to anthropogenic pollutants, in particular SO_2, that render the protective film less effective.

Dry deposition of SO_2 enhances the effects of environmental elements on calcereous stones (limestone, marble, and cement) by converting calcium carbonate (calcite) to calcium sulfate dihydrate (gypsum). The rate of deterioration is determined by the SO_2 concentration, the stone's permeability and moisture content, and the deposition rate; however, the extent of the damage to stones produced by the pollutant species apart from the natural weathering processes is uncertain. Sulfur dioxide also has been found to limit the life expectancy of paints by causing discoloration and loss of gloss and thickness of the paint film layer.

A significant detrimental effect of particle pollution is the soiling of painted surfaces and other building materials. Soiling changes the reflectance of a material from opaque and reduces the transmission of light through transparent materials. Soiling is a degradation process that requires remediation by cleaning or washing, and, depending on the soiled surface, repainting. Available data on pollution exposure indicates that particles can result in increased cleaning frequency of the exposed surface and may reduce the usefulness of the soiled material. Attempts have been made to quantify the pollutants exposure levels at which materials damage and soiling have been perceived. However, to date, insufficient data are available to advance our knowledge regarding perception thresholds with respect to pollutant concentration, particle size, and chemical composition.

4.6.4 Effects of Atmospheric Particulate Matter on Global Warming Processes and Transmission of Solar Ultraviolet Radiation

The physical processes (i.e., scattering and absorption) responsible for airborne particle effects on transmission of solar visible and ultraviolet radiation are the same as those responsible for visibility degradation. Scattering of solar radiation back to space and absorption of solar radiation determine the effects of an aerosol layer on solar radiation.

Atmospheric particles greatly complicate projections of future trends in global warming processes because of emissions of greenhouse gases; consequent increases in global mean temperature; resulting changes in regional and local weather patterns; and mainly deleterious (but some beneficial) location-specific human health and environmental effects. The body of available evidence, ranging from satellite to in situ measurements of aerosol effects on radiation receipts and cloud properties, is strongly indicative of an important role in climate for aerosols.

This role, however, is poorly quantified. No significant advances have been made in reducing the uncertainties assigned to forcing estimates provided by the IPCC for aerosol-related forcing, especially for black carbon-containing aerosol. The IPCC characterizes the scientific understanding of greenhouse gas-related forcing as “high” in contrast to that for aerosol, which it describes as “low” to “very low.”

Quantification of the effect of anthropogenic aerosol on hydrological cycles requires more information than is presently available regarding ecosystems responses to reduced solar radiation and other changes occurring in the climate system. However, several global scale studies indicate that aerosol cooling alone can slow down the hydrological cycle, while cooling plus the nucleation of additional cloud droplets can dramatically reduce precipitation rates.

In addition to direct climate effects through the scattering and absorption of solar radiation, particles also exert indirect effects on climate by serving as cloud condensation nuclei, thus affecting the abundance and vertical distribution of clouds. The direct and indirect effects of particles appear to have significantly offset global warming effects caused by the buildup of greenhouse gases on a globally-averaged basis. However, because the lifetime of particles is much shorter than that required for complete mixing within the Northern Hemisphere, the climate effects of particles generally are felt much less homogeneously than are the effects of long-lived greenhouse gases.

Any effort to model the impacts of local alterations in particle concentrations on projected global climate change or consequent local and regional weather patterns would be subject to considerable uncertainty.

Atmospheric particles also complicate estimation of potential future impacts on human health and the environment projected as possible to occur because of increased transmission of solar ultraviolet radiation (UV-B) through the Earth’s atmosphere, secondary to stratospheric ozone depletion due to anthropogenic emissions of chlorofluorcarbons (CFCs), halons, and certain other gases. The transmission of solar UV-B radiation is affected strongly by atmospheric particles. Measured attenuations of UV-B under hazy conditions range up to 37% of the incoming solar radiation. Measurements relating variations in PM mass directly to UV-B transmission are lacking. Particles also can affect the rates of photochemical reactions occurring in the atmosphere, e.g., those involved in catalyzing tropospheric ozone formation. Depending on the amount of absorbing substances in the particles, photolysis rates either can be increased or decreased. Thus, atmospheric particle effects on UV-B radiation, which vary depending on size and composition of particles, can differ substantially over different geographic areas and from season to season over the same area. Any projection of effects of location-specific airborne PM alterations on increased atmospheric transmission of solar UV radiation (and associated potential human health or environmental effects) due to stratospheric ozone-depletion would, therefore, also be subject to considerable uncertainty.

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Appendix 4A

Colloquial and Latin Names

Alder, hazel	*Alnus serrulata* (Aiton) Willdenow
Alder, red	*Alnus rubra* Bong.
Bean, common	*Phaseolus vulgaris* L.
Beech	*Fagus sylvatica* L.
Birch, yellow	*Betula alleghaniensis* Britt.
Blackhaw	*Viburnum prunifolium* L.
Brush box	*Lophostemon confertus* (R. BR.) P.G. Wilson & Waterhouse
Ceanothus, hoaryleaf	*Ceanothus crassifolius* Torry
Chaparral	*Ceanothus crassifolius*
Coachwood	*Ceratopetalum apetalum*, D.Don
Corn	*Zea mays* L.
Dogwood, flowering	*Cornus florida* L.
Elm	*Ulmus* spp.
Fir, balsam	*Abies balsamea* (L) Mill.
Fir, Douglas	*Pseudotsuga menziesii* (Mirb.) Franco.
Fir, fraser	*Abies fraseri* (Pursh.) Poir
Grape	*Vitis* spp.
Grass, red brome	*Bromus rubens* L.
Grass, purple moor	*Molina caerulea* (L.) Moench.
Greenbriar	*Smilax* spp.
Gum, sweet	*Liquidambar styraciflua* L.
Haw, black	*Viburnum prunifolium* l.
Heather, Scottish	*Calluna vulgaris* Salisb.

Hickory	*Carya* spp.
Hophornbeam	*Ostrya virginiana* (Mill.) Koch
Ivy, English	*Hedera helix* L.
Laurel, mountain	*Kalmia latifolia* L.
Lichen, monks hood	*Hypogymnia physiodes*
Maize	*Zea mays* L.
Maple, red	*Acer rubrum* L.
Maple	*Acer* spp.
Maple, sugar	*Acer saccharum* Marsh.
Mustard, small podded	*Brassica geniculata* L.
Nettle, stinging	*Urtica dioica* L.
Oak, bur	*Quercus macrocarpa* Michx.
Oak, English	*Quercus rober* L.
Oak, chestnut	*Quercus prinus* = Q. *montana* Willd.
Oak, live	*Quercus virginiana* Mill.
Oak, northern red	*Quercus rubra* L.
Oak, turkey	*Quercus laevis* Walt.
Oak, white	*Quercus alba* L.
Oak	*Quercus* spp.
Oats, domestic	*Avena sativa* L.
Oats, wild	*Avena fatua* L
Persimmon, common	*Diosporos virginiana* L.
Pine, eastern white	*Pinus strobus* L.
Pine, jack pine	Pinus *banksiana* Lamb.
Pine, loblolly	*Pinus taeda* L.
Pine, lodgepole	*Pinus contorta* Loud.
Pine, Scots (Scotch)	*Pinus sylvestris* L.
Pine, slash	*Pinus elliotti* Englem.

Pine, lodgepole x jack pine	*Pinus contorta* (Douglas ex Loud) x P. *banksiana* Lamb.
Poplar, black	*Populus nigra L.*
Poplar, white	*Populus alba* L.
Poplar, yellow or tulip	*Liriodendron tulipifera* L.
Privet	*Ligustrum* spp.
Purple Moor Grass	*Molina caerulea* (L.) Moench.
Ragweed	*Ambrosia* spp.
Rhododendron, Catawba	*Rhododendron catawbiense* Michx.
Rhododendron, rosebay	*Rhododendron maximum* L.
Sage, coastal	*Artemisia californica* Less.
Scottish Heather	*Calluna vulgaris* Salisb.
Soybean	*Glycine max* (L.) Merr.
Spruce, Norway	*Picea abies* (L.) Karst.
Spruce, red	*Picea rubens* Sarg.
Spruce, sitka	*Picea sitchensis* (Bong.) Carr.
Spruce, white	*Picea glauca* (Moench.) Voss.
Sunflower	*Helianthus annuus* L.
Sweetgum	*Liquidambar styraciflua* L.
Tulip poplar	*Liriodendron tulipifera* L.

EUMYCOTA-FUNGI

Zygomycota

Vesicular Arbuscular Mycorrhizae

Scutellospora

Gigaspora

Glomus agrigatum

Glomus leptototicum

Ascomycotina

Chaetomium sp.

Fungi Imperfecti

Aureobasidium pullulans

Cladosporium sp.

Epicoccum sp.

Pestalotiopsis

Phialophora verrucosa

Pleurophomella =Sirodothis

5. HUMAN EXPOSURE TO PARTICULATE MATTER AND ITS CONSTITUENTS

5.1 INTRODUCTION

5.1.1 Purpose

The U.S. Environmental Protection Agency's (EPA's) regulatory authority for PM applies primarily to ambient air and those sources that contribute to ambient air PM concentrations. Most of the epidemiological studies, discussed in Chapter 8, relate measured community levels of airborne pollutants to population-based health statistics. Of necessity, these studies have to rely on some simplifying assumptions regarding exposures, usually that air pollutant concentrations measured at community (or population-oriented) monitoring sites (or the average concentration of several such sites) can serve as surrogate indices for the average personal exposure to ambient PM for the population. However, total personal exposure to PM includes both ambient and nonambient components, and both components may contribute to adverse health effects. Thus, a major emphasis must be to develop an understanding of exposure to PM from sources that contribute to ambient air pollution. Ultimately, it will be necessary to account for both ambient and nonambient components of personal exposure in order to fully understand the relationship between PM and health effects. In addition, an individual's personal exposure to ambient, nonambient, and total PM would provide useful information for studies where health outcomes are tracked individually.

Exposure has many definitions. However, for airborne particulate matter (PM), an individual's exposure is ideally based on measurements of the PM concentrations in the air in the individual's breathing zone as the individual moves through space and time. However, epidemiological studies frequently use the ambient concentration as a surrogate for exposure. Therefore, understanding exposure is important because it is the individual who experiences adverse health effects associated with elevated PM concentrations. Human exposure data and models provide the link between ambient concentrations (from monitoring data or estimated with atmospheric transport models) and lung deposition and clearance models to enable estimates of the source-air concentration-exposure-dose relationship for input into dose-response assessments for PM from ambient sources. Personal exposure includes contributions from many different types of particles, from many sources, and in many different environments.

The goal of this chapter is to provide current information on the development of human exposure data and models. This includes information on (a) relationships between PM measured at ambient sites and personal exposures to PM from both ambient and nonambient sources, and (b) factors that affect these relationships. Human exposure data and models presented in this chapter provide critical links between ambient monitoring data and PM dosimetry and between toxicological studies and epidemiologic studies which are presented in other chapters. Specific objectives of this chapter are fourfold:

(1) To provide an overall conceptual framework of exposure science as applied to PM, including the identification and evaluation of factors that determine personal PM exposure;

(2) To provide a concise summary and review of recent data (since 1996) and findings from pertinent PM exposure studies;

(3) To characterize quantitative relationships between ambient air quality measurements (mass, chemical components, number, etc.) as determined by a community monitoring site and total personal PM exposure as well as its ambient and nonambient components; and

(4) To evaluate the implications of using ambient PM concentrations as a surrogate for personal exposure in epidemiologic studies of PM health effects.

5.1.2 Particulate Matter Mass and Constituents

Current EPA PM regulations are based on mass as a function of aerodynamic size. However, EPA also measures the chemical composition of PM in both monitoring and research studies. The composition of PM is variable and, as discussed in Chapters 7 and 8, health effects may be related to PM characteristics other than mass. Since PM from ambient air and other microenvironments may have different physical and chemical characteristics, PM from such different sources may also have different health effects. Ultimately, to understand and control health effects caused by PM exposures from all sources, it is important to quantify and understand exposure to those chemical constituents from various sources that are responsible for adverse health effects.

The National Research Council (NRC) recognized the distinction between measuring exposure to PM mass and to chemical constituents when setting *Research Priorities for Airborne Particulate Matter I: Immediate Priorities and a Long-range Research Portfolio* (NRC, 1998). Specifically, in Research Topic 1, Outdoor Measures versus Actual Human Exposures, NRC recommends evaluating "the relationships between concentrations of particulate matter and gaseous co-pollutants measured at stationary outdoor air monitoring sites and the contributions of these concentrations to actual personal exposures . . ." for PM mass. The NRC Research Topic 2 recommends evaluating exposures to biologically important constituents and specific characteristics of PM that cause responses in potentially susceptible subpopulations and the general population. It also was recognized by the NRC that "a more targeted set of studies under this research topic (#2) should await a better understanding of the physical, chemical, and biological properties of airborne particles associated with the reported mortality and morbidity outcomes" (NRC, 1999). The NRC also stated that the later studies "should be designed to determine the extent to which members of the population contact these biologically important constituents and size fractions of concern in outdoor air, outdoor air that has penetrated indoors, and air pollutants generated indoors" (NRC, 1999). Thus, exposure studies should include contributions from all sources. The emphasis in this chapter on PM mass reflects the current state of the science. Where available, data also have been provided on chemical constituents although in most cases the data are limited. As recognized by the NRC, a better understanding of exposures to PM chemical constituents from multiple sources will be required to more fully identify, understand, and control those sources of PM contributing to adverse health effects and to accurately define the relationship between PM exposure and health outcomes due to either short-term or chronic exposures.

5.1.3 Relationship to Past Documents

Early versions of PM criteria documents did not emphasize total human exposure, but rather focused almost exclusively on outdoor air concentrations. For instance, the 1969 Air Quality Criteria for Particulate Matter (National Air Pollution Control Administration, 1969) did not discuss either *exposure* or *indoor concentrations.* The 1982 EPA PM Air Quality Criteria Document (1982 PM AQCD), however, provided some discussion of indoor PM concentrations reflecting an increase in microenvironmental and personal exposure studies (U.S. Environmental

Protection Agency, 1982). The new data indicated that personal activities along with PM generated by personal and indoor sources (e.g., cigarette smoking) could lead to high indoor levels and high personal exposures to total PM. Some studies reported indoor concentrations that exceeded PM concentrations found in the air outside the monitored microenvironments or at nearby monitoring sites. Between 1982 and 1996, many more studies of personal and indoor PM exposure demonstrated that in most inhabited domestic environments indoor PM mass concentrations and personal PM exposures of the residents were greater than ambient PM mass concentrations measured simultaneously (e.g., Sexton et al., 1984; Spengler et al., 1985; Clayton et al., 1993). As a result, the NRC (1991) recognized the potential importance of indoor sources of contaminants (including PM) in causing adverse health outcomes.

The 1996 AQCD (U.S. Environmental Protection Agency, 1996) reviewed the human PM exposure literature through early 1996 mainly to evaluate the use of ambient air monitors as surrogates for PM exposure in epidemiological studies. Many of the studies cited showed poor correlations between personal exposure or indoor measurements of PM mass and outdoor or ambient site measurements. Conversely, Janssen et al. (1995) and Tamura et al. (1996a) showed that in the absence of major nonambient sources, total PM exposures to individuals tracked through time were highly correlated with ambient PM concentrations. Analyses of these latter two studies led to consideration of ambient and nonambient exposures as separate components of total personal exposure. As a result, the 1996 PM AQCD (U.S. Environmental Protection Agency, 1996) distinguished between ambient and nonambient PM personal exposure for the first time. This chapter builds on the work of the 1996 PM AQCD by further evaluating the ambient and nonambient components of PM and by reporting research that evaluates the relationship between ambient concentrations and total, ambient, and nonambient personal exposure.

5.1.4 Chapter Structure

The chapter is organized to provide information on the principles of exposure, review the existing literature, and summarize key findings and limitations in the information; the specific sections are described below.

- Section 5.2 discusses the basic concepts of exposure including definitions, methods for estimating exposure, and methods for estimating ambient air components of exposure.

- Section 5.3 presents PM mass data including a description of the key available studies, the relationship of PM exposures with ambient concentrations, and factors that affect the relationship.
- Section 5.4 presents data on PM constituents including a description of the key available studies, the relationship with ambient concentrations, and factors that affect the relationship.
- Section 5.5 discusses the implications of using ambient PM concentrations in epidemiologic studies of PM health effects.
- Section 5.6 summarizes key findings and limitations of the information.

5.2 BASIC CONCEPTS OF EXPOSURE

5.2.1 The Concept of Exposure

"There is reasonable agreement that human exposure [to a substance] means contact with the chemical or agent." However, contact can be either with "(a) the visible exterior of the person (skin and openings into the body such as mouth and nostrils), or (b) the so-called exchange boundaries where absorption takes place (skin, lung, gastrointestinal tract)" (Federal Register, 1986). In its 1992 Guidelines for Exposure Assessment (U.S. EPA, 1992), EPA defined exposure as "taking place at the visible external boundary, as in (a) above, [concluding that this definition] is less ambiguous and more consistent with nomenclature in other scientific fields." This was a change from the 1986 Guidelines (Federal Register, 1986).

> Under this definition, it is helpful to think of the human body as having a hypothetical outer boundary separating inside the body from outside the body. This outer boundary of the body is the skin and the openings into the body such as the mouth, the nostrils, and punctures and lesions in the skin. As used in these Guidelines, exposure to a chemical is the contact of that chemical with the outer boundary. An exposure assessment is the quantitative or qualitative evaluation of that contact; it describes the intensity, frequency, and duration of contact, and often evaluates the rates at which the chemical crosses the boundary (chemical intake or uptake rates), the route by which it crosses the boundary (exposure route; e.g., dermal, oral, or respiratory), and the resulting amount of the chemical that actually crosses the boundary (a dose) and the amount absorbed (internal dose) (U.S. EPA, 1992).

When applied to PM exposure by the inhalation route, the concentration of interest is that of PM in the air which enters the respiratory system, not the average concentration of inspired and exhaled air which exists at the mouth or nostrils. Therefore, a measurement of inhalation exposure to PM is based on measurements of the PM concentration near the breathing zone but not affected by exhaled air.

5.2.2 Components of Exposure

The total exposure of an individual over a discrete period of time includes exposures to many different particles from various sources while in different microenvironments. Duan (1982) defined a microenvironment as "a [portion] of air space with homogeneous pollutant concentration." It also has been defined as a volume in space for a specific time interval during which the variance of concentration within the volume is significantly less than the variance between that microenvironment and surrounding ones (Mage, 1985). In general, people pass through a series of microenvironments including outdoor, in-vehicle, and indoor microenvironments as they go through time and space. Thus, total *daily* exposure for a single individual to PM must be expressed as the sum of various exposures for the microenvironments that the person occupies in the day (modified from National Research Council, 1991).

In a given microenvironment, particles may originate from a wide variety of sources. For example, in an indoor microenvironment PM may be generated by (1) indoor activities, (2) outdoor PM entering indoors, (3) the chemical interaction of outdoor air pollutants and indoor air or indoor sources, (4) transport from another indoor microenvironment, or (5) personal activities. All of these disparate sources have to be accounted for when estimating total human exposure to PM.

An analysis of personal exposure to PM mass (or constituent compounds) requires definition and discussion of several classes of particles and exposure. In this chapter, PM metrics may be described in terms of exposure or as an air concentration. PM also may be described according to both its source (i.e., ambient, nonambient) and the microenvironment where exposure occurs. Table 5-1 provides a summary of the terms used in this chapter, the notation used for these terms, and their definition. These terms are used throughout this chapter and provide the terminology for evaluating personal exposure to total PM and to PM from ambient and nonambient sources.

TABLE 5-1. TYPES OF PARTICULATE MATTER USED IN EXPOSURE AND CONCENTRATION VARIABLES

Term	Notation	Definition
		General Definitions
Concentration	C	General term for the average air concentration over some specified time period, used with subscript to indicate concentration of a specific type of PM, usually expressed in µg/m^3 units.
Personal Exposure	E	General term for the average personal exposure over some specified time period, used with subscript to indicate exposure to a specific type of PM, quantified as the concentration at the oral/nasal contact boundary.

Types of Particulate Matter

Term	Subscript	Definition
Ambient PM	a	PM in the atmosphere measured at a community ambient monitoring site either emitted into the atmosphere directly (primary PM) or formed in it (secondary PM). Major sources of PM species are industry, motor vehicles, commerce, domestic emissions such as wood smoke, and natural wind-blown dust or soil. (C without subscript is used for C_a. E_a is used for exposure to ambient PM while outdoors.)
Ambient-Outdoor PM	o	Ambient PM in an outdoor microenvironment. (C_o is frequently considered to be equal to, or at least represented by, C.)
Indoor PM	i	All PM found indoors.
Ambient-Indoor PM	ai	Ambient PM that has infiltrated indoors (i.e., has penetrated indoors and remains suspended). E_{ai} is used for ambient exposure while indoors.
Indoor-generated PM	ig	PM generated indoors.
Indoor-reaction PM	ir	PM formed indoors by pollutants from outdoors reacting with indoor-generated pollutants.
Personal Cloud PM	pc	PM contributing to personal exposure but not contained in indoor or outdoor measurements of PM, usually related to personal activities.
Personal PM (of a subject)	s	PM at the oral/nasal contact zone as the subject moves through time and space.

Concentration and Exposure Variable Used without Subscripts

Term	Notation	Definition
Ambient Concentration	C	Concentration measured at a community ambient air monitoring site (or the average of several such sites).
Total Personal Exposure	T	Total personal exposure as measured by a personal exposure monitor (PEM).
Ambient Exposure	A	Personal exposure to the ambient component of total personal exposure, i.e., personal exposure to that PM measured at an ambient air community monitoring site. Includes exposure to C and C_{ai} but not to resuspended ambient PM previously deposited indoors.
Nonambient Exposure	N	Personal exposure to nonambient PM.

TABLE 5-1 (cont'd). TYPES OF PARTICULATE MATTER USED IN EXPOSURE AND CONCENTRATION VARIABLES

Relationships among Concentration and Exposure Variables for a Two-Compartment Model (indoors and outdoors)

$T = A + N$

$A = E_a + E_{ai}$

$A = yC + (y-1)\ C_{ai}$, where y = fraction of time outside

$N = E_{ig} + E_{ir} + E_{pc}$

Exposures are significant only if they are associated with a biologically relevant duration of contact with a substance of concern. Application of this concept to PM exposure is complicated by a lack of understanding of the biological mechanisms of PM toxicity. It is not certain whether the relevant duration is the instantaneous exposure to a peak concentration, or hourly, daily, or long-term exposure for months or years (or possibly all of the above). Similarly, it is not certain how PM toxicity depends on particle size or particle composition; whether number, surface area, or mass is the appropriate metric; or how PM toxicity may be influenced by conditions that might increase susceptibility (age, pre-existing disease conditions [COPD, asthma, diabetes, etc.], exposure to infectious agents, exposure to heat or cold, stress, etc.). It should be clear that a person's exposure is influenced by the distribution of many variables and parameters. A measurement at a single point in space or time along each distribution cannot easily describe a person's exposure. Thus, it is important to think of exposure as a path function, the instantaneous exposure varying as the PM concentration and composition varies as the person moves through time and space.

The 1997 NAAQS were developed largely on the basis of evidence from epidemiologic studies that found relatively consistent associations between outdoor PM mass concentrations and observed health effects. Thus, an emphasis in this chapter is on the relationship between the PM concentrations measured at ambient sites and personal exposures to the PM measured at those ambient sites (NRC, 1998), i.e., ambient PM exposure. Although this is an emphasis, it should be kept in mind that every particle that deposits in the lung becomes part of a dose delivered to the individual. It is likely that the nonambient component of total exposure also has health effects which would not necessarily be detected using community time-series epidemiological studies.

5.2.3 Quantification of Exposure

Quantification of inhalation exposure to PM or any other air pollutant starts with the concept of the variation in the concentration of the air pollutant in the breathing zone (but unperturbed by exhaled breath) as measured by a personal exposure monitor as a person moves through time and space. The relationships among the various types of exposure quantities can easily be seen in the hypothetical exposure time profile shown in Figure 5-1. The peak exposure, instantaneous exposure, and average exposure have units of concentration, for PM, usually $\mu g/m^3$. The integrated exposure has units of concentration × time.

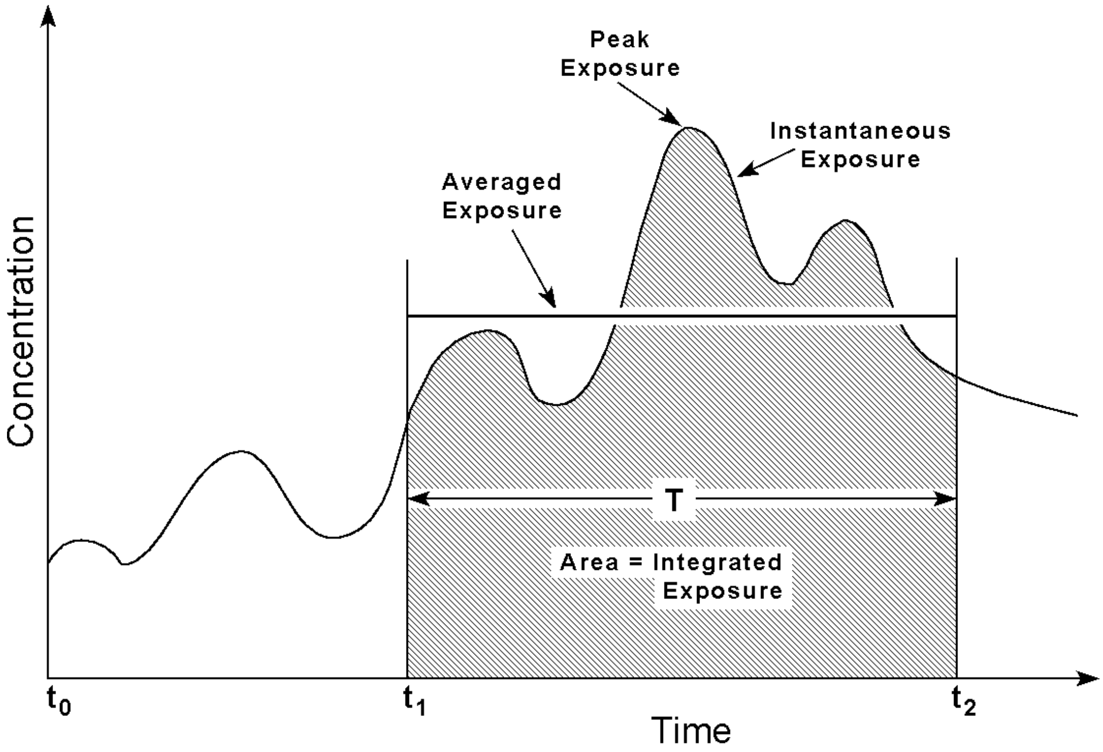


Figure 5-1. Hypothetical exposure time profile: Pollutant exposure as a function of time showing how the averaged exposure, integrated exposure, and peak exposure relate to the instantaneous exposure. (t_2 - t_1 = T.)

Source: Adapted from Duan et al. (1989); Zartarian et al. (1997).

The integrated exposure may be written as

$$\mathcal{E}(t_1, t_2) = \int_{t=t_1}^{t=t_2} C_s(t)dt, \qquad (5\text{-}1)$$

where ∈ is the integrated personal exposure during the time period t_1 to t_2 and C_s is the instantaneous exposure of the subject as the subject moves through space and time (Lioy, 1990; NRC, 1991; Georgopoulos and Lioy, 1994). C_s is a function of both time and space so in general it cannot be correctly approximated by a measurement at a single time or at a single point in space.

For most of the discussion in this chapter we will be interested in the average exposure given as

$$E(t_1, t_2) = \frac{1}{t_2 - t_1} \int_{t=t_1}^{t=t_2} C_s(t)dt, \qquad (5\text{-}2)$$

where E is the average exposure over the time period t_2-t_1. Most studies report 24-hour averages although some studies measure 12-hour or 2 or 3 day averages.

Equations 5-1 and 5-2 apply to a specific individual moving through time and space on a specific path. When treating populations it is necessary to consider the distribution of values of the variables and parameters. Georgopoulos and Lioy (1994) show how these equations can be modified to consider the probability distributions.

5.2.4 Methods To Estimate Personal Exposure

Personal exposure may be estimated using either direct or indirect approaches. *Direct approaches* measure the contact of the person with the chemical concentration in the exposure media over an identified period of time. Direct measurement methods include personal exposure monitors (PEMs) for PM that are worn continuously by individuals as they encounter various microenvironments while performing their daily activities. *Indirect approaches* use models and available information on concentrations of chemicals in microenvironments, the time individuals spend in those microenvironments, and personal PM generating activities to estimate personal exposure. This section describes the methods to directly measure personal exposures and microenvironmental concentrations as well as the models used to estimate exposure. Several approaches to estimate personal exposure to ambient PM also are described.

5.2.4.1 Direct Measurement Methods

5.2.4.1.1 Personal Exposure Monitoring Methods

In theory, personal exposure to total PM is measured by sampling the concentration of PM in inhaled air entering the nose or mouth. Practically, it is defined as that PM collected by a PEM worn by a person and sampling from a point near the breathing zone (but not affected by exhaled breath). PEMs for PM use measurement techniques similar to those used for ambient PM. Most PEMs rely on filter-based mass measurement of a particle size fraction (PM_{10} or $PM_{2.5}$) usually integrated over either a 24- or 12-h period at flow rates of 2 to 4 L/min using battery-operated pumps. PEMs must be worn by study participants; therefore, they must be quiet, compact, and battery-operated. These requirements limit the type of pumps and the total sample volume that can be collected. Generally, small sample volumes limit personal exposure measurements to PM mass and a few elements detected by XRF. In most studies, $PM_{2.5}$ and PM_{10} have not been collected concurrently; thus, there are very few data available with which to estimate personal exposure to coarse thoracic PM (i.e., $PM_{10-2.5}$) exposures.

Other methods used for ambient PM also have been adapted for use as a PEM. For example, a personal nephelometer that measures light scattering has been worn by subjects and used in personal exposure studies to obtain real-time measurements of PM (Quintana et al., 2000; Rea et al., 2001; Magari et al., 2002; Lanki et al., 2002). Light scattering instruments are most sensitive to particles in the accumulation mode size range. A portable condensation nuclei counter (with a lower size limit of 20 nm diameter) has also been used in exposure studies (Abraham et al., 2002).

5.2.4.1.2 Microenvironmental Monitoring Methods

Direct measurements of microenvironmental PM concentrations which are used with models to estimate personal exposure to PM also use methods similar to those for ambient PM. These methods differ from PEMs in that they are stationary with respect to the microenvironment (such as a stationary PEM). Microenvironmental monitoring methods include filter-based mass measurements of particle size fractions (PM_{10}, $PM_{2.5}$) usually integrated over either a 24- or 12-h period. Flow rates vary between various devices from 4 to 20 L/min. Larger sample volumes allow more extensive chemical characterization to be conducted on microenvironmental samples. Because more than one pumping system can be used in a microenvironment, $PM_{2.5}$ and PM_{10} can be collected simultaneously. Other continuous ambient PM measurement methods that have been utilized for microenvironmental monitoring are the Tapered Element Oscillating Microbalance (TEOM) and nephelometers. Various continuous techniques for counting particles by size (Climet, LASX, SMPS, APS) also have also been used. Measurement techniques are discussed in Chapter 2.

5.2.4.2 Indirect or Modeling Methods

5.2.4.2.1 Personal Exposure Models

Exposure modeling for PM mass ($PM_{2.5}$ and $PM_{10-2.5}$) and chemical constituents is a relatively new field facing significant methodological challenges and input data limitations. Exposure models typically use one of two general approaches: (1) a time-series approach that estimates microenvironmental exposures sequentially as individuals go through time or (2) a time-averaged approach that estimates microenvironmental exposures using average microenvironmental concentrations and the total time spent in each microenvironment. Although the time-series approach to modeling personal exposures provides the appropriate structure for accurately estimating personal exposures (Esmen and Hall, 2000; Mihlan et al., 2000), a time-averaged approach typically is used when the input data needed to support a time-series model are not available. However, the time-varying dose profile of an exposed individual can be modeled only by using the time-series approach (McCurdy, 1997, 2000).

Even though the processes that lead to exposure are nonlinear in nature, personal exposure models are often used to combine microenvironmental concentration data with human activity pattern data in order to estimate personal exposures. Time-averaged models can be used to estimate personal exposure for an individual or for a defined population. Total personal exposure models estimate exposures for all of the different microenvironments in which a person spends time, and total average personal exposure is calculated from the sum of these microenvironmental exposures:

$$E = \sum_j E_j = \frac{1}{T}\left(\sum_j C_j t_j \right), \tag{5-3}$$

where E_j is the personal exposure in each microenvironment, j (Duan, 1982). Example microenvironments include outdoors, indoors at home, indoors at work, and in transit. Each microenvironmental exposure, E_j, is calculated from the average concentration in microenvironment j, C_j, weighted by the time spent in microenvironment k, t_j. T is the sum of t_j over all j. This model has been applied to concentration data in a number of studies (Ott, 1984; Ott et al., 1988, 1992; Miller et al., 1998; Klepeis et al., 1994; Lachenmyer and Hidy, 2000).

Many exposure studies use 24-hour average measurements of concentration indoors and outdoors and use these concentrations with the time spent indoors and outdoors in Equation 5-3. It is important to note that although measurement data may be an average concentration over some time period (i.e., 24 h), significant variations in PM concentrations can occur during that time period. Thus, an error may be introduced if real-time concentrations are highly variable and an average concentration for a microenvironment is used to estimate exposure when the individual is in that microenvironment for only a fraction of the total time. This may create large errors if the indoor 24-hour average, e.g., in a house, includes significant time periods when there are no people in the house because the indoor concentrations are increased by the activities of people. In an effort to overcome these errors, the EXPOLIS study (Kousa et al., 2002) turned outdoor samplers off when the subject was indoors and the indoor sampler off with the subject was outdoors. This provides a better estimate of E_a and E_i to compare with the PEM measurement and allows a better calculation of E_{pc}. However, it does not provide data that can be used to regress C or C_o with C_i.

Microenvironmental concentrations used in the exposure models can be measured directly or estimated from one or more microenvironmental models. Microenvironmental models vary in complexity from a simple indoor/outdoor ratio to a multi-compartmental mass-balance model. A discussion of microenvironmental models is presented in Section 5.3.4.2.2.

On the individual level, the time spent in the various microenvironments is obtained from time/activity diaries that are completed by the individual. For population-based estimates, the time spent in various microenvironments is obtained from human activity databases. Many of the largest human activity databases have been consolidated by EPA's National Exposure Research Laboratory (NERL) into one comprehensive database called the Consolidated Human Activity Database (CHAD). CHAD contains over 22,000 person-days of 24-h activity data from 11 different human activity-pattern studies (McCurdy et al., 2000). Population cohorts with diverse characteristics can be constructed from the activity data in CHAD and used for exposure analysis and modeling (McCurdy, 2000). These databases can also be used to estimate inhalation rates based on activity levels, age, gender, and weight for dosimetry calculations. A human activity data base may contain information or location, activity, and other information such as presence of combustion sources (e.g., wood fireplaces, smokers) and the relative exertion rates. However, in exposure studies "activity" frequently refers to a person's location in space, i.e., in what microenvironment at what times. In dosimetry, "activity" is used as an indication of the level of physical exertion and is used to estimate breathing rate and extent of mouth, nose, or combined breathing. Table 5-2 is a summary of the human activity studies in CHAD.

Methodologically, personal exposure models can be divided into three general types: (1) statistical models based on empirical data obtained from one or more personal monitoring studies, (2) simulation models based upon known or assumed physical relationships, and (3) physical-stochastic models that include Monte Carlo or other techniques to explicitly address variability and uncertainty in model structure and input data (Ryan, 1991; MacIntosh et al., 1995). The attributes, strengths, and weaknesses of these model types are discussed by Ryan (1991), National Research Council (1991), Frey and Rhodes (1996), and Ramachandran and Vincent (1999). A review of the logic of exposure modeling is found in Klepeis (1999).

Personal exposure models that have been developed for PM are summarized in Table 5-3. The regression-based models (Johnson et al., 2000; Janssen et al., 1997; Janssen et al., 1998a) were developed for a specific purpose (i.e., to account for the observed difference between personal exposure and microenvironmental measurements) and are based on data from a single study, which limits their utility for broader purposes. Other types of models in Table 5-3 were limited by a lack of data for the various model inputs. For example, ambient PM monitoring data is not generally of adequate spatial and temporal resolution for these models. Lurmann and Korc (1994) assumed a constant relationship between coefficient of haze (COH) and PM_{10} and used site-specific COH information to stochastically develop a time series of 1-h PM_{10} data from every sixth day 24-h PM_{10} measurements. A mass-balance model typically was used for indoor

TABLE 5-2. ACTIVITY PATTERN STUDIES INCLUDED IN THE CONSOLIDATED HUMAN ACTIVITY DATABASE (CHAD)

				Diary				
Study Name	Calendar Time Period of the Study	Age[1]	Days[2]	Type[3]	Time[4]	Rate[5]	Documentation or Reference	Notes
Baltimore	Jan-Feb 1997 Jul-Aug 1998	65+	391	Diary; 15-min blocks	24h Standard	No	Williams et al. (2000a,b)	Multiple days, varying from 5-15; part of a $PM_{2.5}$ PEM study
CARB: Adolescents and Adults	Oct 1987-Sept 1988	12-94	1,762	Retrospective	24h Standard	No	Robinson et al. (1991) Wiley et al. (1991a)	
CARB: Children	Apr 1989-Feb 1990	0-11	1,200	Retrospective	24h Standard	No	Wiley et al. (1991b)	
Cincinnati (EPRI)	Mar-Apr and Aug 1985	0-86	2,614	Diary	24h; nominal 7 pm-7 am	Yes	Johnson (1989)	3 consecutive days; 186 P-D removed[7]
Denver (EPA)	Nov 1982-Feb 1983	18-70	805	Diary	24h; nominal 7 pm-7 am	No	Akland et al. (1985) Johnson (1984)	Part of CO PEM[6] study; 2 consec. days; 55 P-D removed[7]
Los Angeles: Elem. School Children	Oct 1989	10-12	51	Diary	24h Standard	Yes	Spier et al. (1992)	7 P-D removed[7]
Los Angeles: High School Adoles.	Sept-Oct 1990	13-17	43	Diary	24h Standard	Yes	Spier et al. (1992)	23 P-D removed[7]
National: NHAPS-A[8]	Sept 1992-Oct 1994	0-93	4,723	Retrospective	24h Standard	No[9]	Klepeis et al. (1995) Tsang and Klepeis (1996)	A national random-probability survey
National: NHAPS-B[8]	As above	0-93	4,663	Retrospective	24h Standard	No[9]	As above	As above
University of Michigan: Children	Feb-Dec1997	0-13	5,616	Retrospective	24h Standard	No	Institute for Social Research (1997)	2 days of data: one is a weekend day
Valdez, AK	Nov 1990-Oct 1991	11-71	401	Retrospective	Varying 24-h period	No	Goldstein et al. (1992)	4 P-D removed[7]
Washington, DC (EPA)	Nov 1982-Feb 1983	18-98	699	Diary	24h; nominal 7 pm-7 am	No	Akland et al. (1985) Hartwell et al. (1984)	Part of a CO PEM[6] study; 6 P-D removed[7]

[1] All studies included both genders. The age range depicted is for the subjects actually included; in most cases, there was not an upper limit for the adult studies. Ages are inclusive. Age 0 = babies < 1 year old.

[2] The actual number of person-days of data in CHAD after the "flagging" and removal of questionable data. See the text for a discussion of these procedures.

[3] Retrospective: a "what did you do yesterday" type of survey; also known as an ex post survey. Diary: a "real-time" paper diary that a subject carried as he or she went through the day.

[4] Standard = midnight-to-midnight.

[5] Was activity-specific breathing rate data collected?

[6] PEM = a personal monitoring study. In addition to the diary, a subject carried a small CO or $PM_{2.5}$ monitor throughout the sampling period.

[7] P-D removed = The number of person-days of activity pattern data removed from consolidated CHAD because of missing activity *and* location information; completeness criteria are listed in the text.

[8] National Human Activity Pattern Study; A = the air version; B = the water version. The activity data obtained on the two versions are identical.

[9] A question was asked regarding which activities (within each 6-h time block in the day) involved "heavy breathing," lifting heavy objects, and running hard.

TABLE 5-3. PERSONAL EXPOSURE MODELS FOR PARTICULATE MATTER

Study Citation	Model Name	Model Type	Microenvironments or Predictors	Output	Notes
Time-Series Models					
Hayes and Marshall (1999)	PMEX	Deterministic	Indoors: residential, work, school Outdoors: near roadway, other Motor vehicle	Inhaled dose of PM_{10} Hourly for 24 h By age/gender groups Source contributions	Used IAQM Used human activity data with activity-specific breathing rate info
Johnson et al. (2000)		Regression-based	Auto travel, roadside, ETS, food prep. grilling, high ambient PM	$PM_{2.5}$ exposure 24-h average	Developed from scripted activity study (Chang et al., 2000)
Klepeis et al. (1994)		Stochastic	ETS, cooking, cleaning, attached garage, wood burning	Respirable particle ($PM_{3.5}$) exposure	
Lurmann and Korc (1994)	REHEX-II	Stochastic	12 residential with different sources, restaurant/bar, nonresidential indoors, in transit, outdoors	Distribution of PM_{10} exposure for population Three averaging times (1 h, 24 h, season)	Fixed I/O ratio of 0.7 for indoors w/o sources and 1.2 for in transit Reduced form mass balance model for indoors with PM sources
Koontz and Niang (1998)	CPIEM	Stochastic	Indoors: residence, office, industrial plant, school, public building, restaurant/lounge, other. Outdoors, in vehicle	Distribution of PM_{10} exposure for population	Used California activity pattern and breathing rate data. Used either a mass balance model or I/O ratio distribution for indoor microenvironments. Indoor sources included.
Time-Averaged Models					
Clayton et al. (1999a)	SIM	Stochastic		Distribution of annual $PM_{2.5}$ exposures	Based on 3-day ambient measurements
Janssen et al. (1997)		Regression-based	Smoking parent, ETS exposure, outdoor physical activity	Accounts for difference between personal and microenvironmental PM_{10}	Children only
Janssen et al. (1998a)		Regression-based	Number of cigarettes smoked, hours of ETS exposure, residence on busy road, time in vehicle	Accounts for difference between personal and microenvironmental PM_{10}	Adults only
Ott et al. (2000)	RCS	Statistical	Not separated	Distribution of PM_{10} exposure for population	A random-component superposition (RCS) model that uses distribution of ambient PM_{10} and estimated nonambient PM_{10} concentrations Results for Ontario, Canada not corrected for 72-h compared to 24-h averaging time in Riverside, CA and Phillipsburg, NJ

TABLE 5-3 (cont'd). PERSONAL EXPOSURE MODELS FOR PARTICULATE MATTER

Study Citation	Model Name	Model Type	Microenvironments or Predictors	Output	Notes
Time-Averaged Models					
Burke et al. (2001)	SHEDS-PM	Stochastic	Outdoors, indoors: residence, office, stores, school, in vehicle, restaurant/lounge,	$PM_{2.5}$ exposure distributions for population, by age, gender, smoking and employment status; $PM_{2.5}$ exposure uncertainty predictions. Percent contribution from PM of ambient origin to total personal exposures	A 2-stage Monte-Carlo simulation model for predicting population distribution of daily- average personal exposures to PM. Model has been applied to Philadelphia using spatially and temporally interpolated $PM_{2.5}$ ambient measurements from 1992-1993 and 1990 census data. Does not consider $PM_{2.5}$ exposure from active smoking or exposure in subways
Chao and Tung (2001)	None	Mass Balance with Empirical corrections	Indoors in unoccupied residences in Hong Kong	Predictions of ambient PM in indoor microenvironments	Model makes corrections for nonideal mixing (residence with multiple compartments with limited intermixing)

microenvironments when sufficient data were available, such as for a residence. For most other microenvironments, indoor/outdoor ratios were used because of the lack of data for a mass balance model. In addition, only the deterministic model, PMEX, included estimation of inhaled dose from activity-specific breathing rate information. Data from recent PM personal exposure and microenvironmental measurement studies should help in the future to facilitate the development of improved personal exposure models for PM.

An integrated human exposure source-to-dose modeling system that will include exposure models to predict population exposures to environmental pollutants, such as PM, currently is being developed by EPA/NERL. A first-generation population exposure model for PM, called the Stochastic Human Exposure and Dose Simulation (SHEDS-PM) model, recently has been developed. The SHEDS-PM model uses a 2-stage Monte Carlo sampling technique previously applied by MacIntosh et al. (1995) for benzene exposures. This technique allows for separate characterization of variability and uncertainty in the model predictions to predict the distribution of total exposure to PM for the population of an urban/metropolitan area and to estimate the contribution of ambient PM to total PM exposure. Results from a case study using data from Philadelphia have been reported (Burke et al., 2001). Work is underway to link exposure modeling with dosimetry so as to provide estimates of integrated PM doses for different regions of the lung. In the future, both exposure and dose metrics generated for various subgroups of concern should aid evaluation of PM health effects.

5.2.4.2.2 Microenvironmental Models

The mass balance model has been used extensively in exposure analysis to estimate PM concentrations in indoor microenvironments (Calder, 1957; Sexton and Ryan, 1988; Duan, 1982, 1991; McCurdy, 1995; Johnson, 1995; Klepeis et al., 1995; Dockery and Spengler, 1981; Ott, 1984; Ott et al., 1988, 1992, 2000; Miller et al., 1998; Mage et al., 1999; Wilson et al., 2000). The mass balance model describes the infiltration of particles from outdoors into the indoor microenvironment, the removal of particles in indoor microenvironments, and the generation of particles from indoor sources:

$$V\, dC_i / dt = v\, P\, C - v\, C_i - kVC_i + Q_i, \qquad (5\text{-}4)$$

where V = volume of the well-mixed indoor air (m^3);

C_i = concentration of indoor PM ($\mu g/m^3$);

v = volumetric air exchange rate between indoors and outdoors (m^3/h);

P = penetration ratio, the fraction of ambient (outdoor) PM that is not removed from ambient air during its entry into the indoor volume;

C = concentration of PM in the ambient air ($\mu g/m^3$);

k = removal rate (h^{-1}); and

Q_i = indoor sources of particles ($\mu g/h$).

Q_i contains a variety of indoor, particle-generating sources, including combustion or mechanical processes; condensation of vapors formed by combustion or chemical reaction; suspension from bulk material; and resuspension of previously deposited PM. The removal rate, *k*, includes dry deposition to interior surfaces by diffusion, impaction, electrostatic forces, and gravitational fallout. It may include other removal processes, such as filtration by forced air heating, ventilation, or air conditioning (HVAC) or by independent air cleaners. All parameters except V are functions of time. *P* and *k* also are functions of particle aerodynamic diameter, D_a, air exchange rate, ν, and house characteristics such as the surface to volume ratio, type of surface, etc. All variables in Equation 5-3 will have distributions within the population and, in some cases, may vary by a factor of 5 to 10. It is important to determine the distribution of these variables. Sensitivity and uncertainty analyses are necessary when attempting to explain model results.

In addition to the mass balance model, a number of single-source or single-microenvironment models exist. However, most are used to estimate personal exposures to environmental tobacco smoke (ETS). These models include both empirically based statistical models and physical models based on first principles: some are time-averaged; whereas others are time series. These models evaluate the contribution of ETS to total PM exposure in an enclosed microenvironment and can be applied as activity-specific components of total personal exposure models. Examples of ETS-oriented personal exposure models are Klepeis (1999), Klepeis et al. (1996, 2000), Mage and Ott (1996), Ott (1999), Ott et al. (1992, 1995), and Robinson et al. (1994).

5.2.4.3 Methods for Estimating Personal Exposure to Ambient Particulate Matter

In keeping with the various components of PM exposure described in Section 5.3.2, personal exposure to PM can be expressed as the sum of exposure to particles from different sources summed over all microenvironments in which exposure occurs. Total personal exposure may be expressed as

$$T = E_a + E_{ai} + E_{ig} + E_{ir} + E_{pc} \qquad (5\text{-}5)$$

or

$$T = A + N, \qquad (5\text{-}6)$$

where T is the total personal exposure to ambient and nonambient PM, E_a is personal exposure to ambient PM while outdoors, E_{ai} is personal exposure to ambient PM that has infiltrated indoors while indoors, E_{ig} is personal exposure to indoor-generated PM, E_{ir} is exposure to indoor-reaction PM, and E_{pc} is personal exposure to PM from personal activity (personal cloud). T can also be expressed as A + N where A is ambient PM exposure ($E_a + E_{ai}$) and N is nonambient PM exposure ($E_{ig} + E_{ir} + E_{pc}$). Although personal exposure to ambient and nonambient PM cannot be measured directly, they can be calculated or estimated from other measurement data. Approaches for estimating these components of PM exposure are described in the following section.

5.2.4.3.1 Mass Balance Approach

Ambient-Indoor Concentrations of Particulate Matter

The mass balance model described above (Equation 5-4) has been used to estimate PM concentrations in indoor microenvironments. This model also may be used to estimate ambient-indoor (C_{ai}) and indoor-generated (C_{ig}) PM concentrations. The mass balance model can be solved for C_{ai} and C_{ig} assuming equilibrium conditions, i.e., all variables remain constant (Ott et al., 2000; Dockery and Spengler, 1981; Koutrakis et al., 1992) and no indoor reaction PM (C_{ir}). By substituting $a = \nu/V$, where a = the number of air exchanges per hour substituting, $dC_{ai} + dC_{ig}$ for dC_i in Equation 5-4, and assuming that dC_{ai} and $dC_{ig} = 0$, i.e., ambient-indoor PM (C_{ai}) and indoor-generated PM (C_{ig}) are at equilibrium, C_{ai} and C_{ig} are given by Equations 5-7 and 5-8.

$$\mathrm{C}_{\mathrm{ai}} = \mathrm{C}\left[\frac{Pa}{(a+k)}\right] \tag{5-7}$$

$$\mathrm{C}_{\mathrm{ig}} = \frac{Q_i}{V(a+k)} \tag{5-8}$$

Equations 5-7 and 5-8 assume equilibrium conditions and, therefore, are valid only when the parameters P, k, a, C, and Q_i are not changing rapidly and when the Cs are averaged over several hours. It should be understood that equilibrium is a simplification of indoor microenvironments that are occupied by residents. This assumption of equilibrium may only represent a virtual set of individuals or populations at risk. Under certain conditions (e.g., air-conditioned homes, homes with HVAC or air cleaners that cycle on and off, or ambient pollutants with rapidly varying concentrations), nonequilibrium versions of the mass balance model (Ott et al., 2000; Freijer and Bloemen, 2000; Isukapalli and Georgopoulos, 2000) are likely to provide a more accurate estimate of C_{ai} and C_{ig}. However, the equilibrium model provides a useful, if simplified, example of the basic relationships (Ott et al., 2000).

Equation 5-7 may be rearranged further to give $\mathrm{C}_{\mathrm{ai}}/\mathrm{C}$, the equilibrium fraction of ambient PM that is found indoors, defined as the infiltration factor ($\mathrm{F}_{\mathrm{INF}}$) (Dockery and Spengler, 1981).

$$\mathrm{F}_{\mathrm{INF}} = \frac{\mathrm{C}_{\mathrm{ai}}}{\mathrm{C}} = \frac{Pa}{a+k} \tag{5-9}$$

The penetration ratio (P) and the decay rate (k) can be estimated using a variety of techniques. A discussion of these variables and estimation techniques is given in Section 5.4.3.2.2. Both P and k are a function of particle aerodynamic diameter, air exchange rate, and housing characteristics. $\mathrm{F}_{\mathrm{INF}}$ will also be a function of these parameters and as a result $\mathrm{F}_{\mathrm{INF}}$ may vary substantially within a population. Distributions of this parameter should be estimated to understand the uncertainty and variability associated with estimating exposure to PM of ambient origin. The distribution of daytime F_{INF}, as estimated from Particle Total Exposure Assessment Methodology (PTEAM) data, is shown in Figure 5-2a (Wilson et al., 2000).

Personal Exposure to Ambient Particulate Matter

Personal exposure to ambient PM (A) may be estimated using ambient-indoor PM concentration (C_{ai}) from the mass balance model, ambient outdoor PM concentrations (C), and information on the time an individual spent in the various microenvironments. For a two-compartment model, A may be expressed as

$$\begin{aligned} A &= yC + (1 - y)C_{ai} \\ &= yC + (1 - y)C\left[\frac{Pa}{(a + k)}\right], \end{aligned} \tag{5-10}$$

where y is the fraction of time that an individual spent outdoors, and $(1 - y)$ is the fraction of time spent indoors.

It is convenient to express personal exposure to ambient PM (A) as the product of the ambient PM concentration (C) and a personal exposure or attenuation factor. Following the usage in several recent papers (Zeger et al., 2000; Dominici et al., 2000; Ott et al., 2000), the symbol α will be used for this attenuation factor. Equation 5-10 can be rearranged to obtain an expression for α:

$$\alpha = \frac{T}{C} = y + (1 - y)\left[\frac{Pa}{a + k}\right] \tag{5-11}$$

Substituting equation 5-9 in equation 5-11 gives a relationship for α in terms of the infiltration factor F_{INF} and the fraction of time spent in the various microenvironments:

$$a = y + (1 - y)\ F_{INF}. \tag{5-12}$$

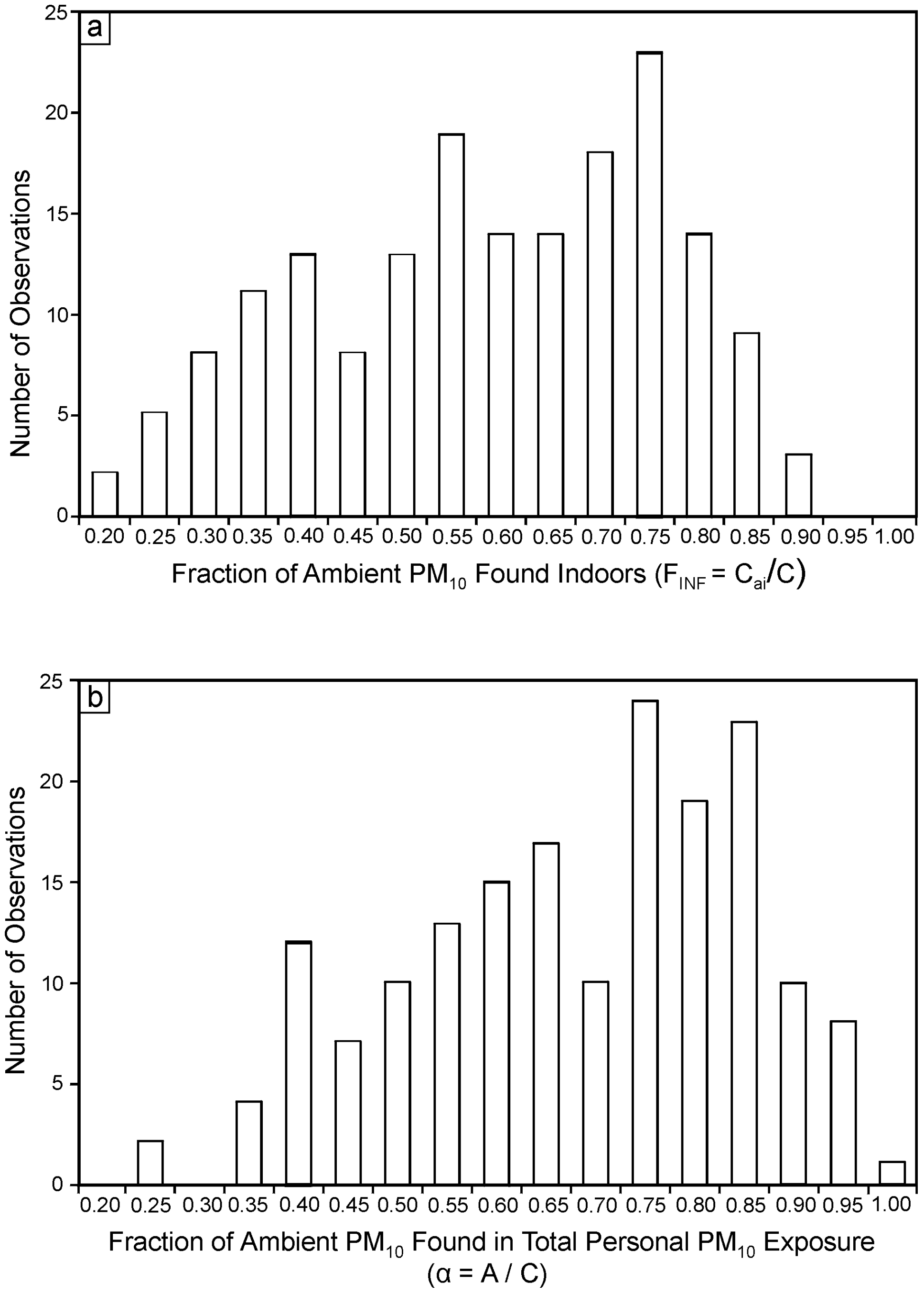


Figure 5-2. Distribution of F_{INF} (a) and α (b) for daytime as estimated from PTEAM study data.

Source: Wilson et al. (2000).

Thus, personal exposures to ambient PM (A) may be calculated from measurable quantities:

$$A = \alpha C. \tag{5-13}$$

The factor α can be measured directly or calculated from measured or estimated values of the parameters *a*, *k*, and *P* and the time spent in various microenvironments from activity pattern diaries (Wilson et al., 2000). Because α depends on housing factors and lifestyle factors, air exchange rate, and PM deposition rate, it could vary to a certain extent from region to region and from season to season. Consequently, predicted exposures based on these physical modeling concepts will provide exposure distributions derived conceptually as resulting from housing, lifestyles, and meteorological considerations. For any given population the coefficient α may represent substantial intra- and inter-personal variability based on personal activities, housing characteristics, particle size, and composition. The distribution of daytime α as estimated from PTEAM data is shown in Figure 5-2b. Note that the distribution of α is shifted to higher values compared to F_{INF} because of the inclusion of time outdoors in α. Distributions of α should be determined using population studies in order to evaluate the uncertainty and variability associated with model exposures.

The mass balance model has been used to separate indoor concentrations into ambient and nonambient components. This approach, based on Equation 5-5 as given in Duan (1982) and called superposition of component concentrations, has been applied using multiple microenvironments to estimate exposures to carbon monoxide (Ott, 1984; Ott et al., 1988, 1992), volatile organic compounds (Miller et al., 1998), and particles (Koutrakis et al., 1992; Klepeis et al., 1994). However, in these studies and in most of the exposure literature, the ambient and nonambient components are added to yield a personal exposure from all sources of the pollutant. The use of the mass balance model, ambient concentrations, and exposure parameters to estimate exposure to ambient PM and exposure to indoor-generated PM separately as different classes of exposure has been discussed in Wilson and Suh (1997) and in Wilson et al. (2000).

5.2.4.3.2 The Sulfate Ratio Technique for Estimating Ambient PM Exposure

The ratio of personal exposure to ambient concentration for sulfate has been recommended as a technique to estimate α (Wilson et al., 2000). If sulfate has no indoor sources, then $A^S = T^S$.

(Superscript S refers to sulfate; superscript 2.5 to $PM_{2.5}$.) As can be seen in Equation 5-11, *P* and *k* depend on particle size, but *a* and *y* do not. Therefore, if sulfate and $PM_{2.5}$ have the same size distribution, $T^S/C^S = A^{2.5}/C^{2.5} = \alpha^S = \alpha^{2.5}$. Sulfate is formed in the ambient air via photochemical oxidation of gaseous sulfur dioxide arising from the primary emissions from the combustion of fossil fuels containing sulfur. It also arises from the direct emissions of sulfur-containing particles from nonanthropogenic sources (e.g., volcanic activity, wind-blown soil). It has been known since the mid-1970s that sulfate and accumulation mode mass have similar size distributions (Whitby, 1978). In the indoor environment, the only common sources of sulfate may be resuspension by human activity of deposited PM containing ammonium sulfates or soil sulfates that were tracked into the home. However, resuspended PM will be mostly larger than $PM_{2.5}$. In some homes, an unvented kerosene heater using a high-sulfur fuel may be a major contributor during winter (Leaderer et al., 1999). Use of matches to light cigarettes or gas stoves can also be a source of sulfates.

Studies that have used the sulfate ratio technique to estimate α and ambient PM exposures are discussed in Section 5.4.3.1. When there are no indoor sources of accumulation-mode sulfates, one may deduce that the ambient-to-personal relationship found for sulfates probably would be the same as that for other PM with the same size range and physical/chemical properties. This assumption has been validated for several homes in Boston (Sarnat et al., 2002). For particle sizes within the accumulation mode size range, the ratio C_{ai}/C was similar for sulfate and $PM_{2.5}$ as estimated from SMPS measurements. However, ambient PM with different physical or chemical characteristics than sulfate will not behave similarly to sulfate. Sulfate has been used as a marker of outdoor air in the indoor microenvironments (Jones et al., 2000; Ebelt et al., 2000). However, the personal exposure of sulfate ($T^s = A^s$) should not be taken as an indicator or surrogate for ambient $PM_{2.5}$ exposure ($A^{2.5}$) unless it has been previously determined that $PM_{2.5}$ and sulfate concentrations are highly correlated. This may be the case in some air sheds with high sulfate concentrations but will not be true in general.

5.2.4.3.3 Source-Apportionment Techniques

Source apportionment techniques provide a method for determining personal exposure to PM from specific sources. If a sufficient number of samples are analyzed with sufficient compositional detail, it is possible to use statistical techniques to derive source category signatures, identify indoor and outdoor source categories, and estimate their contribution to indoor and personal PM. Daily contributions from sources that have no indoor component can be used as tracers to generate exposure to ambient PM of similar aerodynamic size or directly as exposure surrogates in epidemiological analyses. Studies that have used source-apportionment are discussed in Section 5.4.3.3 (i.e., Özkaynak and Thurston, 1987; Yakovleva et al., 1999; Mar et al. 2000; Laden et al., 2000).

5.3 SUMMARY OF PARTICULATE MATTER MASS DATA

5.3.1 Types of Particulate Matter Exposure Measurement Studies

A variety of field measurement studies have been conducted to quantify personal exposure to PM mass, to measure microenvironmental concentrations of PM, to evaluate relationships between personal exposure to PM and PM air concentrations measured at ambient sites, and to evaluate factors that affect exposure. In general, exposure measurement studies are of two types depending on how the participants are selected for the study. In a *probability* study, participants are selected using a probability sampling design where every member of the defined population has a known, positive probability of being included in the sample. Probability study results can be used to make statistical inferences about the target population. In a *purposeful* or *nonprobability* design, any convenient method may be used to enlist participants; and the probability of any individual in the population being included in the sample is unknown. Participants in purposeful samples may not have the same characteristics that would lead to exposure as the rest of the unsampled population. Thus, results of purposeful studies apply only to the subjects sampled on the days that they were sampled and not to other subjects or other periods of time. Although such studies may report significant differences, confidence intervals, and *p* values, they do not have inferential validity (Lessler and Kalsbeek,1992). Purposeful studies, however, may have generalizability (external validity). The extent of generalizability is a matter of judgement based on study participant characteristics. Purposeful studies of PM personal exposure can provide data with which to develop relationships based on important exposure factors and can provide useful information for developing and evaluating either statistical or physical/chemical human exposure models.

Regardless of the sampling design (probability or purposeful), there are three general categories of study design that can be used to measure personal exposure to PM and evaluate the relationship between personal PM exposure levels and ambient PM concentrations measured simultaneously: (1) longitudinal, in which each subject is measured for many days; (2) pooled, in which each subject is measured for only one or two days, different days for different subjects; and (3) daily-average, in which many subjects are measured on the same day. Only one study, in which 14 subjects were measured for 14 days, provides sufficient data for a comparison of longitudinal and daily-average data (Lioy et al., 1990). Longitudinal and pooled studies are discussed in Section 5.4.3.1.1.

5.3.2 Available Data

5.3.2.1 Personal Exposure Data

Table 5-4 gives an overview of the personal exposure studies that have been reported since the 1996 PM AQCD. In addition, major studies that were reported before that time also have been included to provide a comprehensive evaluation of data in this area. Table 5-4 gives information on the sampling and study designs, the study population, the season, number of participants, PM exposure metric, and the PM size fraction measured.

Although there are a number of studies listed in the table, the data available with which to evaluate longitudinal relationships and the factors that influence these are limited. Few studies are based on probability sampling designs that allow study results to be inferred to the general population and to develop distributional data or exposures and the factors that affect exposure. Unfortunately, none of these probability studies used a longitudinal study design. This limits our ability to provide population estimates and distributional data on the relationship between personal PM exposures and ambient site measurements. In addition, most of the probability studies of PM exposure were conducted during a single season; thus, variations in ambient concentrations, air exchange rates, and personal activities are not accounted for across seasons. In these cases, study results are only applicable to a specific time period. Longitudinal studies, on the other hand, generally have small sample sizes and use a purposeful sampling design. Some studies did not include ambient site measurements to allow comparisons with the exposure data. Approximately half of these studies monitored $PM_{2.5}$. Only one or two studies measured both PM_{10} and $PM_{2.5}$ to provide information on $PM_{10-2.5}$.

TABLE 5-4. SUMMARY OF RECENT PM PERSONAL EXPOSURE STUDIES

Study Design	Study Location and Population	No. of Subjects	Study Period	Age Years	Days per Subject	PM Exposure[a] Metrics	PM Size Measured[b]	Co-Pollutant Metrics	Reference
Probability Studies									
Pooled[c]	Riverside, CA, PTEAM	178	Fall 1990	10-70	1 (12 h)	P, I, O, A	PM_{10}		Clayton et al. (1993) Özkaynak et al. (1996a,b)
Pooled	Basel, Switzerland, EXPOLIS	50	1997		1 (48 h)	P, I, P	$PM_{2.5}$	VOC, CO, NO_2, S, K, Pb, Br, Ca	Oglesby et al. (2000) Jantunen et al. (1998)
Pooled	Toronto, Canada	732	Sept 1995-Aug 1996	16+	3	P, I, O, A	$PM_{2.5}$ (12 mo) PM_{10} (3 mo)		Clayton et al. (1999a), Pellizzari et al. (1999)
Pooled	Mexico City	66	1992	< 65	1	P, I, O	PM_{10}		Santos-Burgoa et al. (1998)
Pooled	Baltimore, MD nonsmoke exposed adults, children, COPD patients	20 Adults 21 Children 15 COPD	Summer 1998 Winter 1999	A 75 Ch 9-13 COPD 65	12-days 8-days for children in summer	P, A	$PM_{2.5}$ PM_{10}	O_3, NO_2, SO_2, VOCs, ED/OC, CO	Sarnat et al. (2001)
Purposeful Studies									
Longitudinal[d]	Wageningen, Netherlands, school children	13	1995	10-12	6	P, A, School	$PM_{2.5}$, PM_{10}		Janssen et al. (1999a)
Longitudinal	Amsterdam (Am), Helsinki (Hls), elderly angina or coronary heart disease	41 (Am) 49 (Hls)	Winter 1998 Spring 1999	50-84	22 (Am) 27 (Hls)	P, I, O	$PM_{2.5}$		Janssen et al. (2000)
Longitudinal	Baltimore, elderly healthy and COPD	21	July-Aug 1998	72-93	5-22	P, I, O, A	$PM_{2.5}$, PM_{10}	CO, O_3, NO_2, SO_2	Williams et al. (2000a,b)
Longitudinal	Fresno I Fresno II (elderly)	5 16	Feb 1999 Apr-May 1999	60+	24 24	P, I, O, A P, I, O, A	$PM_{2.5}$, PM_{10} $PM_{2.5}$, PM_{10}	CO, O_3	Evans et al. (2000)
Longitudinal	Los Angeles, elderly COPD subjects	30	Summer/Fall 1996	56-83	4	P, I, O	$PM_{2.5}$		Linn et al. (1999)
Longitudinal	Boston, COPD subjects	18	Winter 1996-7 Summer 1996		12	P, I, O, A	$PM_{2.5}$, PM_{10}		Rojas-Bracho et al. (2000)

TABLE 5-4 (cont'd). SUMMARY OF RECENT PM PERSONAL EXPOSURE STUDIES (SINCE 1996)

Study Design	Study Location and Population	No. of Subjects	Study Period	Age Years	Days per Subject	PM Exposure[a] Metrics	PM Size Measured[b]	Co-Pollutant Metrics	Reference
Purposeful Studies (cont'd)									
Longitudinal	Nashville, TN, COPD subjects	10	Summer 1995	36-88	6	P, I, O	$PM_{2.5}$, PM_{10}		Bahadori et al. (2001)
Longitudinal	Vancouver, British Columbia, COPD	16	April-Sept 1998	54-86	7	P, A	$PM_{2.5}$, PM_{10}		Ebelt et al. (2000)
Longitudinal	Amsterdam and Wageningen, Neth., school children	45	1994-1995	10-12	4-8	P, A, School	PM_{10}		Janssen et al. (1997)
Longitudinal	Amsterdam, adults	37	1994	51-70	5-8	P, I, A	PM_{10}		Janssen et al. (1998a)
Longitudinal	Baltimore, elderly subjects	15	Summer 1998 Spring 1999	75 ± 6.8	12	P	$PM_{2.5}$, PM_{10}	O_3, NO_2, SO_2 VOCs	Sarnat et al. (2000)
Longitudinal	Baltimore, elderly, COPD, children	56	Summer 1998 Winter 1999	Adults: 75 ± 6.8 Children: 9-13 COPD: 65 ± 6.6	12	P, I, O, A	$PM_{2.5}$	O_3, NO_2, SO_2, CO, EC,/OC. VOC	Sarnat et al. (2000)
Longitudinal	Tokyo, Japan, elderly housewives	18	1992		3	P, I, O, A	SPM	NO_2	Tamura et al. (1996a)
Longitudinal	Osaka, Japan	26	Fall 1990-1995		Multiple days	P, I, O	PM_2,$PM_{2\text{-}10}$, $PM_{>10}$		Tamura et al. (1996b)
Pooled	Milan, Italy, office workers	100	Spring/Summer and Winter, year not stated		1	P, Home, Office, Commuting	PM_{10}	NO_2, CO, VOCs	Carrer et al. (1998)
Probability Sample, Pooled	Indianapolis, IN	240	1996	16 - ?	One 72-h sample/subject	P, I, A, O	$PM_{2.5}$, PM_{10}	Mn, Al, Ca	Pellizzari et al. (2001)
Pooled	Banská Bystrica, Slovakia	49	1997-1998	15 - 59	1	P, I, O, A	PM_{10}, $PM_{2.5}$	SO_4^{-2}, nicotine	Brauer et al. (2000)
Longitudinal	Wageningen, NL	13	Mar-June 1995	12 - 14	5-8	P, A, I at school	$PM_{2.5}$, PM_{10}	None	Janssen et al. (1999a)
Longitudinal µE diary	Mpala, Kenya	252	1996-1998	5 - 75	2 years	I	Undefined Optical MIE	CO	Ezzati and Kammen (2001)

TABLE 5-4 (cont'd). SUMMARY OF RECENT PM PERSONAL EXPOSURE STUDIES (SINCE 1996)

Study Design	Study Location and Population	No. of Subjects	Study Period	Age Years	Days per Subject	PM Exposure[a] Metrics	PM Size Measured[b]	Co-Pollutant Metrics	Reference
Longitudinal	London, UK	10	1997	9-11	5day/season 3 seasons	P, I, O	$PM_{2.5}$, PM_{10}	None	Wheeler et al. (2000)
Pooled	Zurich, CH	10	1998	Adults	12h/day for 3 days	P, I, O	Pollen	None	Riediker et al. (2000)
Pooled	Minneapolis/St. Paul, MN Volunteers	32	Spring, Summer, fall 1999	24 - 64	2-15	P, I, O	$PM_{2.5}$	None	Adgate et al. (2002)
Pooled	Birmingham, UK - healthy adults, children and susceptibles	11 healthy adults, 18 susceptible	Season and year not given	Adults, Adults > 65 Child 10	adults and children 10. susceptibles 5, daytime only	P, I, O	PM_{10}	CO, NO_2	Harrison et al. (2002)
Pooled	Santiago, Chile children	8 in 1998 20 in 1999	Winters 1998 & 1999	10 -12	5	P, I, O	$PM_{2.5}$ PM_{10}	NO_2, O_3	Rojas-Bracho et al. (2002)
Pooled	Copenhagen, DK non-smoking students	68 subjects	Winter 1999, Spring, Summer, Fall 2000	20 -33	2	P, A	$PM_{2.5}$ BS (from $PM_{2.5}$ filter)	None	Sørensen, et al. (2003)

[a] All based on gravimetric measurements.
[b] P = personal, I = indoors, O = outdoors, A = ambient.
[c] pooled; data from many subjects with only a few days per subject.
[d] longitudinal; one subject measured for many days.

Four large-scale probability studies that quantify personal exposure to PM under normal ambient source conditions have been reported in the literature. These include the EPA's PTEAM study (Clayton et al., 1993; Özkaynak et al., 1996a,b); the Toronto, Ontario, study (Clayton et al., 1999a and Pellizzari et al., 1999); the Air Pollution Exposure Distribution within Adult Urban Populations in Europe (EXPOLIS) study (Jantunen et al., 1998, 2000; Oglesby, et al., 2000; Gotshi et al., 2002; Kousa et al., 2002); and a study of a small, highly polluted area in Mexico City (Santos-Burgoa et al., 1998). A fifth study conducted in Kuwait during the last days of the oil-well fires (Al-Raheem et al., 2000) is not reported here because the ambient PM levels were not representative of normal ambient source conditions.

Recent longitudinal exposure studies have focused on potentially susceptible subpopulations such as the young and elderly with preexisting respiratory and heart diseases (hypertension, chronic obstructive pulmonary disease, and congestive heart disease). This is in keeping with epidemiological studies that indicate mortality associated with high levels of ambient $PM_{2.5}$ is greatest for elderly people with cardiopulmonary disease (U.S. Environmental Protection Agency, 1996). Longitudinal studies were conducted in the Netherlands by Janssen (1998) and Janssen et al. (1997, 1998a,b, 1999b,c) on purposefully selected samples of adults (50 to 70 years old) and children (10 to 12 years old). School children have also been studied in Chile (Rojas-Bracho et al., 2002). Several additional studies have focused on nonsmoking elderly populations in Amsterdam and Helsinki (Janssen et al., 2000), Tokyo (Tamura et al., 1996a), Baltimore, MD (Liao et al., 1999; Williams et al., 2000a,b,c), and Fresno, CA (Evans et al., 2000). These cohorts were selected because of the low incidence of indoor sources of PM (such as combustion or cooking). This should allow an examination of the relationship between personal and ambient PM concentrations without the large influences caused by smoking, cooking, and other indoor particle-generating activities. The EPA has a research program focused on understanding PM exposure characteristics and relationships. Within the program, longitudinal studies are being conducted on elderly participants with underlying heart and lung disease (COPD, patients with cardiac defibrillator, and myocardial infarction), an elderly environmental justice cohort, and asthmatics. These studies are being conducted in several cities throughout the United States and over several seasons (Rodes et al., 2001; Conner et al., 2001; Landis et al., 2001; Rea et al., 2001).

A series of studies by Phillips et al. (1994, 1996, 1997a,b, 1998a,b, 1999) examined personal ETS exposure in several European cities. Participants varied by age and occupation. Respirable particulate matter (RSP) concentrations were reported. These studies are not included in Table 5-4 because of their focus on ETS exposure (which is not the focus of this chapter). A small personal exposure study in Zurich, Switzerland, was reported by Monn et al., (1997) for PM_{10}. This study also is not listed in Table 5-4 because indoor and outdoor measurements were not taken simultaneously with the personal measurements and other details of the study were not published.

5.3.2.2 Microenvironmental Data

Usually, personal PM monitoring is conducted using integrated measurements over a 12- or 24-h period. As such, total PM exposure estimates based on PEM measurements do not capture data from individual microenvironments. Recent studies have examined PM concentrations in various microenvironments using a number of different types of instruments ranging from filter-based to continuous particle monitors. Details on the instruments used, measurements collected, and findings of these studies according to microenvironment (residential indoor, nonresidential indoor, and traffic-related) are summarized in Table 5-5. Those studies which collected microenvironmental data as part of a personal exposure monitoring study are summarized in Table 5-4. In general, the studies listed in Table 5-5 are relatively small, purposeful studies designed to provide specific data on the factors that affect microenvironmental concentration of PM from both ambient and nonambient sources.

Recently published studies have used various types of continuous monitors to examine particle concentrations in specific microenvironments and resulting from specific activities. Continuous particle monitors such as the scanning mobility particle sizer (SMPS), aerodynamic particle sizer (APS), and Climet have been used to measure particle size distributions in residential microenvironments (Abt et al., 2000a; Long et al., 2000a; Wallace et al., 1997; Wallace, 2000a; McBride et al., 1999; Vette et al., 2001; Wallace and Howard-Reed, 2002). These studies have been able to assess penetration efficiency for ambient particles to indoor microenvironments, as well as penetration factors and deposition rates. Continuous instruments are also a valuable tool for assessing the impact of particle resuspension caused by human activity. A semi-quantitative estimate of PM exposure can be obtained using personal

TABLE 5-5. SUMMARY OF RECENT MICROENVIRONMENTAL PM MEASUREMENT STUDIES

Reference	Study Description	Instrument(s)	Size Fraction (µm)	Summary of Measurements	Notes
Residential Indoor: Nonsmoking Homes					
Abt et al. (2000a) Boston, MA	2 homes, 2 seasons, 6 days	SMPS APS		Detailed indoor/outdoor traces of PM in various size classes for different air exchange rates (< 1h^{-1} to > 2 h^{-1}).	Major indoor sources of PM: cooking, cleaning, human activity.
Long et al. (2000a) Boston, MA	9 homes, 2 seasons	SMPS APS	0.02-10 µm	Continuous PM distributions and size distributions obtained for indoor and outdoor air using SMPS and APS monitors.	Sources of fine particles: cooking and outdoor particles; Sources of coarse particles: cooking, cleaning, indoor activities. 50% of particles by volume generated by indoor events were ultrafine particles.
Anuszewski et al. (1998) Seattle, WA	9 homes, 18 days	Nephelometer (radiance)	PM$_{1}$	Simultaneous indoor and outdoor PM measured continuously; 1-h avg time, I/O = 0.98; air exchange rate: 0.7-1.7 h^{-1}.	Homes contained asthmatic children, heavy wood burning. Dominant source of fine particles was outdoor air.
Leaderer et al. (1999) Southwest, VA	58 homes, summer		PM$_{10}$	24 h mean: Regional air 26.0 ± 11.5 µg/m^3 (n = 47); Outdoor homes 28.0 ± 17.7 µg/m^3 (n = 43); Indoor w/ AC 28.9 ± 18.7 µg/m^3 (n = 49); Indoor w/o AC 33.3 ± 14.2 µg/m^3 (n = 8).	Epidemiologic study of maternal and infant health effects associated with indoor air pollution.
			PM$_{2.5}$	24 h mean: Regional air 20.2 ± 9.9 µg/m^3 (n = 50); Outdoor homes 21.8 ± 14.8 µg/m^3 (n = 43); Indoor w/ AC 18.7 ± 13.2 µg/m^3 (n = 49); Indoor w/o AC 21.1 ±7.5 µg/m^3 (n = 9).	Indoor PM concentrations were lower for homes with air conditioning (AC) than non-air-conditioned homes.
Wallace et al. (1997); Wallace (2000b) Reston, VA	1 home, 4 years	SMPS Climet PAHs Black carbon	6 size bins; 100 size channels 0.01-0.4 µm	Time activity data, whole-house air exchange rates. Continuous carbon monoxide; descriptive data for monitored pollutants; size profiles for six indoor particle sources.	0.3- to 0.5-µm particles linked to outdoor concentrations, frying, broiling; 0.5- to 2.5-µm particles related to cooking events; > 2.5-µm particles influenced by physical movement.
Howard-Reed et al. (2000) Fresno, CA Baltimore, MD	15 participants	Nephelometer (personal MIE) PEM	0.1-10 µm PM$_{2.5}$	Continuous (15-min avg) PM and time activity data; 24-h PM mass; participants from Baltimore and Fresno PM panel studies. Descriptive statistics from each study for five microenvironments.	Time-series plots of personal nephelometer data showed that each participant's PM exposure consisted of a series of short-term peaks, imposed on a background caused by ambient PM concentrations.

TABLE 5-5 (cont'd). SUMMARY OF RECENT MICROENVIRONMENTAL PM MEASUREMENT STUDIES

Reference	Study Description	Instrument(s)	Size Fraction (µm)	Summary of Measurements	Notes
Residential Indoor: Nonsmoking Homes (cont'd)					
Rea et al. (2001) Baltimore, MD Fresno, CA	15 participants	Nephelometer (personal MIE) PEM	0.1-10 µm $PM_{2.5}$ and PM_{10}	54 ± 31% of average daily $PM_{2.5}$ exposure occurred indoor residences, where participants spent 83 ± 10% of their time. A significant portion of $PM_{2.5}$ exposure occurred where participants spent 4-13% of their time.	Continuous (15-min avg) PM and time activity data; 24-h PM mass; modeled PM mass and time activity data to apportion time spent in a location. Good comparison with nephelometer mass (6-20%).
Quintana et al. (2000) San Diego, CA	Asthmatic children indoor and outdoor 9 homes	Nephelometer (personal MIE) Harvard impactors TEOM	0.1-10 µm $PM_{2.5}$ and PM_{10}	Nephelometer correlates best with $PM_{2.5}$: vs. Indoor $PM_{2.5}$ $r = 0.66$, vs. indoor PM_{10} $r = 0.13$, vs. outdoor $PM_{2.5}$ $r = 0.42$, vs. outdoor PM_{10} $r = 0.20$.	Indoor and outdoor measurements collected using passive, active, and active heated nephelometers for comparison to PM mass measurements.
Chang et al. (2000) Baltimore, MD	1 person performing predetermined activities	"Roll around" monitor (RAS) ($PM_{2.5}$, CO, VOC, O_3, NO_2, SO_2)	$PM_{2.5}$	1-h personal O_3 exposures were significantly lower in indoor than outdoor microenvironments. 1-h personal CO exposures were highest in vehicles. Personal and ambient $PM_{2.5}$ correlations were strongest for outdoor microenvironments and those with high air exchange rates (i.e., vehicles).	1-h personal exposures measured simultaneously. Personal and ambient concentrations were compared.
Lioy et al. (1999) NA	10 vacuum cleaners		0.3-0.5 µm	Vacuum cleaners ranged in collection efficiency from 29-99%. Substantial fine particle emissions from motors with emission rates from 0.028 - 128.8 µg/min.	
Ezzati and Kammen (2001) Mpala, Kenya	55 Native huts 2- years	MiniRam (MIE)	Not specified. Optical device detects particles 1-10 µm, but it is not PM_{10}	Measured PM surrounding wood fires in unvented huts. PM measures were up to 8000 µg/m^3, but uncalibrated against wood smoke.	Exposures were related to ARI.
Chao and Tung (2001) Hong Kong	5 unoccupied homes measured indoors and outdoors, along with air exchange rates	Dust-Trak (TSI)	$PM_{2.5}$ real time, calibrated against an Andersen Mark II	In the limit as air exchange goes to zero, there appears to be a residual source, perhaps from drafts or thermal effects. Above air exchange rates of 4.5/hr penetration goes to 1, but indoor turbulence resuspends previously settled $PM_{2.5}$.	Developed an excellent model for ambient PM infiltration in the absence of anthropogenic indoor sources.

TABLE 5-5 (cont'd). SUMMARY OF RECENT MICROENVIRONMENTAL PM MEASUREMENT STUDIES

Reference	Study Description	Instrument(s)	Size Fraction (µm)	Summary of Measurements	Notes
Residential Indoor: Nonsmoking Homes (cont'd)					
Fischer et al. (2000) Amsterdam, NL	Measured traffic related differences of PM and VOCs, indoor/outdoor in 18 paired homes at varying distances from traffic	Harvard Impactors	$PM_{2.5}$ and PM_{10}. EC was measured by reflectance of the $PM_{2.5}$ filters. PAH also measured as indicator of diesel traffic.	Outdoor PM_{10} and $PM_{2.5}$ were approximately 15-20% higher at higher traffic streets than at the quiet streets on the same days. However, much larger differences were found for PAH and EC which are traffic specific.	"This [study] supports the use [of] traffic related pollution mapping as an exposure proxy in large-scale epidemiologic studies into health effects of motorized traffic emissions."
Kingham et al. (2000) Huddersfield, UK	Measured PM at ten homes of non-smokers, < 50 m and > 300 m from traffic	Harvard Impactors	$PM_{2.5}$ and PM_{10} and PAH. EC measured by filter reflectance.	Median Indoor/outdoor ratio =1 (no indoor combustion sources).	Found an absence of a spatial gradient, perhaps due to wind direction effects (e.g. sometimes upwind and sometimes downwind of traffic).
Morawska et al. (2001) Brisbane, Australia	Measured PM indoors and outdoors at 16 homes while residents were absent. Air exchange rate estimated, not measured	Scanning mobility particle sizer, aerodynamic particle sizer, and a TSI dust-trak	Submicron PM, Supramicron PM, $PM_{2.5}$	For supra and sub micron particles, indoor = outdoor for normal ventilation conditions of > 2 air changes/hour.	Average outdoor PM concentrations are good estimates of average indoor concentrations of PM of ambient origin for air exchange rates of > 0.5/h.
Abraham et al. (2002)	Measured ultrafine PM in various home and traffic microenvironments	TSI 8525	< 1 µm optical diameter	1-second readings collected while noting presence of sources.	The TSI 8525 is a useful instrument for screening UFPM in microenvironments.
Geller et al. (2002)	Comparison of indoor and outdoor PM in homes in Coachella Valley, CA	USC Personal PM 5 Lpm	$PM_{2.5}$ and $PM_{10-2.5}$	I2.5 = 4.3 + 0.74 O I10-2.5 = 3 + 0.3 O I EC = 0.84 O EC I OC > O OC.	13 volunteers had two to four 23-h measurements I and O analyzed for elemental carbon (EC) and organic carbon (OC). Some unoccupied homes measured.
Gotschi et al. (2002)	Measured Black Smoke (BS) by reflection from $PM_{2.5}$ filters for 4 European cities, indoor and outdoor.	XPOLIS PM monitor and EEL 43 reflectometer.	$PM_{2.5}$	PM measured I and O for two nights while subject was home (5 pm - 8 am). 183 sampled $PM_{2.5}$ and BS were compared for these samples.	BS is a supplementary measurement that can be made on $PM_{2.5}$ filters as an indication of EC.
Sarnat et al. (2002)	Measured $PM_{2.5}$ for sulfate analysis in and out of 6 Boston homes	Harvard Impactors with SMPS and APS particle counters	$PM_{2.5}$	The ratio of I/O $PM_{2.5}$, sulfate and size sub-fractions are developed as a function of season and Air Exchange Rate.	Sulfur is primarily of outdoor origin and can be used to track ambient PM of similar (0.06-0.5 µm) AD, but different relations exist for ultrafine PM and coarse mode PM < 2.5 µm AD.
Wallace and Howard-Reed (2002)	Measured ultrafine, fine and coarse PM in one Reston, VA tri-level home for 18 months with air exchange and meteorologic data	TSI 3071 SMPS TSI 3320 APS Climet 500-I MIE pDR-1000	10 nm to > 10 µm	Analysis of particle counts as a function of Air Exchange Rate and meteorological variables.	Wind speed has little influence on AER. The home sometimes acts as 1 compartment and sometimes multiple compartments.

TABLE 5-5 (cont'd). SUMMARY OF RECENT MICROENVIRONMENTAL PM MEASUREMENT STUDIES

Reference	Study Description	Instrument(s)	Size Fraction (µm)	Summary of Measurements	Notes
Residential Indoor: Other Home Types					
Brauer et al. (1996) Mexico	22 rural Mexican homes (smoking and nonsmoking)	Inertial impactor Radiance nephelometer	PM_{10} $PM_{2.5}$	Indoor $PM_{2.5}$: 132-555 µg/m^3 PM_{10}: 282-768 µg/m^3. Outdoor $PM_{2.5}$: 37 µg/m^3 PM_{10}: 68 µg/m^3; I/O $PM_{2.5}$: 1.8-12.4; PM_{10}: 4.7-10.0.	Variety of cooking fuels used Nephelometer data were highly correlated with $PM_{2.5}$ and PM_{10} indoors (r = ≈0.87-0.95).
Jenkins et al. (1996 a,b) 16 U.S. Cities	Smoking and nonsmoking homes	Fluoropore membrane filters	Particle phase ETS markers	Mean $PM_{3.5}$ concentrations were 17-20 µg/m^3 in smoking homes over nonsmoking homes.	
McBride et al. (1999) NA	Combustion source (incense) and walking (1 room, carpeted)	Met-One laser particle counter		Ratios of particle counts a 1.0 and 5.7 m from the combustion source/activity were obtained.	Proximity to source may help explain the existence of a personal cloud.
Vette et al. (2001) Fresno, CA	Detached semioccupied residence	SMPS LASX	0.01-2.5 µm	Temporal relationships between indoor and outdoor aerosol concentrations evaluated; penetration factors and deposition rates estimated. Fresno panel study empty residence.	Diurnally variable indoor/outdoor aerosol concentration ratios because of resuspension from daytime activities. Penetration factors ranged from 0.5 to 0.9.
Douce et al. (2001)	ETS measured by 4 methods in smokers homes and offices	37 mm filter and XAD-4 resin backup	PM_5	Samples extracted and analyzed for UV aborption, fluorescence, solanesol, and scopoletin.	Solanesol is best method of 4, but needs study of solanesol stability on filter.
Nonresidential Microenvironments					
Bohadana et al. (2000)	Manufacturing plant, woodworkers		Not given	443 personal time-weighted average occupations samples of airborne dust.	
Donham et al. (2000) San Francisco, CA	34 poultry workers	NIOSH Method 0600 monitors probed respirators	PM_5	Total dust sampled indoor respiratory masks. Personal monitoring: 630 ± 980 µg/m^3 (n = 210) ranging from 10-7,730 µg/m^3.	Respirable dust constituted about 10% of total dust measured.
Klepeis et al. (1996) San Francisco, CA	Airport lounge, ETS	TSI 8510 piezobalance	$PM_{3.5}$	Estimated cigarette emission rate of 1.43 mg/min/cigarette.	Personal exposures to ETS can be modeled in these types of microenvironments.
Nieuwenhuijsen et al. (1999)	Agricultural activities		PM_4	Average respirable fraction: 4.5 mg/m^3.	
Teschke et al. (1999)	Wood production, wood finishing, wood construction workers		PM ≈50	1,632 observations from 1979-1997. Arithmetic mean exposure: 7.93 mg/m^3. Geometric mean exposure: 1.86 mg/m^3.	

TABLE 5-5 (cont'd). SUMMARY OF RECENT MICROENVIRONMENTAL PM MEASUREMENT STUDIES

Reference	Study Description	Instrument(s)	Size Fraction (µm)	Summary of Measurements	Notes
Nonresidential Microenvironments (cont'd)					
Baek et al. (1997) Korea	Indoor and outdoor smoking restaurants		$PM_{3.5}$	Indoor concentrations: 33-475 $\mu g/m^3$ Outdoor concentrations: 12-172 $\mu g/m^3$ I/O: 2.4.	No significant correlation between indoor and outdoor measurements.
Ott et al. (1996) California	Bar before and after smoking prohibited	Piezobalance	$PM_{3.5}$	Smoking permitted: indoor 26.3-182 $\mu g/m^3$; outdoor < 5-67 $\mu g/m^3$ Smoking prohibited: indoor 4-82 $\mu g/m^3$; outdoor 2-67 $\mu g/m^3$.	I/O nonsmoking: 2.2. I/O smoking: 3.4.
Houseman et al. (2002) Boston, MA	Indoor and outdoor restaurants, stores	TSI DusTrak		Indoor restaurants: 14-278 $\mu g/m^3$ Outdoor restaurants: 7-281 $\mu g/m^3$ Indoor stores: 12-206 $\mu g/m^3$ Outdoor stores: 7-281 $\mu g/m^3$.	Avg I/O for restaurants: 2.3. Not known if the restaurants allowed smoking. In stores, indoor and outdoor measurements were correlated, avg I/O: 0.83.
Brauer and Mannetje (1998) Vancouver, BC	Indoor restaurants, various smoking policies		$PM_{2.5}$ PM_{10}	Nonsmoking: $PM_{2.5}$ 7-65 $\mu g/m^3$; PM_{10} < 10-74 $\mu g/m^3$ Restricted smoking (> 40% nonsmoking) $PM_{2.5}$ 11-163 $\mu g/m^3$; PM_{10} 24-89 $\mu g/m^3$ Unrestricted smoking: $PM_{2.5}$ 47-253 $\mu g/m^3$; PM_{10} 51-268 $\mu g/m^3$.	
Lee and Chang (1999) Hong Kong	Indoor and outdoor 5 classrooms		PM_{10}	Indoor PM_{10}: 30-470 $\mu g/m^3$ Outdoor PM_{10}: 20-617 $\mu g/m^3$	
Chan (2002)	A Hong Kong Office monitored indoor and outdoor	TEOM 1400a	$PM_{2.5}$	Daily 9 a.m - 6 p.m. weekday for 9 months.	Temp, RH and solar intensity influence In/Out. Wind speed has no effect.
Levy et al. (2002)	Arbitrary choice of one library, coffee shop, urban shopping mall, food court, apartment, hospital, subway, diesel bus in Boston, MA	TSI DustTrak 8520 TSI P-Trak 8525	PM counter calibrated to $PM_{2.5}$ < 1 µm OD	Measured inside and outside the various microenvironments tested, weekdays morning and afternoon. At least 3 visits, several 10 min averages.	10 min outdoor averages are poor predictors of indoor values.

TABLE 5-5 (cont'd). SUMMARY OF RECENT MICROENVIRONMENTAL PM MEASUREMENT STUDIES

Reference	Study Description	Instrument(s)	Size Fraction (µm)	Summary of Measurements	Notes
Traffic-Related Microenvironments (TRM)					
Praml and Schierl (2000) Munich, Germany	Trams and buses, rural and urban	Continuous millipore polycarbonate filter	PM_{10}	n = 201 4-h trips, mean concentration 155 $\mu g/m^3$ range: 13-686 $\mu g/m^3$ I/O: 2.8.	Tram > circular bus route > radial bus route Day > night
Monn et al. (1997) Switzerland	Spatial scale from a city street	Harvard microenvironment monitor	PM_{10}	48- or 72-h avg times; horizontal distance from street: 0, 15, 50, and 80 m; vertical distance from street: 20 m. Mean PM_{10} 27.3 ± 3.0 $\mu g/m^3$.	No vertical gradient (0-20 m) and horizontal gradient (0-80 m) in distance from road, each about 13%. No significant differences between wet and dry periods.
Rodes et al. (1998) Saevanenso, Los Angeles, CA	In-vehicle, various road types, 2-h trips		$PM_{2.5}$ PM_{10}	Vehicles in front of the monitored vehicle accounted for most of the in-vehicle commuting exposure; average I/O: 0.6-0.8 h^{-1} for $PM_{2.5}$; carpool lane concentrations were 30-60% lower than noncarpool lane concentrations.	Air exchange rates measured at various ventilation settings and speeds. Monitoring vehicle followed a diesel bus or truck.
Roorda-Knape et al. (1998) van Vliet et al. (1997) Netherlands	Gradient in distance from roadway	Harvard impactor	$PM_{2.5}$ PM_{10} Black smoke	PM monitoring at 50, 100, 150, and 300 m from roadway; 1-week avg time.	No concentration gradient with increasing distance from the roadways for $PM_{2.5}$ and PM_{10}; concentration gradient did exist for black smoke, also found an effect with wind direction.
Houseman et al. (2002) Boston, MA	Indoor and outdoor vehicles buses, subways	TSI DusTrak	PM_{10}	Vehicle concentrations ranged from 33-170 $\mu g/m^3$. Outdoor vehicle concentrations ranged from 40-144 $\mu g/m^3$. Bus concentrations: 17-268 $\mu g/m^3$; outdoor 10-203 $\mu g/m^3$. Subway: 28-174 $\mu g/m^3$; outdoor 8-203 $\mu g/m^3$.	The average in-vehicle to outdoor ratio was 0.99. Average I/O: 3; subway values were correlated with outdoor concentrations.
Brauer et al. (1999) Vancover, BC	Commuting environments	APC-1000		PM < 5: greatest concentrations by combustion powered vehicles. PM > 5: greatest concentrations by bicycling and buses.	
Janssen et al. (1997) Netherlands	Background and roadway		$PM_{2.5}$ PM_{10}	$PM_{2.5}$ background: 21-35 $\mu g/m^3$; roadway 23-43 $\mu g/m^3$. PM_{10} background:13-32 and 29-62 $\mu g/m^3$; roadway 16-56 and 30-75 $\mu g/m^3$.	Average roadway/background ratio: 3 for $PM_{2.5}$ and PM_{10}. Average increase in concentration at the roadway 7.2-12.7 $\mu g/m^3$.

TABLE 5-5 (cont'd). SUMMARY OF RECENT MICROENVIRONMENTAL PM MEASUREMENT STUDIES

Reference	Study Description	Instrument(s)	Size Fraction (µm)	Summary of Measurements	Notes
Traffic-Related Microenvironments (TRM) (cont'd)					
Adams et al. (2001)	PM by volunteers in TRM in London, UK	16 lpm personal monitor. Porous foam size selector	PM$_{2.5}$	Volunteers rode/cycled along fixed routes repetitively.	Personal exposures were generally double those at fixed-site ambient station. Subway exposures are maximal.
Alm et al. (1999) Kuopio, Finland	9-km commuter route, rush hours 1/mo	Climet	6 channels	Windows closed, vents open air exchange rate 36-47 h^{-1}.	Morning commutes were generally higher than afternoon commutes; relationships determined between PM and wind speed and vehicle speed.
Chan et al. (2002)	PM measured in TRM in Hong Kong	TSI 8520 DustTrac Calibrated to Partisol PM$_{2.5}$ HiVol PM$_{10}$	PM$_{2.5}$ and PM$_{10}$	Repetitive sampling over 8 fixed routes.	Highly variable by mode. Tram exposures are maximal.
Hoek et al. (2001) Hoek et al. (2002)	BS in Netherlands interpolated to outdoor locations relative to traffic at subject's homes	Black Smoke measured from filters	Not Recorded	GIS used to interpolate background and regional ambient BS with added increment for distance to traffic < 50 m and < 100 m.	May be useful technique. Estimates not validated with BS measurements at interpolated loci.
Jinsart et al. (2002)	PM Exposure of traffic police at intersection post in Bangkok, Thailand	Sibata personal single nozzle 2.5 lpm	PM$_{2.5}$ and PM$_{10}$	Sampled 12-h while on duty at post at intersection.	Exposures of both PM$_{2.5}$ and PM$_{10}$ higher than ambient PM measured at station with β gauge. Not comparable to U.S. conditions.
Lena et al. (2002)	PM$_{2.5}$ and EC in the Bronx, NY in area of high Diesel truck traffic	PM$_{2.5}$ @ 4 lpm 3 Lpm quartz filter for EC EEL for BS	PM$_{2.5}$	Sampled 10-h at sidewalk locations while counting cars and trucks for 3-weeks in summer of 1999.	EC is a large component of Diesel PM$_{2.5}$ and varies with truck traffic.
Zhu et al. (2002)	Ultrafine near Interstate Highway in Los Angeles, CA with heavy Diesel traffic	CPC TSI 3022A SMPS TSI 3936 BC aethalometer	6 nm-220 nm	200 m upwind and 17, 20, 30, 90, 150 and 300 m downwind.	Ultrafine PM decreased exponentially from the freeway and was equal to upwind at 300 m.

nephelometers that measure PM using light-scattering techniques. Recent PM exposure studies have used condensation nuclei counters (1 s averaging time) and personal nephelometers (1 min averaging time) to measure PM continuously (Howard-Reed et al., 2000; Quintana et al., 2000; Magari et al., 2002; Lanki et al., 2002) in various microenvironments. These data have been used to identify the most important ambient and nonambient sources of PM, to provide an estimate of source strength, and to compare modeled time activity data and PEM 24-h mass data to nephelometer measurements (Rea et al., 2001).

5.3.2.3 Traffic-Related Microenvironments

There has been increasing interest in the possible role of traffic-related pollutants. Distance to roadways has been used as a surrogate for exposure to traffic-related pollutants (Hoek et al., 2001), and this exposure indicator was subsequently used in an epidemiological study (Hoek et al., 2002). A traffic model, using traffic volume, direct exhaust emissions rate, and a re-entrainment rate has been used to estimate concentrations of traffic-related emissions at several schools in East Los Angeles (Korenstein and Piazza, 2002). Personal exposure studies have been made in a variety of commuting situations including vehicle traffic (Adams et al., 2001; Chan et al., 2002). Other studies have measured various indicators of traffic near roadways (Lena et al., 2002), inside vehicles in traffic (Abraham et al., 2002), and in several types of traffic related microenvironments (Levy et al., 2002). Table 5-5 provides a brief description of these studies, instruments used, measurements made, and key findings.

5.3.2.4 Reanalyses of Previously-Reported Particulate Matter Exposure Data

Papers that have reanalyzed and interpreted the data collected in previous PM exposure studies are summarized in Table 5-6. These reanalyses are directed toward understanding the personal cloud, the variability in total PM exposure, and the personal exposure-to-ambient concentration relationships for PM. Brown and Paxton (1998) determined that the high variability in personal exposure to PM makes the personal-to-ambient PM relationship difficult to predict. Wallace (2000b) used data from a number of studies to test two hypotheses: elderly COPD patients have (1) smaller personal clouds and (2) higher correlations between personal exposure and ambient concentrations compared to healthy elderly, children, and the general population. The analysis by Wallace (2000a) and three subsequent longitudinal studies

TABLE 5-6. PAPERS REPORTING REANALYSES OF PARTICULATE MATTER EXPOSURE STUDIES

Reference	Study Cited	Objectives/Hypotheses	Findings
Wallace (2000a)	PTEAM (Özkaynak et al., 1990; Spengler et al., 1989; Wiener 1988, 1989; Wiener et al., 1990) THEES (Lioy et al., 1990) Nashville COPD (Bahadori et al., 2001) Amsterdam COPD (Janssen et al., 1997, 1998a) Boston COPD (Rojas-Bracho et al., 2000)	Examines the differences between pooled and longitudinal correlations in personal and ambient (or outdoor) data for $PM_{2.5}$ and PM_{10}. Discusses the personal cloud for $PM_{2.5}$ and PM_{10}. Hypothesizes that COPD patients have (1) smaller personal clouds (supported) and (2) higher correlations of personal exposure with outdoor concentrations because of reduced mobility (not supported).	Median longitudinal correlation coefficient is much higher than the pooled correlation coefficient for the same data sets. Personal cloud for PM_{10}: 3-67 μg/m^3; $PM_{2.5}$ 6-27 μg/m^3. Personal cloud for elderly COPD was much smaller (PM_{10}: 6-11 μg/m^3; $PM_{2.5} \approx$ 6 g/m^3) than for other healthy populations (PM_{10}: 27-56 μg/m^3; $PM_{2.5}$: 11-27 μg/m^3) of elderly, children, and the general population. However, correlations of personal exposure with ambient concentrations were not higher for elderly COPD than for other groups.
Özkaynak and Spengler (1996)	Dockery and Spengler, 1981 PTEAM (Özkaynak et al., 1996a,b) Netherlands (Janssen et al., 1995)	Uses statistical modeling techniques to examine the relationship between ambient PM concentrations and personal exposures. Data analysis involves use of air exchange rates, penetration factors, and indoor/outdoor ratios, as well as examining exposure in various microenvironments (traveling, working, outdoors, indoors) activities (exposure to smoke, cooking), and source strengths.	The important components of personal exposures are received during contact with indoor sources, mainly in homes and work places. Ambient aerosols contribute about 50% or more to the personal PM_{10} exposures of the general population. The contribution of ambient aerosols to the total toxicity of inhaled particles is significant.
Brown and Paxton (1998)	THEES (Lioy et al., 1990) PTEAM pilot (Wallace, 1996) Boston and Nashville COPD (Rojas-Bracho et al., 2000); Bahadori et al., 2001)	Cross-sectional and longitudinal regression analysis on data sets.	Individual personal PM exposure is subject to high variability, which makes the personal-to-ambient PM relationship difficult to predict.
Wilson and Suh (1997)	Philadelphia (Burton et al., 1996; Suggs and Burton, 1983) EPA AIRS database	Determines the utility of fine and coarse PM concentrations as indicators of time-series epidemiology with regard to day-to-day variability, area uniformity, and indoor/outdoor PM ratios. Necessary to treat personal exposure to ambient PM and personal exposure to nonambient PM as separate components of total personal PM exposure.	Fine and coarse particles should be considered separate classes of pollutants. Fixed-site ambient fine-particle measurements likely give a reasonable indication of the variability in the concentration of ambient fine particles across the community. Coarse-particle measurements most likely will not.
Wilson et al. (2000)	New Jersey (Lioy et al., 1990) Japan (Tamura et al., 1996a) PTEAM (Clayton et al., 1993; Özkaynak et al., 1996a,b) Netherlands (Janssen, 1998a; Suh et al., 1992)	Synoptic review of the "exposure paradox": Low correlations between personal exposure and ambient PM concentrations in spite of the existence of statistical association between ambient PM and epidemiologic health effects. Uses personal exposure equation, mass balance, regression analysis, and deductive logic.	Personal PM exposure needs to be divided into different classes according to source type: exposure to ambient PM (outdoor and indoors) and exposure to nonambient PM (indoor source and personal activity). Correlations are higher between personal exposure and ambient PM concentrations when PM exposures from nonambient sources are removed.

TABLE 5-6 (cont'd). PAPERS REPORTING REANALYSES OF PARTICULATE MATTER EXPOSURE STUDIES

Reference	Study Cited	Objectives/Hypotheses	Findings
Mage et al. (1999)	Japan (Tamura et al., 1996a) State College (Suh et al., 1995) Netherlands (Janssen et al., 1997, 1998a, 1999a) New Jersey (Lioy et al., 1990) PTEAM (Clayton et al., 1993; Özkaynak et al., 1996a,b)	Examines the influence of nonambient PM on total PM concentrations and how it may confound the outdoor/personal PM relationship. Missing data and outlier values created using an algorithm. Linear regression analysis of subsequent data sets.	Variation in daily personal exposure for subjects with similar lifestyles and no ETS exposure are driven by variations in ambient PM concentrations. Exposure to ambient PM is highly correlated in time with ambient PM concentrations measured at a community site. Indoor PM does not confound the relationship between daily mortality and ambient PM.
Mage (1998)	PTEAM (Clayton et al., 1993; Özkaynak et al., 1993, 1996a,b)	Uses a reduced-form mass-balance model to predict the average fraction of ambient PM to which the average person is exposed.	On average, a person is exposed to > 75% of ambient $PM_{2.5}$ and > 64% of ambient PM_{10} measured by the community monitor.
Monn (2001)	Multiple Literature Review	To make an objective review of literature published since 1996 as an implicit update to the 1996 U.S. EPA PM AQCD. Emphasis on European studies.	"It is important to note that a personal measurement does not *a priori* provide more valid data than a stationary ambient measurement, i.e. a personal sample in a study investigating effects from outdoor combustion particles is often influenced by sources other than outdoor sources and may thus confound the exposure-effect outcome." "Despite some lack of correlation between personal (PM_{10}) and outdoor values, outdoor fine particle concentrations were strongly associated with mortality and morbidity indicating that outdoor sources (e.g. vehicular emissions) emit the toxic entity (Dockerey et al., 1993; Schwartz et al., 1996)."
Rotko et al. (2000a)	Jantunen et al. (1998) Carrer et al. (1997) Koistinen et al. (1999)	To make a comparison of exposure relationships between the six EXPOLIS European cities (Athens, Basel, Grenoble, Helsinki, Milan, Prague).	Demographic bias exists because women and more-educated individuals are more likely to respond to survey. Socioeconomic bias exists in low SES subjects less likely to participate in diary keeping and exposure monitoring. Weighting is required for inter-city comparisons. Selection bias is not a problem for characterizing physical factors influencing personal exposure.
Rotko et al. (2000b)	Rotko et al. (2000a), Jantunen et al. (1998)	To determine sociodemographic influences of exposure in Helsinki.	Distinct male vs female differences: males had higher exposures to $PM_{2.5}$, related to ETS, and a larger variance between sociodemographic groupings. No sociodemographic differences existed in outdoor $PM_{2.5}$ concentrations. Lower occupational status contributed to greater $PM_{2.5}$ exposures than higher (professional) occupational status.
Rodes et al. (2001)	EPA Baltimore and Fresno 1 and 2	To investigate relationships between the different retirement centers and identify most likely factors influencing personal and indoor concentrations.	Mean personal exposure $PM_{2.5}$ was higher than their apartment concentrations. Personal cloud of 3 $\mu g/m^3$ for $PM_{2.5}$ was negligible but cloud for PM_{10} was 20 $\mu g/m^3$. Indoor $PM_{2.5}$ data were less than ambient concentrations.

(Williams 2000a,b,c; Ebelt et al., 2000; Sarnat et al., 2000) supported hypothesis 1 but not hypothesis 2. Özkaynak and Spengler (1996) showed that at least 50% of personal PM_{10} exposure for the general population comes from ambient particles. Wilson and Suh (1997) concluded that fine and coarse particles should be treated as separate classes of pollutants because of differences in characteristics and potential health effects. Wilson et al. (2000) gave a review of what they call the "exposure paradox" and determine that personal PM needs to be divided into different classes according to source type and that correlations between personal and ambient PM will be higher when nonambient sources of PM are removed from the personal PM concentration. Mage (1998) conducted analysis using the PTEAM data and showed that the average person in PTEAM (Riverside, CA in the fall) was exposed to > 75% of ambient $PM_{2.5}$ and > 64% of ambient PM_{10}. Mage et al. (1999) used an algorithm to fill in missing data and outliers to analyzed data sets and show that variation in daily personal exposures for subjects with similar activity patterns and no ETS exposure are driven by variation in ambient PM concentrations.

5.3.3 Factors Influencing and Key Findings on Particulate Matter Exposures

5.3.3.1 Relationship of Personal/Microenvironmental Particulate Matter with Ambient Particulate Matter

Understanding the relationship between ambient site measurements and personal exposure to PM is important for several reasons. First, it allows us to examine the extent to which ambient measurements for PM and various PM constituents can serve as surrogates for exposure to ambient PM or ambient constituents of PM in epidemiological studies. Second, it provides information that may improve surrogate exposure measurements and, hence, increase the power of epidemiologic studies. Finally, because compliance with the NAAQS is based on ambient monitoring, it can be used to understand the effect of regulation on exposures to PM and its constituents and, hence, can help link the effect of regulations to health outcomes. Many of the studies summarized in Table 5-4 have analyzed this relationship using measurements of personal PM exposures and ambient PM concentrations. Of primary interest are the PM concentrations measured in ambient, indoor, and outdoor air; personal exposure measurements; the statistical correlations between measurements; and the attenuation and/or infiltration factors developed for personal exposure and indoor microenvironments. Attenuation and infiltration factors are discussed in Section 5.3.4.3.1. Information on correlation analysis is provided below.

5.3.3.1.1 Types of Correlations

The three types of correlation data that will be discussed in this section are longitudinal, "pooled," and daily-average correlations. *Longitudinal correlations* are calculated when data from a study includes measurements over multiple days for each subject (longitudinal study design). Longitudinal correlations describe the temporal relationship between daily personal PM exposure or microenvironment concentration and daily ambient PM concentration for each individual subject. The longitudinal correlation coefficient, r, may differ for each subject. An analysis of the variability in r across subjects can be performed with this type of data. Typically, the median r is reported along with the range across subjects in the study. *Pooled correlations* are calculated when a study involves one or only a few measurements per subject and when different subjects are studied on subsequent days. Pooled correlations combine individual subject/individual day data for the correlation calculation. Pooled correlations describe the relationship between daily personal PM exposure and daily ambient PM concentration across all subjects in the study. For some studies, the multiple days of measurements for each subject were assumed to be independent (after autocorrelation and sensitivity analysis) and combined together in the correlation calculation (Ebelt et al., 2000). *Daily-average correlations* are calculated by averaging exposure across subjects for each day. Daily-average correlations then describe the relationship between the daily average exposure and daily ambient PM concentration. Cross-sectional is used to refer to both pooled and daily average correlations, so the meaning of this term must be determined from context.

Pooled correlations have been simulated from longitudinal data by using a random-sampling procedure to select a random day from each subject's measurements for use in the correlation. This procedure was repeated many times, and statistics (such as the mean and standard deviation of the pooled correlation coefficient) were reported (Janssen et al., 1997, 1998a, 1999c).

The type of correlation analysis can have a substantial effect on the resulting correlation coefficient. Mage et al. (1999) mathematically demonstrated that very low correlations between personal exposure and ambient concentrations could be obtained when people with very different nonambient exposures are pooled, even though their individual longitudinal correlations are high. The longitudinal studies conducted by Tamura et al. (1996a) and Janssen et al. (1997, 1998a, 1999c) determined that the longitudinal correlations between personal exposure and ambient PM concentrations were higher than the correlations obtained from a pooled data set. Wallace (2000a) reviewed a number of longitudinal studies and found that the median longitudinal correlation coefficient was higher than the pooled correlation coefficient for the same data (see Tables 1 and 2, Wallace, 2000a).

Mage et al. (1999) examined three longitudinal exposure data sets where several subjects were measured each day. They showed that by averaging daily exposures across subjects, daily-average correlations could be obtained. These were all higher than the median longitudinal correlations. Williams et al. (2000a,b) and Evans et al. (2000) have also reported higher correlation coefficients for daily-average correlations compared to longitudinal correlations. The higher correlations found between daily-average personal exposures and ambient PM concentrations, as opposed to lower correlations found between individual exposures and ambient PM levels, have been attributed to the statistical process of averaging (Ott et al., 2000). Personal exposures include contributions from nonambient as well as ambient PM concentrations. When several subjects are measured on the same day, the mean variability due to variations in nonambient exposures is reduced due to averaging. Therefore, the correlation between personal exposure and ambient concentrations increases as the number of subjects measured daily increases. Ott et al. (2000), using the theory on which their Random Component Superposition (RCS) model is based, predict expected correlations above 0.9 for the PTEAM study and above 0.70 for the New Jersey study (Lioy et al., 1990) if 25 subjects had been measured daily in each study.

5.3.3.1.2 Correlation Data from Personal Exposure Studies

Measurement data and correlation coefficients for the personal exposure studies described in Section 5.4.2.1 are summarized in Table 5-7. All data are based on mass measurements. The studies are grouped by the type of study design, longitudinal or pooled. For each study in Table 5-7, summary statistics for the total personal PM exposure measurements are presented as well as statistics for residential indoor, residential outdoor, and ambient PM concentrations when available. The correlation coefficients (r) between total personal PM exposures and

TABLE 5-7. PERSONAL MONITORING STUDIES FOR PARTICULATE MATTER: MEASURED CONCENTRATIONS AND CORRELATION COEFFICIENTS

		Measured Concentration Levels (µg/m^3)						Personal-Ambient[2] Correlation Coefficients (r)			Other Correlation Coefficients (r)	
Size Fraction	Avg. Time	Statistic	Sample Size[1]	Personal	Residential Indoor	Residential Outdoor	Ambient	Type[3]	Value (Range)	Notes	Type[3]	Value (Range)
Longitudinal Studies												
Ebelt et al. (2000) – Vancouver, BC												
$PM_{2.5}$	24 h	$\bar{x}$ ± SD Range	106	18.2 ± 14.6 2 - 91			11.4 ± 4.1 4 - 29	Median L P	0.48 (−0.68-0.83) 0.15	n = 16 COPD subjects		
Evans et al. (2000) – Fresno, CA												
$PM_{2.5}$	24 h	$\bar{x}$ Range	24	13.3 1 - 24	9.7 4 - 17	20.5 4 - 52	21.7 6 - 37	P	0.41[4]	Fresno-1 study	P_{p-i} P_{p-o}	0.81[4] 0.80[4]
$PM_{2.5}$	24 h	$\bar{x}$ Range	12	11.1 7 - 16	8.0 4 - 12	10.1 5 - 20	8.6 4 - 16	P	0.84[4]	Fresno-2 study	P_{p-i} P_{p-o}	0.95[4] 0.80[4]
Janssen et al. (1997) – Netherlands												
PM_{10}	24 h	$\bar{x}$ ± SD Range	301	105.2 ± 28.7 57 - 195			38.5 ± 5.6 25 - 56	Median L Median L Median L Mean P Mean P Mean P	0.63 (0.1-0.9) 0.63 0.59 0.28 (0.12)[5] 0.45 (0.16)[5] 0.20 (0.19)[5]	n = 45 school children With nonsmoking parents With smoking parents All With nonsmoking parents With smoking parents		
Janssen et al. (1998a) – Netherlands												
PM_{10}	24 h	$\bar{x}$ ± SD Range	262	61.7 ± 18.3 38 - 113	35.0 ± 9.4 19 - 65		41.5 ± 4.3 32 - 50	Median L Median P Median P	0.50 (−0.41-0.92) 0.50 (0.07-0.83)[5] 0.34 (−0.09-0.67)[5]	n = 37 adults No ETS exposure All	Med. L_{p-i} Med. L_{i-a}	0.72 (−0.10-0.98) 0.73 (−0.88-0.95)
Janssen et al. (1999c) – Netherlands												
$PM_{2.5}$	24 h	$\bar{x}$ ± SD Range	77	28.3 ± 11.3 19 - 60			17.1 ± 2.8 14 - 22	Median L Median P	0.86 (-0.11-0.99) 0.41 (-0.28-0.93)[5]	n = 13 school children		
$PM_{2.5}$	24 h	$\bar{x}$ ± SD Range	55	24.4 ± 4.9 19 - 33			17.1 ± 2.6 15 - 22	Median L Median P	0.92 0.82[5]	With nonsmoking parents		
$PM_{2.5}$	24 h	$\bar{x}$ ± SD Range	22	37.0 ± 17.4 21 - 60			17.1 ± 3.7 14 - 21			With smoking parents		

TABLE 5-7 (cont.). PERSONAL MONITORING STUDIES FOR PM: MEASURED CONCENTRATIONS AND CORRELATION COEFFICIENTS

		Measured Concentration Levels (µg/m^3)						Personal-Ambient[2] Correlation Coefficients (r)			Other Correlation Coefficients (r)	
Size Fraction	Avg. Time	Statistic	Sample Size[1]	Personal	Residential Indoor	Residential Outdoor	Ambient	Type[3]	Value (Range)	Notes	Type[3]	Value (Range)
Janssen et al. (2000) – Netherlands												
PM$_{2.5}$	24 h	x̄ ± SD	338	24.3 ± 25.7	28.6 ± 41.8		20.6 ± 4.0	Median L	0.79 (−0.41-0.98)	n = 36 elderly w/CV disease	Med. L$_{p-i}$	0.91 (−0.28-1.0)
		Range		9 - 134	9 - 239		13 - 31	Median L	0.85	No ETS exposures	Med. L$_{i-a}$	0.84 (−0.00-0.98)
Janssen et al. (2000) – Finland												
PM$_{2.5}$	24 h	x̄ ± SD	336	10.8 ± 4.4	11.0 ± 4.0		12.6 ± 2.0	Median L	0.76 (−0.12-0.97)	n = 46 elderly w/CV disease	Med. L$_{p-i}$	0.89 (0.14-1.0)
		Range		4 - 33	3 - 27		10 - 18				Med. L$_{i-a}$	0.70 (−0.15-0.94)
Linn et al. (1999) – Los Angeles												
PM$_{2.5}$	24 h	x̄ ± SD	60	23.8 ± 15.1	23.5 ± 15.3	24.8 ± 14.5		P	0.26[6]		P$_{i-a}$	0.26[6]
		Range		4 - 65	4 - 92	4 - 63					P$_{o-a}$	0.47[6]
PM$_{10}$	24 h	x̄ ± SD	59	34.8 ± 14.8	32.6 ± 15.6	39.8 ± 18.3	33 ± 15	P	0.22[6]		P$_{i-a}$	0.32[6]
		Range		5 - 85	9 - 105	7 - 97	9 - ??				P$_{o-a}$	0.66[6]
Rojas-Bracho et al. (2000) – Boston												
PM$_{2.5}$	12 h	x̄ ± SD	224	21.6 ± 13.6	17.5±14.1	14.2 ± 11.2		Median L	0.61 (0.10-0.93)[6]	n = 17 adults	Med. L$_{p-i}$	0.87[6]
		Range		1 - 128	2 - 73	1 - 57					Med. L$_{i-o}$	0.74[6]
PM$_{10}$	12 h	x̄ ± SD	225	37.2 ± 22.8	31.9 ± 25.2	22.2 ± 18.7		Median L	0.35 (0.0-0.72)[6]		Med. L$_{p-i}$	0.71[6]
		Range		9 - 211	2 - 329	3 - 76					Med. L$_{i-o}$	0.50[6]
PM$_{10-2.5}$	12 h	x̄ ± SD	222	15.6 ± 14.6	14.5 ± 9.2	8.1 ± 6.8		Median L	0.30 (0.0-0.97)[6]		Med. L$_{p-i}$	0.42[6]
		Range		−11 - 103	−3 - 255	−2 - 64					Med. L$_{i-o}$	0.20[6]

TABLE 5-7 (cont.). PERSONAL MONITORING STUDIES FOR PM: MEASURED CONCENTRATIONS AND CORRELATION COEFFICIENTS

		Measured Concentration Levels (µg/m^3)						Personal-Ambient [2] Correlation Coefficients (r)			Other Correlation Coefficients (r)	
Size Fraction	Avg. Time	Statistic	Sample Size[1]	Personal	Residential Indoor	Residential Outdoor	Ambient	Type[3]	Value (Range)	Notes	Type[3]	Value (Range)
Sarnat et al. (2000) – Baltimore												
$PM_{2.5}$	24 h	x̄ ± SD	37	26.7 ± 13.7			25.2 ± 11.5	Median L	0.76 (−0.21-0.95)[7]	n = 15 adults;		
		x̄ ± SD	36	18.5 ± 11.2			5.6 ± 49.0	Median L	0.25 (−0.38-0.81)[7]	summer		
								P	0.89[8]	n = 15 adults; winter		
								P	0.75[8]	High ventilation;		
								P	0.50[8]	summer		
								P	0.44[8]	Med. ventilation;		
										summer		
										Low ventilation;		
										summer		
										WINTER		
PM_{10}	24 h	x̄ ± SD	37	33.9 ± 11.7			34.0 ± 12.8	Median L	0.64 (0.08-0.86)[7]	SUMMER		
		x̄ ± SD	36	28.0 ± 16.5			7.5 ± 73.2	Median L	0.53 (−0.79-0.89)[7]	WINTER		
$PM_{10-2.5}$	24 h	x̄ ± SD	37	7.2 ± 4.0			8.4 ± 2.3	Median L	0.11 (−0.60-0.64)[7]	SUMMER		
		x̄ ± SD	36	9.6 ± 7.9			−1.3 ± 24.2	Median L	0.32 (−0.48-0.68)[7]	WINTER		
Tamura et al. (1996a) – Tokyo												
PM_{10}	48 h							P	0.83	n = 7 elderly adults		
Williams et al. (2000a,b) – Baltimore												
$PM_{2.5}$	24 h	x̄	23	13.0	9.4	22.0	22.0	Median L	0.80 (0.38-0.98)[6]	n = 21 elderly adults	P_{p-i}	0.90[4]
		Range		7 - 25	4 - 19	7 - 52	8 - 59	P	0.89[4]		P_{p-o}	0.95[4]
											P_{i-o}	0.94[4]
											P_{i-a}	0.87[4]
											P_{o-a}	0.96[4]
PM_{10}	24 h	x̄	28		11.0	30.0	29.9				P_{i-o}	0.82[4]
		Range			4 - 23	13 - 66	13 - 74				P_{i-a}	0.81[4]
											P_{o-a}	0.94[4]
$PM_{10-2.5}$	24 h	x̄	26		1.0	8.0	8.0				P_{i-o}	0.18[4]
		Range			-3 - 5	−2 - 16	1 - 15				P_{i-a}	0.08[4]
											P_{o-a}	0.45[4]

TABLE 5-7 (cont.). PERSONAL MONITORING STUDIES FOR PM: MEASURED CONCENTRATIONS AND CORRELATION COEFFICIENTS

		Measured Concentration Levels (µg/m^3)						Personal-Ambient [2] Correlation Coefficients (r)			Other Correlation Coefficients (r)	
Size Fraction	Avg. Time	Statistic	Sample Size[1]	Personal	Residential Indoor	Residential Outdoor	Ambient	Type[3]	Value (Range)	Notes	Type[3]	Value (Range)
Williams et al. (2000a,b) – Baltimore (cont'd)												
Keeler et al. (2002) Detroit, MI		Mean (Std)	20 asthmatic children	68.4 (39.2)	52.2 (30.6)		25.8 (11.8)					
PM_{10} 24-h $PM_{2.5}$ 24-h					34.4 (21.7)		15.6 (8.2)					
Landis et al. (2001) Baltimore, MD		Mean	10 elderly retirees	12.8	10.2	21.0		Pearson	r = 0.82 (0.51-0.92)		P vs I	r = 0.60 (.41-.85)
$PM_{2.5}$ 24-h Sulfate 24-h				4.5	4.0	10.2			r = 0.95 (0.74-0.97)			r = 0.95 (.73-.97)
Pooled Studies												
Bahadori (1998) – Nashville												
$PM_{2.5}$	12 h	$\bar{x}$ ± SD Range	30	21.7 ± 10.5 10 - 67	15.5 ± 6.6 5 - 40	23.4 ± 6.8 3 - 61		P	0.09	n = 10 COPD subjects; daytime	P_{p-i} P_{i-o}	0.72 0.31
PM_{10}	12 h	$\bar{x}$ ± SD Range	30	33.0 ± 16.9 5 - 88	21.6 ± 10.7 9 - 77	32.5 ± 8.1 7 - 76		P	−0.08	n = 10 COPD subjects; daytime	P_{p-i} P_{i-o}	0.43 0.06
Pellizzari et al. (1999) – Toronto												
$PM_{2.5}$	3 d	$\bar{x}$	922	28.4	21.1	15.1		P	0.23	n = 178; n for indoor, outdoor lower than personal	P_{p-i} P_{i-o}	0.79 0.33
PM_{10}	3 d	$\bar{x}$	141	67.9	29.8	24.3				No correlations reported		
Oglesby et al. (2000) – EXPOLIS Basel												
$PM_{2.5}$	48 h	$\bar{x}$ ± SD	44 20	23.7 ± 17.1 17.5 ± 13.0		19.0 ± 11.7 17.7 ± 7.1		P P	0.07 0.21	All No ETS exposure		
Santos-Burgoa et al. (1998) – Mexico City												
PM_{10}	24 h	$\bar{x}$ ± SD	66	97 ± 44	99 ± 50			P	0.26		P_{p-i} P_{i-a}	0.47 0.23
Tamura et al. (1996b) – Osaka												
PM_2	48 h							P	0.74			
PM_{10}	48 h							P	0.67			

TABLE 5-7 (cont.). PERSONAL MONITORING STUDIES FOR PM: MEASURED CONCENTRATIONS AND CORRELATION COEFFICIENTS

		Measured Concentration Levels (µg/m^3)						Personal-Ambient [2] Correlation Coefficients (r)			Other Correlation Coefficients (r)	
Size Fraction	Avg. Time	Statistic	Sample Size[1]	Personal	Residential Indoor	Residential Outdoor	Ambient	Type[3]	Value (Range)	Notes	Type[3]	Value (Range)
Pellizzari et al. (2001) – Indianapolis												
$PM_{2.5}$	72-h	Median	250	23	18	18	18	P	0.102	Between the Logarithms of concentrations	P vs outdoor	0.138 0.923
											P vs Indoor	
Brauer et al. (2000) Banska Bystrica												
$PM_{2.5}$	24-h	Mean	PM_{10}	122	79		35	P PM_{10}	$r^2 < 0.17$	Multivar with	P indoor	$r^2 = 0.15$
PM_{10}			Summer	120	66		45			nicotine	$PM_{2.5}$	$r^2 = 0.23$
			PM_{10} Winter	88	55		22				P	
			$PM_{2.5}$	69	53		32				Personal	
			Summer	6.5	4.6		5.7				SO_4 vs	
			$PM_{2.5}$ Winter								Amb. SO_4	
			SO_4 Winter									
Kousa et al. (2002)												
Helsinki + 3 cities $PM_{2.5}$48-h								Pearson non-work pooled	$r^2 = 0.69$		P vs I	r = 0.60 (0.41-0.85)
								Helsinki				r = 0.95 (0.73-0.97)

Abbreviations used:

Avg. = Averaging (time)
Conc. = Concentration
CV = Cardiovascular
d = Day
ETS = Environmental tobacco smoke

h = Hour
i-a = Indoor-ambient correlation
i-o = Indoor-outdoor correlation
L = Longitudinal correlation
Med. = Median
o-a = Outdoor-ambient correlation

P = Pooled correlation
p-i = Personal-indoor correlation
p-o = Personal-outdoor correlation
SD = Standard deviation
Stat. = Statistic
x̄ = Mean

Notes:

1. Sample size is for personal concentrations; indoor, outdoor and ambient sample sizes may differ.
2. Correlation coefficient is for personal-residential outdoor if no ambient concentration data reported.
3. See text for description of types of correlations.
4. Daily-averaged correlation (values for individual subjects averaged for each day).
5. Pooled correlations estimated using a Monte Carlo sampling procedure, n = 1000. If mean P is shown, then SD given; if median P is shown, then range is given.
6. Obtained from a regression equation; $r = \sqrt{(R^2)}$.
7. Spearman rank correlations.
8. Calculated, $r = \sqrt{(R^2)}$, from R^2 from a mixed model regression.

ambient PM concentrations also are presented and classified as longitudinal or pooled correlations. When reported, *p*-values for the correlation coefficients are included. Correlation coefficients between personal, indoor, outdoor, and ambient also are reported when available.

5.3.3.1.3 Correlations Between Personal Exposures, Indoor, Outdoor, and Ambient Measurements

Longitudinal and pooled correlations between personal exposure and ambient or outdoor PM concentrations varied considerably between study and study subjects. Most studies report longitudinal correlation coefficients that range from < 0 to ≈1, indicating that an individual's activities and residence type may have a significant effect on total personal exposure to PM. General population studies tend to show lower correlations because of the higher variation in the levels of PM generating activities. In contrast, the absence of indoor sources for the populations in several of the longitudinal studies resulted in high correlations between personal exposure and ambient PM within subjects over time for these populations. But even for these studies, correlations varied by individual depending on their activities and the microenvironments that they occupied.

Probability Studies

In the Toronto study (Pellizzari et al., 1999), pooled correlations were derived for personal, indoor, outdoor, and fixed-site ambient measurements. This study was conducted in Toronto on a probability sample of 732 participants who represented the general population of people 16 years and older. The study included between 185 and 203 monitoring periods with usable PM data for personal, residential indoor, and outdoor measurements. For PM_{10} measurements, the mean concentrations were 67.9 $\mu g/m^3$ for personal, 29.8 $\mu g/m^3$ for indoor air, and 24.3 $\mu g/m^3$ for outdoor air samples. For $PM_{2.5}$, the mean concentrations were 28.4 $\mu g/m^3$ for personal, 21.1 $\mu g/m^3$ for indoor air, and 15.1 $\mu g/m^3$ for outdoor air samples. A low but significant correlation ($r = 0.23$, $p < 0.01$) was reported between personal exposure and ambient measurements. The correlations between indoor concentrations and the various outdoor measurements of $PM_{2.5}$ ranged from 0.21 to 0.33. The highest correlations were for outdoor measurements at the residences with the ambient measurements made at the roof site (0.88) and the other fixed site (0.82). Pellizzari et al. (1999) state that much of the difference among the data for personal/indoor/outdoor PM:

> . . . can be attributed to tobacco smoking, since all variables reflecting smoking . . . were found to be highly correlated with the personal (and indoor) particulate matter levels, relative to other variables that were measured . . . none of the outdoor concentration data types (residential or otherwise) can adequately predict personal exposures to particulate matter. (p. 729)

Using a Random Component Superposition (RCS) statistical model, Ott et al. (2000) calculated an attenuation factor of 0.61 for personal exposure for PM_{10} for the Toronto study. The mean nonambient exposure component for PM_{10} was estimated as 52.62 $\mu g/m^3$ with a standard deviation of 84.82 $\mu g/m^3$. Although the data were available for $PM_{2.5}$, similar calculations were not made.

PM_{10} data from the PTEAM study were analyzed using the same approach (Ott et al., 2000). For PTEAM, an attenuation factor of 0.55 was calculated for personal exposure. Infiltration factors were calculated for each residence with an average of 0.56 and a standard deviation of 0.15. Values ranged from a minimum of 0.19 to a maximum of 0.87 showing the substantial variability that can be seen between homes depending upon the housing characteristics and operation of the HVAC system. The mean nonambient exposure component for PM_{10} was estimated as 59 $\mu g/m^3$ with a standard deviation of 46 $\mu g/m^3$.

Santos-Burgoa et al. (1998) describe a 1992 study of personal exposures and indoor concentrations to a randomly sampled population near Mexico City. The sample of 66 monitored subjects included children, students, office and industrial workers, and housewives. None of the people monitored were more than 65 years old. The mean 24-h personal exposure and indoor concentrations were 97 ± 44 and 99 ± 50 $\mu g/m^3$, respectively, with an $r_{Personal/Ambient} = 0.26$ ($p = 0.099$). Other correlations of interest were $r_{Personal/Indoor} = 0.47$ ($p = 0.002$) and $r_{Indoor/Ambient} = 0.23$ ($p = 0.158$). A strong statistical association was found between personal exposure and socioeconomic class ($p = 0.047$) and a composite index of indoor sources at the home ($p = 0.039$).

Correlation analysis for personal exposure has not yet been reported for EXPOLIS. Some preliminary results (Jantunen et al., 2000) show that in Basel and Helsinki a single ambient monitoring station was sufficient to characterize the ambient $PM_{2.5}$ concentration in each city. Using microenvironmental concentration data collected while the subjects were at home, at work, and outdoors, they calculated the sum of the time-weighted-averages of these data and found the results closely match the personal $PM_{2.5}$ exposure data collected by the monitors carried by most of the subjects although a few subjects (mostly smokers) were noticeable exceptions.

Longitudinal Studies

A number of longitudinal studies using a purposeful sampling design have been conducted and reported in the literature since 1996. A number of these studies (Janssen et al., 1998a, 1999b, 2000; Williams et al., 2000b; Evans et al., 2000) support the previous work by Janssen et al. (1995) and Tamura et al. (1996a) and demonstrate that for individuals with little exposure to nonambient sources of PM, correlations between total PM exposure and ambient PM measurements are high. Other studies (Ebelt et al., 2000; Sarnat et al., 2000) show strong correlations for the SO_4^{-2} component of $PM_{2.5}$ but poorer correlations for $PM_{2.5}$ mass. Still other studies show only weak correlations (Rojas-Bracho et al., 2000; Linn et al., 1999; Bahadori et al., 2001). Even when strong longitudinal correlations are demonstrated for individuals in a study, the variety of living conditions may lead to variations in attenuating factors or the fraction of ambient PM contributing to personal exposure. Groups with similar living conditions, especially if measurements are conducted during one season, may have similar α and, therefore, very high correlations between personal exposure and ambient concentrations, even for pooled correlations. However, when studies contain subjects with homes of very different ventilation characteristics or cover more than one season, variations in α can be high across subjects, thus, showing poor pooled correlations even in the absence of indoor sources.

Elderly Subjects. Janssen et al. (2000) continued their longitudinal studies with measurements of personal, indoor, and outdoor concentrations of $PM_{2.5}$ for elderly subjects with doctor-diagnosed angina pectoris or coronary heart disease. Studies were conducted in Amsterdam, Holland, and Helsinki, Finland, in the winter and spring of 1998 and 1999. In the Amsterdam study with 338 to 417 observations, mean $PM_{2.5}$ concentrations were 24.3, 28.6, and 20.6 $\mu g/m^3$ for personal, indoor, and outdoor samples, respectively. If the measurements with ETS in the home were excluded, the mean indoor concentration dropped to 16 $\mu g/m^3$, which was lower than outdoor concentrations. In the Helsinki study, the mean $PM_{2.5}$ concentrations were 10.8 $\mu g/m^3$ for personal, 11.0 $\mu g/m^3$ for indoor air, and 12.6 $\mu g/m^3$ outdoor air samples. The authors note that for this group of subjects, personal exposure, indoor concentrations, and ambient concentrations of $PM_{2.5}$ were highly correlated within subjects over time. Median Pearson's correlation coefficients between personal exposure and outdoor concentrations were 0.79 in Amsterdam and 0.76 in Helsinki. The median Pearson's r for the indoor/outdoor relationship was 0.85 for the Amsterdam study when homes with ETS were excluded. The correlation for indoors versus outdoors was 0.70 for all homes.

Results from the correlation analysis can be used to estimate infiltration factors and penetration factors for these two groups of subjects. In Amsterdam, the attenuation factor was 0.43 and the infiltration factor was 0.47. Very similar results were seen in Helsinki for the attenuation factor (0.45) and the infiltration factor (0.51).

A series of PM personal monitoring studies involving elderly subjects was conducted in Baltimore County, MD, and Fresno, CA. The first study was a 17-day pilot (January-February 1997) to investigate daily personal and indoor $PM_{1.5}$ concentrations, and outdoor $PM_{2.5}$ and $PM_{2.5\text{-}10}$ concentrations experienced by nonsmoking elderly residents of a retirement community located near Baltimore (Liao et al., 1999; Williams et al., 2000c). The 26 residents were aged 65 to 89 (mean = 81), and 69% of them reported a medical condition such as hypertension or coronary heart disease. In addition, they were quite sedentary: on average, less than 5 h day^{-1} were spent on ambulatory activities. Because most of the residents ate meals in a communal dining area, the average daily cooking time in the individual apartments was only 0.5 h (range = 0 to 4.5 h). About 96% of the residents' time was spent indoors (Williams et al., 2000c). Personal monitoring, conducted for five subjects, yielded longitudinal correlation coefficients between ambient concentrations and personal exposure ranging from 0.00 to 0.90.

The Baltimore main study and the Fresno study were conducted using similar monitoring techniques and study design. Concentrations measured in these studies are summarized in Table 5-8. For $PM_{2.5}$, personal exposure and indoor air concentrations are similar for all three studies even though outdoor air concentrations for Fresno in the spring are only half of those measured for Fresno in the winter and for Baltimore. This result is presumably due to high penetration efficiencies in the spring in Fresno when the weather was warm and participants kept the windows and doors of their homes open. These data also show that even when correlations are high, the use of an ambient monitor as a surrogate for exposure in epidemiologic studies can bias the strength of the health effect found due to differing exposure levels.

TABLE 5-8. MEAN CONCENTRATION FOR PM MASS REPORTED FOR THE BALTIMORE (Williams et al., 2000a,b,c) AND THE FRESNO (Evans et al., 2000) STUDIES

	$PM_{2.5}$ Concentration (µg/m^3)			PM_{10} Concentration (µg/m^3)		
Study	**Personal**	**Indoors**	**Outdoors**	**Personal**	**Indoors**	**Outdoors**
Baltimore	13.0 ± 4.2	10.5 ± 4.9	22.0 ± 12.0	—	13.5 ± 6.3	30.0 ± 13.7
Fresno-Winter	13.3 ± 5.9	9.7 ± 5.0	20.5 ± 13.4	—	15.1 ± 4.1	28.2 ± 15.9
Fresno-Spring	11.1 ± 2.8	8.0 ± 1.8	10.1 ± 3.2	37.3	16.7 ± 3.1	28.7 ± 6.6

Calculated correlation coefficients are summarized in Tables 5-9 and 5-10. In Table 5-9, results for Baltimore show excellent daily average correlations for both $PM_{2.5}$ and PM_{10}. These results primarily represent the behavior of fine-particle regional sulfate for a group of participants who have few indoor or personal sources. However, even for this group, there was a wide range of individual correlation coefficients. The Fresno data, on the other hand, shows much poorer daily average correlations. Of special note are the poorer correlations for the ambient to outdoor residential monitors. This could be due to the higher concentrations of nitrate in the samples. In addition, the residential site may have been influenced by highway traffic.

TABLE 5-9. DAILY-AVERAGE CORRELATION COEFFICIENTS REPORTED FOR THE BALTIMORE (Williams et al., 2000a,b,c) AND THE FRESNO (Evans et al., 2000) STUDIES

	$PM_{2.5}$ r^2			PM_{10} r^2
Study	**Ambient/Outdoor**	**Personal/Ambient**	**Personal/Indoors**	**Ambient/Outdoor**
Baltimore	0.92	0.80 (0.14-0.80)[a]	0.98 (0.20-0.99)[a]	0.89
Fresno-Winter	0.48	—	—	0.48
Fresno-Spring	0.53	0.70	0.77	0.61

[a] Range for individual participants.

TABLE 5-10. REGRESSION ANALYSIS REPORTED FOR INDOOR/OUTDOOR RELATIONSHIPS FOR $PM_{2.5}$ IN THE BALTIMORE (Williams et al., 2000a,b,c) AND FRESNO (Evans et al., 2000) STUDIES

	Daily Average			Individual		
Study	r^2	**slope**	**Intercept ($\mu g/m^3$)**	r^2	**slope**	**Intercept ($\mu g/m^3$)**
Baltimore	0.92	0.39	1.5	0.73 ± 0.16	0.43 ± 0.15	0.9 ± 2.6
Fresno-Winter	0.86	nr	nr	0.55 ± 0.25	0.25 ± 0.17	4.4 ± 3.2
Fresno-Spring	0.56	nr	nr	0.39 ± 0.21	0.49 ± 0.38	3.0 ± 3.7

The correlation analysis in Table 5-10 shows correlation coefficients as well as the slope (infiltration factor) and the intercept (indoor concentration due to nonambient sources) for the Baltimore and Fresno studies. These data show strongest correlations for Baltimore where there are very low indoor concentrations from nonambient sources. Correlations are not as strong for Fresno, where there are higher concentrations from nonambient sources. The infiltration factors for Baltimore and Fresno-Spring are very similar at approximately 0.5. The infiltration factors for Fresno-Winter are considerably lower.

Subjects with COPD. Linn et al. (1999) describe a 4-day longitudinal assessment of personal $PM_{2.5}$ and PM_{10} exposures (on alternate days) in 30 COPD subjects aged 56 to 83. Concurrent indoor and outdoor monitoring was conducted at their residences. This study occurred in the summer and autumn of 1996 in the Los Angeles area. PM_{10} data from the nearest fixed-site monitoring station to each residence also was obtained. Pooled correlations for personal exposure to outdoor measurements gave R^2 values of 0.26 and 0.22 for $PM_{2.5}$ and PM_{10}, respectively. Correlations of day-to-day changes in $PM_{2.5}$ and PM_{10} measured outside the homes and correlated with concurrent PM_{10} measurements at the nearest ambient monitoring location gave R^2 values of 0.22 and 0.44, respectively. Correlations of day to day changes in PM mass measured indoors correlated with outdoor measurements at the homes gave R^2 values of 0.27 and 0.19 for PM_{10} and $PM_{2.5}$.

Personal, indoor, and outdoor $PM_{2.5}$, PM_{10}, and $PM_{2.5-10}$ correlations were reported by Rojas-Bracho et al. (2000) for a study conducted in Boston, MA, on 18 individuals with COPD. Both the mean and median personal exposure concentrations were higher than the indoor concentrations, which were higher than outdoor concentrations for all three PM measurement parameters. Geometric mean indoor/outdoor ratios were 1.4 ± 1.9 for PM_{10}, 1.3 ± 1.8 for $PM_{2.5}$, and 1.5 ± 2.7 for $PM_{2.5\text{-}10}$. Median longitudinal R^2s between personal exposure and ambient PM measurements were 0.12 for PM_{10}, 0.37 for $PM_{2.5}$ and 0.07 for $PM_{2.5\text{-}10}$. The relationship between the indoor and outdoor concentrations was strongest for $PM_{2.5}$, with a median R^2 of 0.55 and 11 homes having significant R^2 values. For PM_{10}, the median R^2 value was 0.25, with significant values for eight homes. Only five homes had significant indoor/outdoor associations for $PM_{2.5\text{-}10}$, with an insignificant median R^2 value of 0.04. The poor correlations for $PM_{10\text{-}2.5}$ are a result of poorer penetration efficiencies, higher decay rates, and spatial inhomogeneities.

Bahadori et al. (2001) report a pilot study of the PM exposure of 10 nonrandomly chosen COPD patients in Nashville, TN, during the summer of 1995. Each subject alternately carried a personal $PM_{2.5}$ or PM_{10} monitor for a 12-h daytime period (8 am to 8 pm) for 6 consecutive days. These same pollutants were monitored simultaneously indoors and outdoors at their homes. All of the homes were air-conditioned and had low air exchange rates (mean = 0.57 h^{-1}), which may have contributed to the finding that mean indoor $PM_{2.5}$ was 66% of the mean ambient $PM_{2.5}$. This can be contrasted with the PTEAM study in Riverside, CA, where no air conditioners were in use and the mean indoor $PM_{2.5}$ was 98% of the mean ambient $PM_{2.5}$ (Clayton et al., 1993). Data sets were pooled for correlation analysis. Resulting pooled correlations between personal and outdoor concentrations were $r = 0.09$ for $PM_{2.5}$ and $r = -0.08$ for PM_{10}.

5.3.3.1.4 Personal Exposure to Sulfate Compared to Personal Exposure to Ambient Particulate Matter

A study conducted in Vancouver involving sixteen COPD patients aged 54 to 86 reported low median longitudinal ($r = 0.48$) and pooled ($r = 0.15$) correlation coefficients between personal exposures and ambient concentrations of $PM_{2.5}$ (Ebelt et al., 2000). However, the mean correlation between personal exposures to sulfate and ambient concentrations of sulfate was much higher ($r = 0.96$). Because there are typically minimal indoor sources of sulfate, the relationship between ambient concentrations and personal exposures to sulfate would not be weakened by variability in an indoor-generated sulfate component as for example in the case of $PM_{2.5}$ for which there are many primary indoor sources as well as some secondary indoor sources. Correlations of ambient concentrations versus personal exposures for $PM_{2.5}$ and sulfate are compared in Figure 5-3.

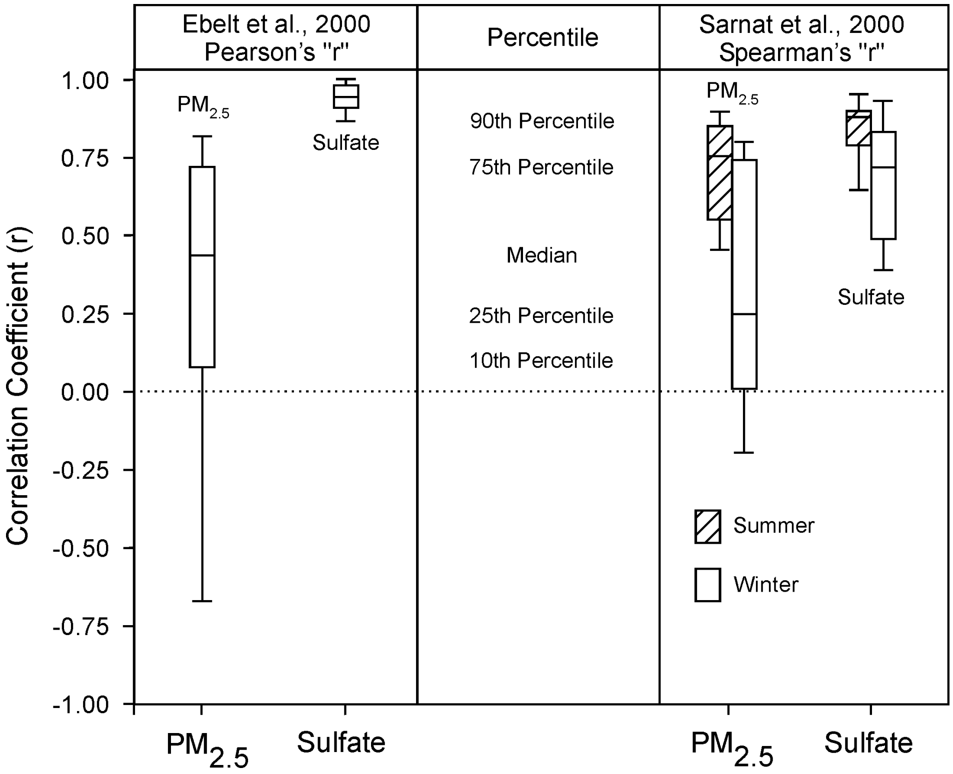


Figure 5-3. Comparison of correlation coefficients for longitudinal analyses of personal exposure versus ambient concentrations for individual subjects for $PM_{2.5}$ and sulfate.

Another study, conducted in Baltimore, MD, involved 15 nonsmoking adult subjects (> 64 years old) who were monitored for 12 days during Summer 1998 and Winter 1999 (Sarnat et al., 2000). All subjects (nonrandom selection) were retired, physically healthy, and lived in nonsmoking private residences. Each residence, except one, was equipped with central air-conditioning; however, not all residences used air-conditioning throughout the summer. The average age of the subjects was 75 years (± 6.8 years). Sarnat et al. (2000) reported higher longitudinal and pooled correlations for $PM_{2.5}$ during summer than winter. Similar to Ebelt et al. (2000), Sarnat et al. (2000) reported stronger associations between personal exposure to SO_4^{-2} and ambient concentrations of SO_4^{-2} than for total personal $PM_{2.5}$ exposure and ambient $PM_{2.5}$ concentrations. The ranges of correlations are shown in Figure 5-1 along with similar data from Ebelt et al. (2000).

The higher correlation coefficients and the narrower range of the correlation coefficient for sulfate suggest that removing indoor-generated and personal activity PM from total personal PM would result in a higher correlation with ambient concentrations. If, as discussed in 5.3.4.3.1, there are no indoor sources, a personal exposure measurement for sulfate gives the ambient exposure of sulfate; the ratio of personal sulfate to ambient sulfate gives the attenuation coefficient on an individual, daily basis; and the attenuation coefficient times the ambient $PM_{2.5}$ concentration gives the individual, daily values of ambient $PM_{2.5}$ exposures (Wilson et al., 2000). This technique applies only to the nonvolatile components of fine PM, as measured by $PM_{2.5}$. It requires that the sulfate concentration be large enough so that it can be measured with reasonable accuracy. It does not require that sulfate be correlated with $PM_{2.5}$ or the non-sulfate components of $PM_{2.5}$ because the sulfate data is used to estimate the attenuation coefficient not $PM_{2.5}$. The technique does require that there be minimal indoor sources of sulfate, as indicated by a near-zero intercept for the regression, and that the size distribution of $PM_{2.5}$ and sulfate be similar.

Sarnat et al. (2001) subsequently extended the Baltimore study to include 20 older adults, 21 children, and 15 individuals with COPD for a total of 56 subjects. In both studies (Sarnat et al., 2000, 2001), they used their personal and ambient sulfate data to estimate the ambient $PM_{2.5}$ exposure. They used this information in mixed-model analysis (mixed models account for differences among individual subjects), but did not report correlations between ambient $PM_{2.5}$ exposure and ambient $PM_{2.5}$ concentrations based on the pooled data set. However, Sarnat et al. (2001) did report slopes from the mixed model analyses. The t-statistic for the slope of ambient exposure versus ambient concentration as compared to total personal exposure versus ambient concentration increased from 9.96 to 11.12 (total exposure vs. ambient concentration) for the summer period and from 4.36 to 19.88 (ambient exposure vs. ambient concentration) for the winter period.

The study conducted by Sarnat et al. (2000) also illustrates the importance of ventilation on personal exposure to PM. During the summer, subjects recorded the ventilation status of every visited indoor location (e.g., windows open, air-conditioning use). As a surrogate for the air exchange rate, personal exposures were classified by the fraction of time the windows were open while a subject was in an indoor environment (F_v). Sarnat et al. (2000) report regression analyses of personal exposure on ambient concentration for $PM_{2.5}$ and for sulfate for each of the three ventilation conditions (Figure 5-4). The correlation between personal exposure and ambient concentration is higher for sulfate than for $PM_{2.5}$, presumably because $PM_{2.5}$ has indoor sources as well as ambient sources but sulfate has only ambient sources. As expected, the improvement is better for the lower ventilation conditions because under these conditions the ambient concentration is larger. For the lowest ventilation condition, R^2 improves from 0.25 to 0.72.

5.3.3.1.5 Personal Exposure to Ambient and Nonambient Particulate Matter

The utility of treating personal exposure to ambient PM, A, and personal exposure to nonambient PM, N, as separate and distinct components of total personal exposure to PM, T, was pointed out by Wilson and Suh (1997). The PTEAM study measured, in addition to indoor, outdoor, and personal PM_{10}, the air exchange rate for each home and collected information on the time spent in various indoor and outdoor microenvironments. This information is available for 147 12-h daytime periods. With this information and statistically estimated values of *P* and *k*, it is possible to estimate the daytime A and N as described in Section 5.2.4.3. Various examples of this information have been reported (Mage et al., 1999; Wilson et al., 2000). Graphs showing the relationships between ambient concentration and the various components of personal exposure (T, A, and N) are shown in Figure 5-5. The correlation coefficient for the pooled data set improves from r = 0.377 for T versus C (Figure 5-5a) to r = 0.856 for A versus C (Figure 5-5b) because of the removal of the N, which, as shown in Figure 5-5c, is highly variable and independent of C. The correlation between A and C is less than 1.0 because of the day-to-day variation in the α of each individual. The regression of T on C gives $\overline{\alpha} = 0.711$ and $\overline{N} = 81.6\ \mu g/m^3$. The regression of A on C gives $\overline{\alpha} = 0.625$. The regression of N on C gives $\overline{N} = 79.2\ \mu g/m^3$. The finite intercept in the regression with A must be attributed to bias or error in some of the measurements. No reported studies, other than PTEAM, have provided the quantity of data on individual, daily values of T, C, C_i, and *a* that are required to conduct an analysis comparable to that shown in Figure 5-5. It should be noted that the PTEAM study was conducted in southern California in the fall, when houses were open and air exchange rates were high and relatively uniform. These are best case conditions for showing high correlations between ambient site measurements and personal correlations. Such high correlations are not usually found and would not be expected with lower and more variable air exchange rates.

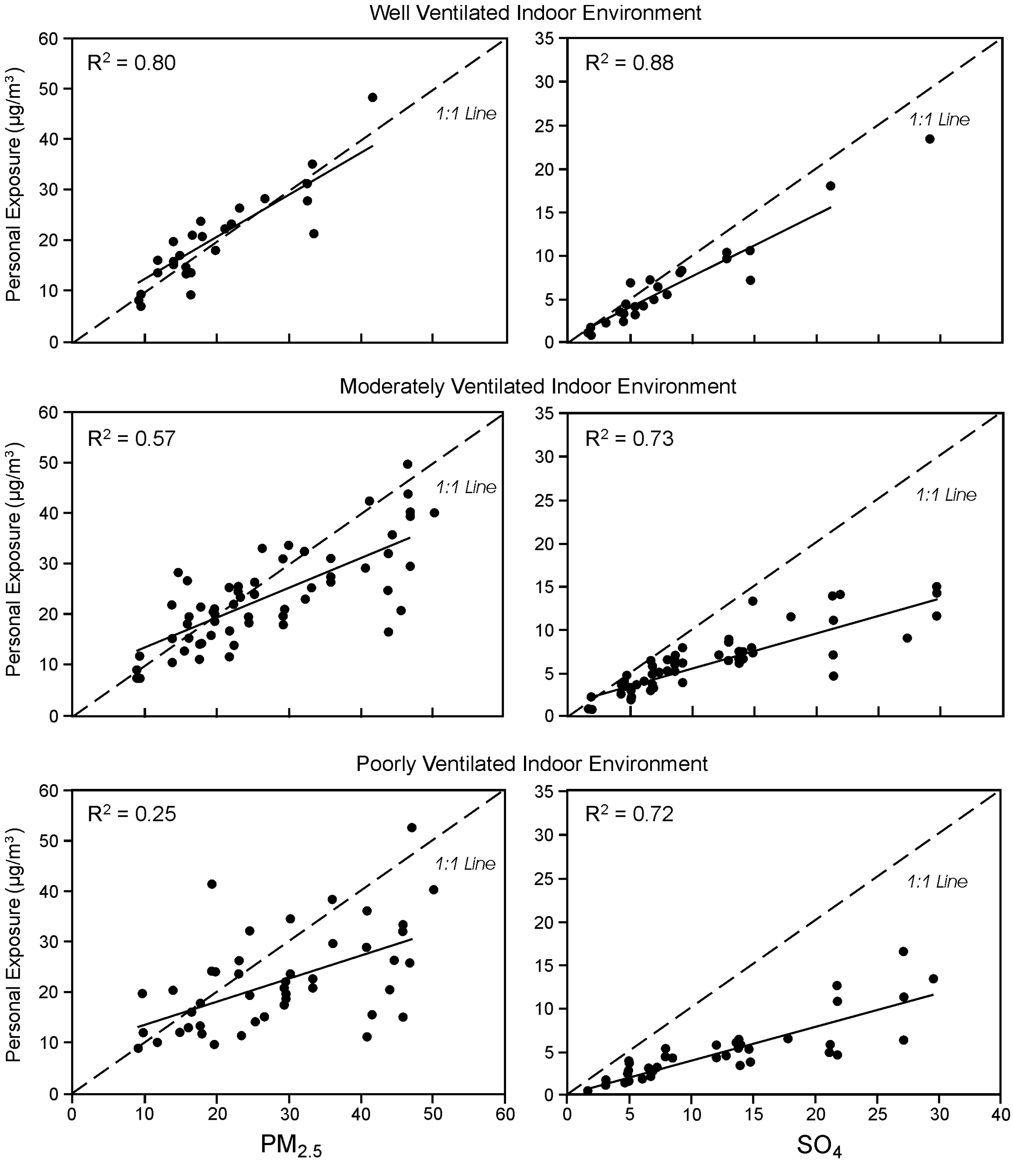


Figure 5-4. Personal exposure versus ambient concentrations for $PM_{2.5}$ and sulfate. (Slope estimated from mixed models).

Source: Sarnat et al. (2000).

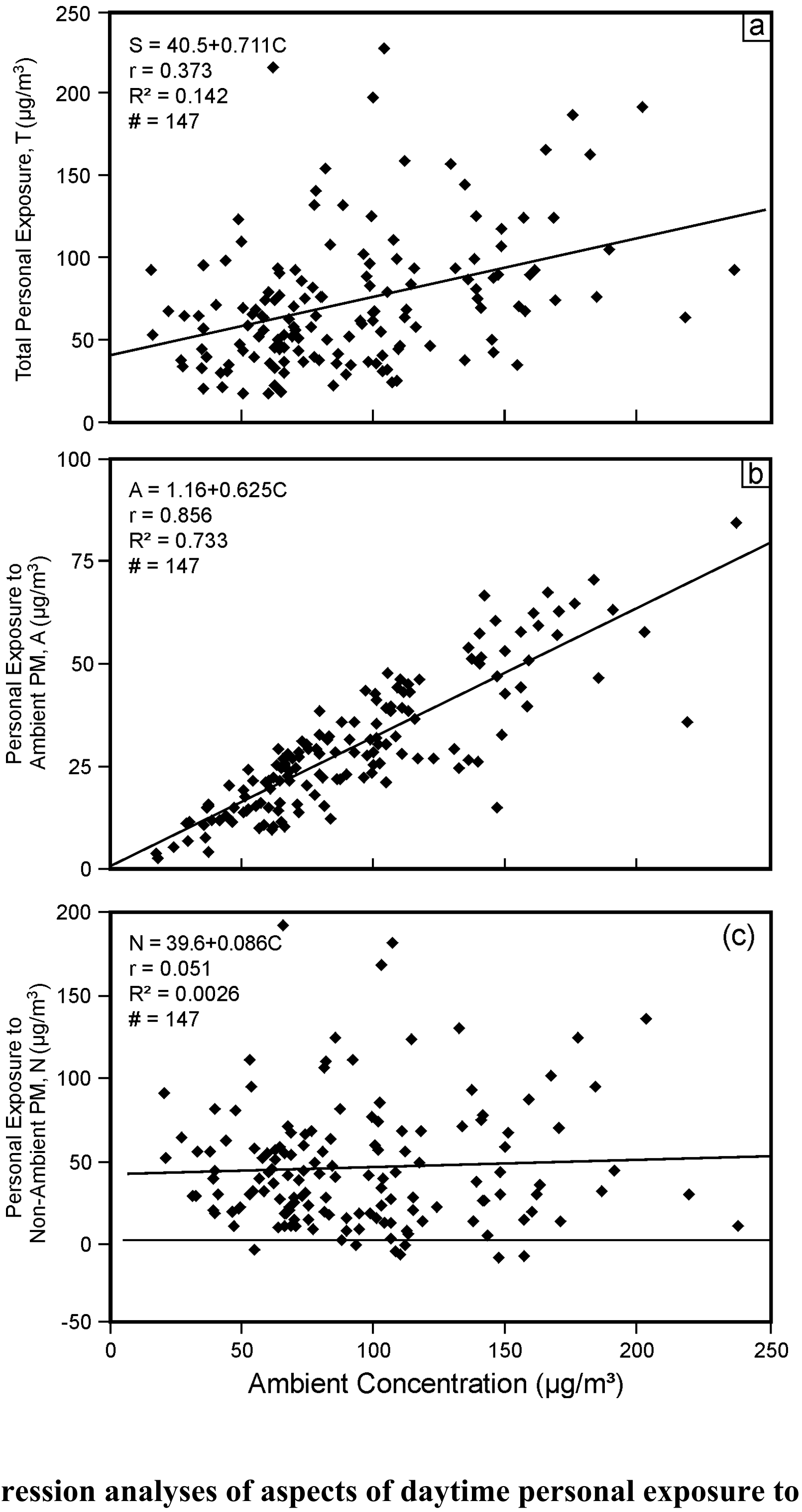


Figure 5-5. Regression analyses of aspects of daytime personal exposure to PM_{10} estimated using data from the PTEAM study. (a) Total personal exposure to PM, T, regressed on ambient concentration, C. (b) Personal exposure to ambient PM, A regressed on C. (c) Personal exposure to nonambient PM, N regressed on C.

Source: Data taken from Clayton et al. (1993). Adapted from Mage et al. (1999) and Wilson et al. (2000).

The RCS model introduced by Ott et al. (2000) presents a modeling framework to determine the average contribution of ambient PM_{10} and indoor-generated PM_{10} to average personal exposures in large urban metropolitan areas. The model has been tested using personal, indoor, and outdoor PM_{10} data from three urban areas (Riverside, CA; Toronto; and Phillipsburg, NJ). Results suggest that it is possible to separate the average ambient and nonambient PM contributions to personal exposures on a community-wide basis. However, as discussed in the paper, the authors make some assumptions that require individual consideration in each-city specific application of the model for exposure or health effects investigations. Primarily, housing factors, air-conditioning, seasonal differences, and complexities in time-activity profiles specific to the cohort being studied have to be taken into account prior to adopting the model to a given situation. Finally, this and other available exposure-based analyses presented here do not yet predict the relative contribution of indoor and outdoor PM to particle mass burden to the lung as a function of human activities and different microenvironmental sources and concentrations of PM and its co-pollutants.

5.3.3.2 Factors That Affect Relationships Between Personal Exposure and Ambient PM

A number of factors will affect the relationship between personal exposure and PM measured at ambient-site community monitors. Spatial variability in outdoor microenvironmental concentrations and variations in penetration into indoor microenvironments will influence the relationship to ambient PM. Air exchange rates and decay rates in indoor microenvironments will influence the relationship to both ambient and total PM whereas personal activities will influence the relationship to total PM but not ambient PM. Information on these effects is presented in detail in the following sections.

5.3.3.2.1 Spatial Variability and Correlations Over Time

Chapter 3, Section 3.2.3, presents information on the spatial variability of PM mass and chemical components at fixed-site ambient monitors; for purposes of this chapter, this spatial variability is called an "ambient gradient." The data presented in Section 3.2.3 indicate that ambient gradients of PM and its constituents exist in urban areas to a greater or lesser degree. This gradient and any that may exist between a fixed-site monitor and the outdoor microenvironments near where people live, work, and play obviously affects exposure. The purpose of this section is to review the available data on ambient monitor-to-outdoor microenvironmental concentration gradients or relationships that have been measured by researchers since 1996. These analyses below are, in general, consistent with the previous studies covered in the 1996 PM AQCD. A few outdoor-to-outdoor monitoring studies also are included to highlight relationships among important microenvironment categories. To assess spatial variability or gradients, the spatial correlations in the data are usually analyzed. However, it should be noted that high temporal correlation between two monitoring locations does not imply low spatial variability or low ambient gradients. High temporal correlation between two sites indicates that changes in concentrations at one site can be estimated from data at another site.

In a paper on the EXPOLIS-EAS study, Oglesby et al. (2000) conclude that in Basel, Switzerland little spatial variability exists between PM levels measured at fixed site monitors and the participants' outdoor microenvironments. The authors report a high correlation between home outdoor $PM_{2.5}$ levels (48-h measurements beginning and ending at 8:00 a.m.) and the corresponding 24-h average PM_4 (time-weighted values calculated from midnight to midnight) measured at a fixed monitoring station ($n = 38$, $r_{sp} = 0.96$, $p < 0.001$). They considered each home outdoor monitor as a temporary fixed monitor and concluded that "the $PM_{2.5}$ level measured at home outdoors . . . represents the fine particle level prevailing in the city of Basel during the 48-h measuring period."

In a study conducted in Helsinki, Finland, Buzorius et al. (1999) concluded that a single monitor may be used to adequately describe the temporal variations in concentration across the metropolitan area. Particle size distributions were measured using a differential mobility particle sizer (DMPS; Wintlmayer) coupled with a condensation particle counter (CPC TSI 3010, 3022) at four locations including the official air monitoring station, which represented a "background" site. The monitoring period varied between 2 weeks and 6 months for the sites, and data were reported for 10-min and 1-, 8-, and 24-h averages. As expected, temporal variation decreased as the averaging time increased. The authors report that particle number concentration varied in magnitude with local traffic intensity. Linear correlation coefficients computed for all possible site-pairs and averaging times showed that the correlation coefficient improved with increasing averaging time. Using wind speed and direction vectors, lagged correlations were calculated and were generally higher than the "raw" data correlations. Weekday correlations were higher than weekend correlations as “traffic provides relatively uniform spatial distribution of particulate matter” (p. 565). The authors conclude that, even for time periods of 10 min and 1 h, sampling at one station can describe temporal variations across relatively large areas of the city with a correlation coefficient > 0.7.

Dubowsky et al. (1999) point out that, although the variation of $PM_{2.5}$ mass concentration across a community may be small, there may be significant spatial variations of specific components of the total mass on a local scale. An example is given of a study of concentrations of polycyclic aromatic hydrocarbons (PAH) at three indoor locations in a community: (1) an urban site, (2) a semi-urban site 1.6 km away, and (3) a suburban site located further away. The authors found the geometric mean PAH concentrations at these three locations varied respectively as 31:19:8 ng/m^3 and suggest that the local variations in traffic density were responsible for this gradient. Note that these concentrations are 1,000 times lower than the total PM mass concentration so that such a small gradient would not be detectable for total $PM_{2.5}$ mass measurements on the order of 25 $\mu g\ m^{-3}$.

The Total Human Environmental Exposure Study (THEES) reported by Waldman et al. (1991) measured indoor, outdoor, and personal benzo(a)pyrene (BaP) levels and found that the outdoor BaP was the same at all outdoor sites across the three sampling periods. This study showed the seasonal differences versus BaP levels and exposures due to indoor and outdoor sources and individual activities.

Leaderer et al. (1999) monitored 24-h PM_{10}, $PM_{2.5}$, and sulfates during the summers of 1995 and 1996 at a regional site in Vinton, VA (6 km from Roanoke, VA). One similar 24-h measurement was made outdoors at residences in the surrounding area at distances ranging from 1 km to > 175 km from the Vinton site, at an average separation distance of 96 km. The authors reported significant correlations for $PM_{2.5}$ and sulfates between the residential outdoor values and those measured at Vinton on the same day. In addition, the mean values of the regional site and residential site $PM_{2.5}$ and sulfates showed no significant differences in spite of the large distance separations and mountainous terrain intervening in most directions. However, for the concentrations of $PM_{2.5\text{-}10}$ estimated as PM_{10}-$PM_{2.5}$, no significant correlation among these sites was found ($n = 30$; $r = -0.20$).

Lillquist et al. (1998) found no significant gradient in PM_{10} concentrations in Salt Lake City, UT, when levels were low, but a gradient existed when levels were high. PM_{10}

concentrations were measured outdoor at three hospitals using a Minivol 4.01 sampler (Airmetrics, Inc.) operating at 5 L min^{-1} and at the Utah Department of Air Quality (DAQ) ambient monitoring station located between 3 and 13 km from the hospitals for a period of about 5 mo.

Pope et al. (1999) monitored ambient PM_{10} concentrations in Provo, UT (Utah Valley), during the same time frame the following year and reported nearly identical concentrations at three sites separated by 4 to 12 km. Pearson correlation coefficients for the data were between 0.92 and 0.96. The greater degree of variability in the Salt Lake City PM_{10} data relative to the Provo data may be related to the higher incidence of wind-blown crustal material in Salt Lake City. Pope et al. (1999) reported that increased adverse health effects in the Utah Valley were associated with stagnation and thermal inversions trapping anthropogenically derived PM_{10}; whereas, no increases in adverse health effects were observed when PM_{10} levels were increased during events of wind blown crustal material.

Väkevä et al. (1999) found significant vertical gradients in submicron particles existed in an urban street canyon of Lahti, Finland. Particle number concentrations were measured using a TSI screen diffusion battery and a condensation particle counter at 1.5 and 25 m above the street at rooftop level. The authors found a fivefold decrease in concentration between the two sampling heights and attributed the vertical gradient to dilution and dispersion of pollutants emitted at street level.

White (1998**)** suggests that the higher random measurement error for the coarse PM fraction compared to the error for the fine PM fraction may be responsible for a major portion of the apparent greater spatial variability of coarse ambient PM concentration compared to fine ambient PM concentration in a community (e.g., Burton et al., 1996; Leaderer et al., 1999). When $PM_{2.5}$ and PM_{10} are collected independently, and the coarse fraction is obtained by difference ($PM_{2.5\text{-}10} = PM_{10}\text{-}PM_{2.5}$), the expected variance in the coarse fraction is influenced by the variances of the PM_{10} and $PM_{2.5}$ measurements. When a dichotomous sampler collects $PM_{2.5}$ and $PM_{2.5\text{-}10}$ on two separate filters, the coarse fraction also is expected to have a larger error than the fine fraction. There is a possible error caused by loss of mass below the cut-point size and a gain of mass above the cut-point size that is created by the asymmetry of the product of the penetration times PM concentration about the cut-point size. Because a dichotomous PM sampler collects coarse mass using an upper and lower cut-point, it is expected to have a larger variance than for fine mass collected using only one cut-point.

Wilson and Suh (1997) conclude that $PM_{2.5}$ and PM_{10} concentrations are correlated more highly across Philadelphia than are $PM_{2.5\text{-}10}$ concentrations. Ambient monitoring data from 1992 to 1993 was reviewed for $PM_{2.5}$, $PM_{2.5\text{-}10}$, and PM_{10}, as well as for $PM_{2.5}$ and $PM_{2.5\text{-}10}$ dichotomous data for 212 site-years of information contained in the AIRS database (U.S. Environmental Protection Agency, 2000). The authors also observed that PM_{10} frequently was correlated more highly with $PM_{2.5}$ than with $PM_{2.5\text{-}10}$. The authors note that $PM_{2.5}$ constitutes a large fraction of PM_{10} and that this is the likely reason for the strong agreement between $PM_{2.5}$ and PM_{10}. Similar observations were made by Keywood et al. (1999) in six Australian cities. The authors reported that PM_{10} was more highly correlated with $PM_{2.5}$ than with coarse PM ($PM_{2.5\text{-}10}$) suggesting that "variability in PM_{10} is dominated by variability in $PM_{2.5}$."

Lippmann et al. (2000) examined the site-to-site temporal correlations in Philadelphia (1981 to 1994) and found the ranking of median site-to-site correlation was O_3 (0.83), PM_{10} (0.78), TSP (0.71), NO_2 (0.70), CO (0.50), and SO_2 (0.49). The authors explain that O_3 and a fraction of TSP and PM_{10} (e.g., sulfate) are secondary pollutants that would tend to be distributed more uniformly spatially within the city than primary pollutants such as CO and SO_2 which are more likely to be influenced by local emission sources. Lippman et al. (2000) conclude "Thus, spatial uniformity of pollutants may be due to area-wide sources, or to transport (e.g., advection) of fairly stable pollutants into the urban area from upwind sources. Relative spatial uniformity of pollutants would therefore vary from city to city or region to region."

Goswami et al. (2002) used data collected at outdoor monitors of homes in a large exposure study in Seattle, WA to analyze the spatial variability of outdoor $PM_{2.5}$ concentrations. The day-to-day variability between sites was 10 times higher than the spatial variability between sites. However, differences between sites was sufficient to potentially contribute to measurement error. An examination of the spatial characteristics of the monitoring sites showed that the most representative monitoring sites were located at elevations of 80-120 m above sea level and at distances of 100-300 m from the nearest arterial road.

5.3.3.2.2 Physical Factors Affecting Indoor Microenvironmental Particulate Matter Concentrations

Several physical factors affect ambient particle concentrations in the indoor microenvironment including air exchange, penetration, and particle deposition. Combined, these factors are critical variables that describe ambient particle dynamics in the indoor microenvironments and, to a large degree, significantly affect an individual's personal exposure to ambient particles while indoors. The relationship between the concentrations of ambient particles outdoors, C, and ambient particles that have infiltrated indoors, C_{ai}, is given by

$$C_{ai} / C = Pa / (a + k), \qquad (5\text{-}14)$$

where P is the penetration factor; a is the air exchange rate; and k is the particle deposition rate. (As discussed in Section 5.3.2.3.1, use of this model assumes equilibrium conditions and assumes that all variables remain constant.) Particle penetration is a dimensionless quantity that describes the fraction of ambient particles that effectively penetrates the building shell. "Air exchange" is a term used to describe the rate at which the indoor air in a building or residence is replaced by outdoor air. The dominant processes governing particle penetration are air exchange and deposition of particles as they traverse through cracks and crevices and other routes of entry into the building. Although air exchange rates have been measured in numerous studies, very few field data existed prior to 1996 to determine size-dependent penetration factors and particle deposition rates. All three parameters (P, a, and k) may vary substantially depending on building type, region of the country, and season. In the past several years, researchers have made significant advancements in understanding the relationship between particle size and penetration factors and particle deposition rates. This section will highlight the studies that have been conducted to better understand physical factors affecting indoor particle dynamics.

Air Exchange Rates

The air exchange rate, a, in a residence varies depending on a variety of factors, including geographical location, age of the building, the extent to which window and doors are open, and season. Murray and Burmaster (1995) used measured values of a from households throughout the United States to describe empirical distributions and to estimate univariate parametric probability distributions of air exchange rates. Figure 5-6 shows the results classified by season and region. In general, *a* is highest in the warmest region and increases from the coldest to the warmest region during all seasons. Air exchange rates also are quite variable within and between seasons, as well as between regions (Figure 5-6). Data from the warmest region in summer should be viewed cautiously as many of the measurements were made in Southern California in July when windows were more likely to be open than in other areas of the country where air-conditioning is used. Use of air-conditioning generally results in lowering air exchange rates. In a separate analysis of these data, Koontz and Rector (1995) suggested that a conservative estimate for air exchange in residential settings would be 0.18 h^{-1} (10th percentile) and a typical air exchange would be 0.45 h^{-1} (50th percentile).

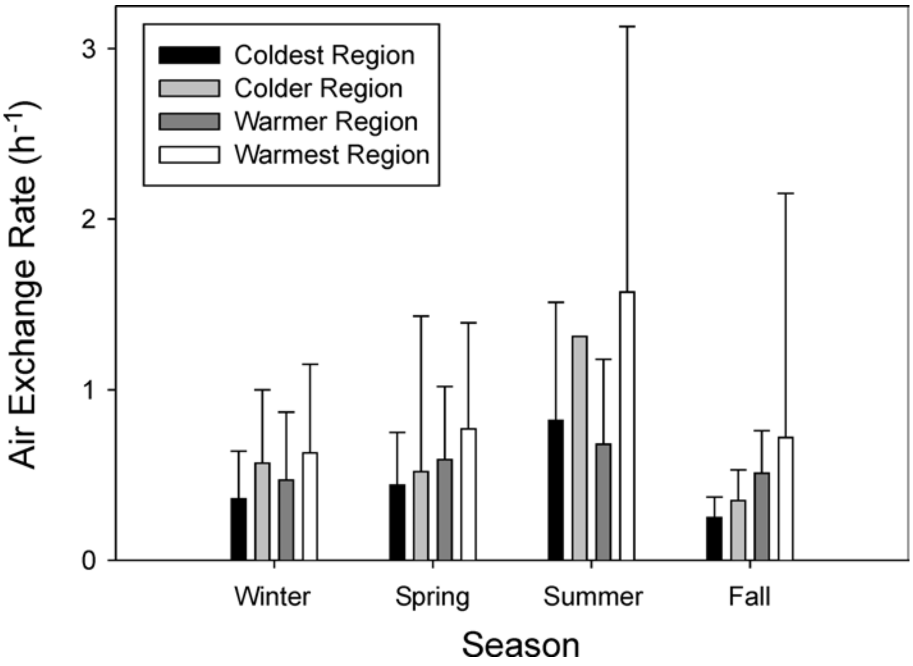


Figure 5-6. Air exchange rates measured in homes throughout the United States. Climatic regions are based on heating-degree days: Coldest region ≥ 7000, Colder region = 5500 to 6999, Warmer region = 2500 to 4999, and Warmest region ≤ 2500 heating-degree days.

Source: Adapted from Murray and Burmaster (1995).

These data provide reasonable experimental evidence that *a* varies by season in locations with distinct seasons. As a result, infiltration of ambient particles may be more efficient during warmer seasons when windows are likely to be opened more frequently and air exchange rates are higher. This suggests that the fraction of ambient particles present in the indoor microenvironment would be greater during warmer seasons than colder seasons. For example, in a study conducted in Boston, MA, participants living in non-air-conditioned homes kept the windows closed except during the summer (Long et al., 2000). This resulted in higher and more variable air exchange rates in summer than during any other season (Figure 5-7). During nighttime periods when indoor sources are negligible, the indoor/outdoor concentration ratio or infiltration factor may be used to determine the relative contribution of ambient particles in the indoor microenvironment. Particle data collected during this study were used to determine the indoor/outdoor concentration ratios by particle size (Figure 5-8). For these nine homes in Boston the fraction of ambient particles penetrating indoors was higher during summer when air exchange rates were higher than during fall when air exchange rates were lower (Long et al., 2001a).

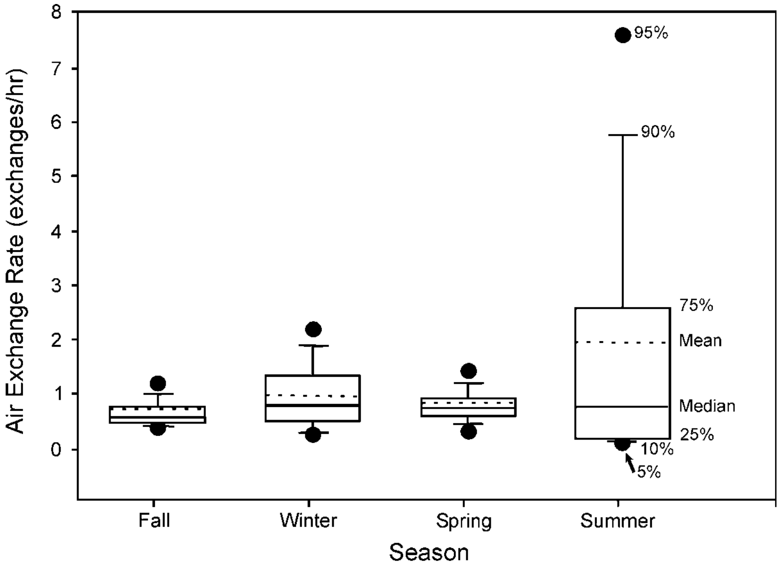


Figure 5-7. Box plots of hourly air exchange rates stratified by season in Boston, MA, during 1998.

Source: Long et al. (2000).

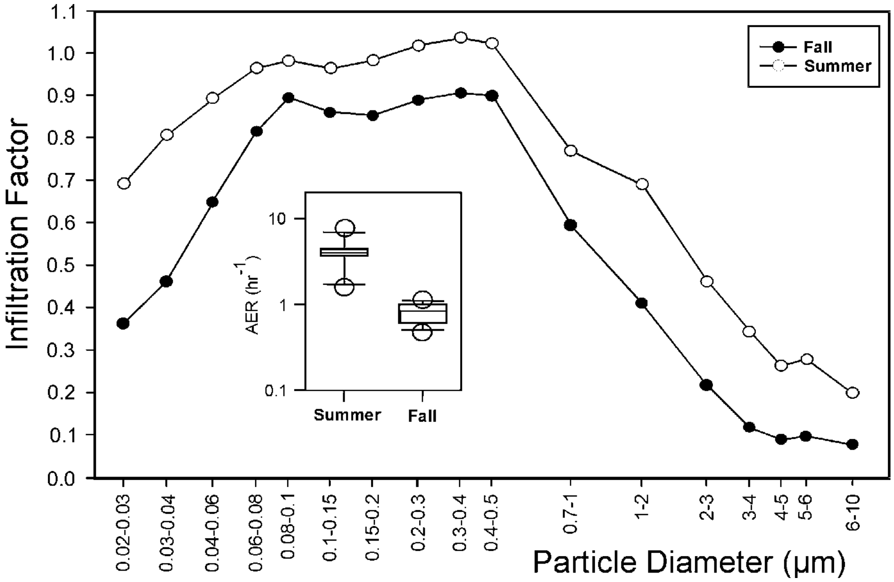


Figure 5-8. Geometric mean infiltration factor (indoor/outdoor ratio) for hourly nighttime, nonsource data for two seasons. Box plots of air exchange rates are shown as inserts for each plot. (Boston, 1998)

Source: Long et al. (2001a).

Wallace et al. (2002) conducted a year-long investigation of air rates in an occupied house to establish the effects of temperature, wind velocity, use of exhaust fans, and window-opening behavior. Air exchange rates were calculated by periodically injecting a tracer gas (SF_6) into the return air duct and measuring the concentration in 10 indoor locations sequentially every minute by a gas chromatograph equipped with an electron capture detector. Temperature and relative humidity were measured outdoors and in multiple indoor locations. Wind speed and direction in the horizontal plane were also measured. Use of the thermostat-controlled attic fan was recorded automatically. Indoor temperatures increased from 21 °C in winter to 27 °C in summer. Windows were open only a few percent of the time in winter but more than half the time in summer. About 4600 hour-long average air exchange rates were calculated from the measured tracer gas decay rates. The mean (SD) rate was 0.65 (0.56) h^{-1}. Tracer gas decay rates in different rooms were very similar, ranging only from 0.62 to 0.67 h^{-1}, suggesting that conditions were well mixed throughout the year. The strongest influence on air change rates was opening windows, which could increase the rate to as much as 2 h^{-1} for extended periods, and up to 3 h^{-1}

for short periods of a few hours. The use of the attic fan also increased air change rates by amounts up to 1 h^{-1}. Use of the furnace fan had no effect on air change rates (ducts were all inside the house). A clear effect of indoor-outdoor temperature difference (ΔT) could be discerned. However, wind speed and direction were found to have very little influence on air change rates at the house where the measurements were made.

The air exchange rate, *a*, is a critical parameter in determining the fraction of ambient PM found indoors and the extent of build-up of indoor PM due to indoor sources. Wallace et al. (2002) provide a brief review of the existing literature on the theory and measurement of air exchange rates. Open windows and frequent opening of doors lead to higher values of *a*. However, many homes are kept closed for heating in winter and air-conditioning in summer. Windows may or may not be opened during moderate weather conditions. In some areas, however, heating or air-conditioning may not be required and ventilation by open windows may be more frequent. Thus, *a* may vary geographically with climate. However, wind speed and direction were found to have very little influence on air exchange rates at the house where measurements were made. The variation of *a* with ΔT, as shown in Figure 5-9, is given by a (h^{-1}) = 0.176 + 0.0162 ΔT (°C). Thus, an increase of 10 °C in ΔT would lead to an increase in *a* of 0.164 h^{-1}, almost a doubling of the value of *a* for no indoor/outdoor temperature difference and no open windows or forced ventilation.

The observation of a minimal effect of wind speed on *a* is an important finding. If *a* were strongly dependent on wind speed, especially at low wind speeds, there might be a correlation between the indoor-generated PM found indoors and the ambient concentration outdoors. Such a correlation could lead to a confounding of the relationship of ambient PM with health outcomes by indoor-generated PM. Wallace et al. (2002) suggest that "the generally tighter construction of homes and the use of vapor barriers may have reduced the effect of wind speed and direction on residential air change rates compared to earlier studies."

Wind speed might be expected to have a larger effect on *a* in a home with open windows. Under conditions of large *a*, the ambient infiltrated indoors PM concentration will be a large fraction of the outdoor PM and the two concentrations will be highly correlated. However, the indoor-generated PM concentration will be kept low by the high *a* so a significant correlation between ambient PM concentrations and indoor-generated PM concentrations would not be likely. The observed lack of a strong wind effect on *a* in closed houses (Wallace et al., 2002;

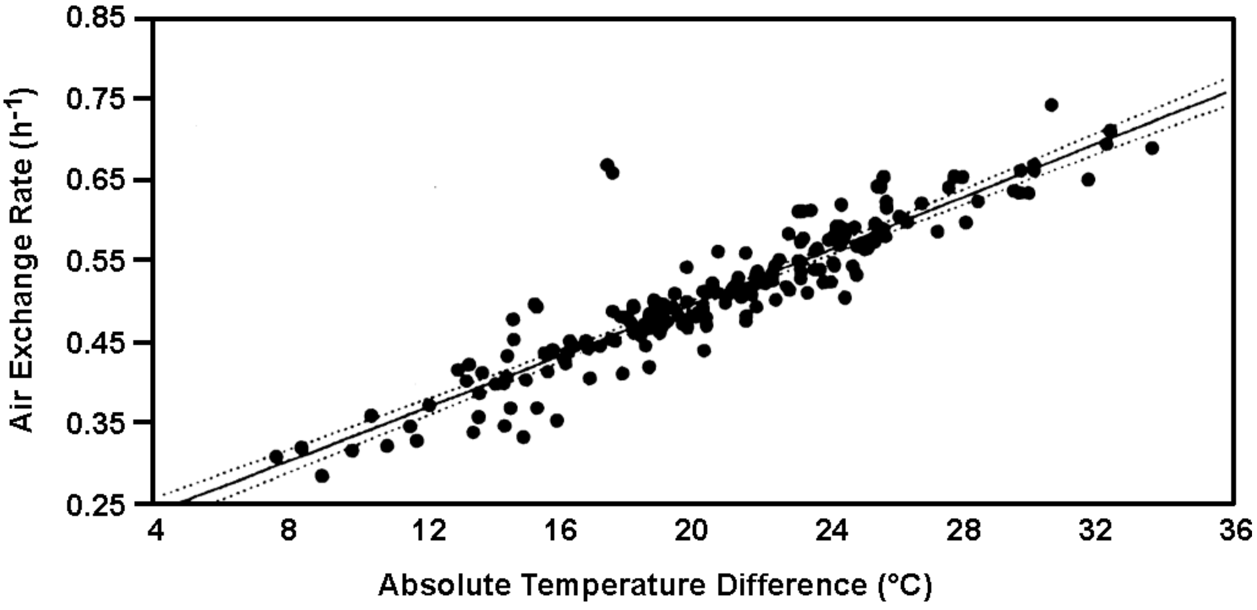


Figure 5-9. Regression of air exchange rate on absolute indoor-outdoor temperature difference. Overnight values (midnight-8 a.m.) in winter (January-March 2000). a (h^{-1}) = 0.176 (0.011 SE) + 0.0164 (0.0005) $\triangle T$ C°) (N = 183, R^2 = 0.82).

Howard-Reed et al., 2002) and the observed lack of correlation between ambient PM concentrations and indoor-generated PM concentrations indicate that the possibility of correlation of ambient and indoor-generated PM concentrations can be discounted.

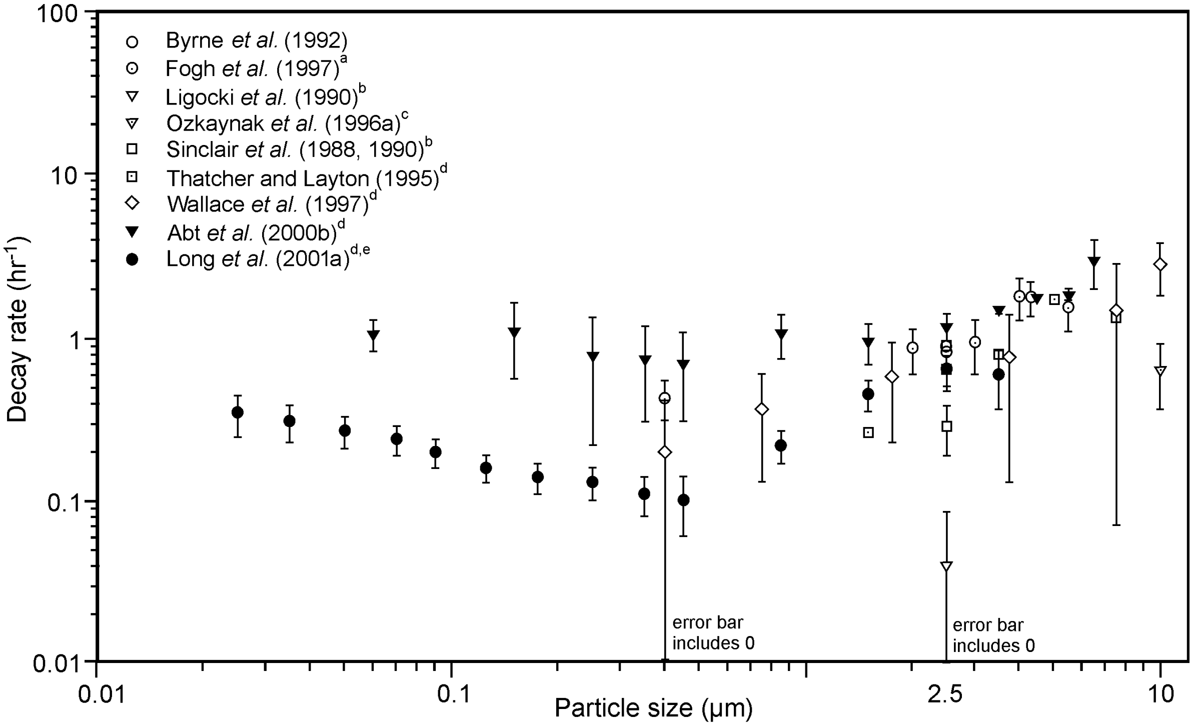
Particle Deposition Rates and Penetration Factors

Physical factors affecting indoor particle concentrations including particle deposition rates, *k*, and penetration factors, *P*, are possibly the most uncertain and variable quantities. Although *k* can be modeled with some success, direct measurements are difficult, and results often vary from study to study. Particle deposition rates vary considerably depending on particle size because of the viscous drag of air on the particles hindering their movement to varying degrees. The nature and composition of particles also affect deposition rates. Surface properties of particles, such as their electrostatic properties, can have a significant influence on deposition rates. In addition, thermophoresis can also affect *k*, but probably to a lesser degree in the indoor microenvironment because temperatures generally vary over a small range. Combined, these effects can produce order of magnitude variations in *k* between particles of different size and, in the case of electrophoresis and thermophoresis, particles of the same size.

Particle penetration efficiency into indoor microenvironments depends on particle size and air exchange rates. Penetration varies with particle size because of the size-dependent deposition of particles caused by impaction, interception, and diffusion of particles onto surfaces as they traverse through cracks and crevices. Penetration also is affected by air exchange rates. When air exchange rates are high, *P* approaches unity because the majority of ambient particles have less interaction with the building shell. In contrast, when air exchange rates are low, P is governed by particle deposition as particles travel through cracks and crevices.

Significant advancements have been made in the past few years to better characterize particle deposition rates and penetration factors. Several new studies, including two in which semi-continuous measurements of size distributions were measured indoors and outdoors, have produced new information on these quantities, which are key to understanding the contributions of ambient PM to indoor PM concentrations (Equation 5-7).

Studies involving semi-continuous measurements of indoor and outdoor particle size distributions have been used to estimate *k* and *P* as a function of particle size (Vette et al., 2001; Long et al., 2001a; Abt et al., 2000b). These studies each demonstrated that the indoor/outdoor concentration ratios (C_{ai}/C in Equation 5-9) were highest for accumulation mode particles and lowest for ultrafine and coarse-mode particles. Various approaches were used to estimate size-specific values for *k* and *P*. Vette et al. (2001) and Abt et al. (2000b) estimated *k* by measuring the decay of particles at times when indoor levels were significantly elevated. Vette et al. (2001) estimated *P* using measured values of *k* and indoor/outdoor particle measurements during nonsource nighttime periods. Long et al. (2001a) used a physical-statistical model, based on Equation 5-12, to estimate *k* and *P* during nonsource nighttime periods. The results for *k* reported by Long et al. (2001a) and Abt et al. (2000b) are compared with other studies in Figure 5-10. Although not shown in Figure 5-10, the results for *k* obtained by Vette et al. (2001) were similar to the values of *k* reported by Abt et al. (2000b) for particle sizes up to 1 μm. Results for *P* by Long et al. (2001a) show that penetration was highest for accumulation-mode particles and decreased substantially for coarse-mode particles (Figure 5-11). The results for *P* reported by Vette et al. (2001) show similar trends, but are lower than those reported by Long et al. (2001a). This likely is because of lower air exchange rates in the one Fresno, CA, test



[a] Decay Rates represent Summary Estimates from the four houses examined.

[b] Decay rates are based on sulfate and are presented as < 2.5 µm. Estimates were computed using a surface-to-volume ratio of 2 m^{-1} (Koutrakis *et al.*, 1992).

[c] Data represents $PM_{2.5}$.

[d] Particle sizes are the midpoint of the ranges examined.

[e] Decay rates presented are estimates of k for nightly average data from all nine study homes.

[f] Decay rates are theoretically modeled deposition values for smooth indoor surfaces and homogeneous and isotropically turbulent air flow. Presented curves assume typical room dimensions (3 m x 4 m x 5 m) and a friction velocity of 1.0 cm/s.

Figure 5-10. Comparison of deposition rates from Long et al., 2001a with literature values (from Abt et al., 2000b). Error bars represent standard deviations for same-study estimates.

Source: Adapted from Abt et al. (2000b); Long et al. (2001a).

home (a ≈ 0.5 h^{-1}; Vette et al., 2001) than in the nine test homes in Boston, MA, study ($a > 1$ h^{-1}; Long et al., 2001a). These data for *P* and *k* illustrate the role that the building shell may provide in increasing the concentration of particles because of indoor sources and reducing the concentration of indoor particles from ambient sources especially for homes with low air exchange rates.

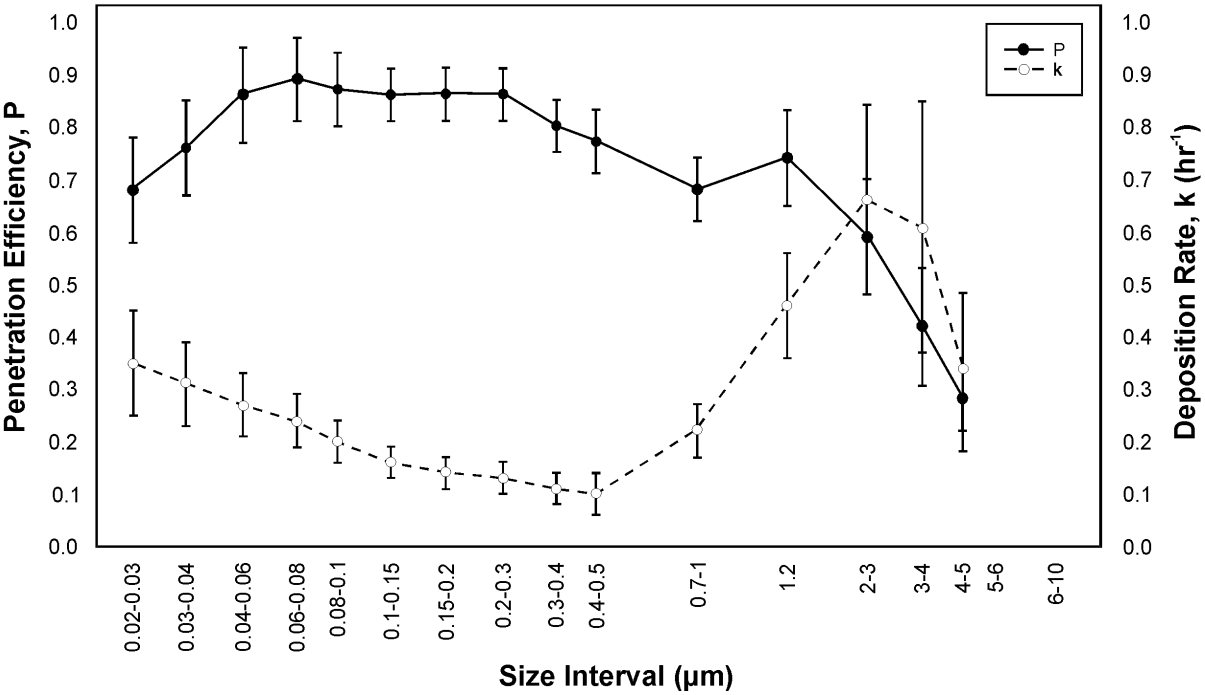


Figure 5-11. Penetration efficiencies and deposition rates from models of nightly average data. Error bars represent standard errors. (Boston, 1998, winter and summer).

Source: Long et al. (2001a).

Several other studies have investigated particle loss as a function of particle size. The penetration of particles across building envelopes has been modeled for several sizes of idealized rectangular cracks (Liu and Nazaroff, 2001). Particles of 0.1 to 1.0 µm diameter had penetration efficiencies near 1.0. Supermicron and ultrafine particles were removed to a greater degree by gravitational settling and Brownian diffusion. Thatcher et al. (2002) conducted an experimental study of the effects of room furnishings and air speed on particle deposition rates indoors. The deposition loss rate (*k*) increased by as much as a factor of 2.6 in going from a bare room (35 m^2 surface area) to a fully furnished room (12 m^2 additional surface area) with the greatest increase seen for the smallest particles. Air speed increases from < 5 to 19 cm/s increased the deposition rates by factors of 1.3 to 2.4 with greater effects on large particles than small particles. The authors state that, “The significant effect of particle size and room conditions on deposition loss rates argues against using a single first-order loss-rate coefficient to represent deposition for integrated mass measurements ($PM_{2.5}$ or PM_{10}).” Riley et al. (2002) have modeled the infiltration of particles into two building types: offices and residences. They developed representative values of *P*, *k*, and ventilation-system filter efficiencies for particle sizes from 0.001 to 10 µm. They then used a typical rural and urban outdoor size distribution and calculated predicted indoor concentrations for number, surface area, and volume distributions.

Compositional Differences Between Indoor-Generated and Ambient Particulate Matter

Wilson et al. (2000) discuss the differences in composition between particles from indoor and outdoor sources. They note that, because of the difficulty in separating indoor PM into ambient and nonambient PM, there is little direct experimental information on the composition differences between the two. Although experimental data are limited, Wilson et al. (2000) suggest the following.

> Photochemistry is significantly reduced indoors; therefore, most secondary sulfate [H_2SO_4, NH_4HSO_4, and $(NH_4)_2SO_4$] and nitrate (NH_4NO_3) found indoors come from ambient sources. Primary organic emissions from incomplete combustion may be similar, regardless of the source. However, atmospheric reactions of polyaromatic hydrocarbons and other organic compounds produce highly oxygenated and nitrated products, so these species are also of ambient origin. Gasoline, diesel fuel, and vehicle lubricating oil all contain naturally present metals or metal additives. Coal and heavy fuel oil also contain more metals and nonmetals, such as selenium and arsenic, than do materials such as wood or kerosene burned inside homes. Environmental tobacco smoke (ETS), however, with its many toxic components, is primarily an indoor-generated pollutant.

Particles generated indoors may have different chemical and physical properties than those generated by anthropogenic ambient sources. Siegmann et al. (1999) have demonstrated that elemental carbon in soot particles generated indoors has different properties than in those generated outdoors by automotive or diesel engines. In the United States, combustion-product PM in the ambient/outdoor air generally is produced by burning fossil fuels (e.g., coal, gasoline, fuel oil) and wood; whereas combustion-product PM from indoor sources is produced by biomass burning (e.g., tobacco, wood, foods, etc.). However, some indoor sources of PM (such as cigarette smoking, meat cooking, and coal burning) occur both indoors and outdoors and may constitute an identifiable portion of measured ambient PM (Cha et al., 1996; Kleeman and Cass, 1998).

Indoor Air Chemistry

Gas- and aerosol-phase chemical reactions in the indoor microenvironment are responsible for secondary particle formation and modification of existing particles. This process could be complex and may influence the interpretation of exposures to indoor generated particles in instances when particles are generated by outdoor gases reacting with gases generated or released indoors to produce fresh particles. For example, homogeneous gas phase reactions involving ozone and terpenes (specifically d-limonene, α-terpinene, and α-pinene) have been identified as an important source of submicron particles (Weschler and Shields, 1999). Terpenes are present in several commonly available household cleaning products, and d-limonene has been identified in more than 50% of the buildings monitored in the Building Assessment and Survey Evaluation (BASE) study (Hadwen et al., 1997). Long et al. (2000) found that when PineSol (primary ingredient is α-pinene) was used indoors, indoor $PM_{2.5}$ mass concentrations increased from 11 to 32 $\mu g\ m^{-3}$ (indoor ozone concentrations unknown, but ambient ozone concentrations were 44 to 48 ppb). Similarly, a 10-fold increase in number counts of 0.1 to 0.2 μm particles was observed in an experimental office containing supplemented d-limonene and normally encountered indoor ozone concentrations (< 5 to 45 ppb), resulting in an average increase in particle mass concentration of 2.5 to 5.5 $\mu g\ m^{-3}$ (Weschler and Shields, 1999). Ozone appears to be the limiting reagent as particle number concentration varied proportionally to ozone concentrations (Weschler and Shields, 1999). Other studies showed similar results (e.g., Jang and Kamens, 1999; Wainman et al., 2000). Such particles, if toxic, would represent an increased health risk due to ambient air pollution. However, the concentration would depend on the ambient O_3 concentration, the O_3 infiltration factor, and the indoor generation rate of terpenes. Because the concentration of the resulting particles would not be expected to be correlated with ambient PM on an individual or population basis, it seems more appropriate to consider indoor-reaction particles as part of nonambient exposure.

Indoor Sources of Particles

The major sources of indoor PM in nonsmoking residences and buildings include suspension of PM from bulk material, cooking, cleaning, and the use of combustion devices such as stoves and kerosene heaters. Human and pet activities also lead to PM detritus production (from tracked-in soil, fabrics, skin and hair, home furnishings, etc.) that is found ubiquitously in house dust deposited on floors and other interior surfaces. House dust and lint particles may be resuspended indoors by agitation (cleaning) and turbulence (HVAC systems, human activities, etc.). Ambient particles that have infiltrated into the indoor microenvironments also may be resuspended after deposition to indoor surfaces. Typically, resuspension of particles from any source involves coarse particles (> 1 μm); particles with smaller diameters are not resuspended efficiently. On the other hand, cooking produces both fine and coarse mode particles whereas combustion sources typically produce ultrafine particles.

Environmental tobacco smoke (ETS) is also a major indoor source of PM. It is, however, beyond the scope of this chapter to review the extensive literature on ETS. A number of articles provide source-strength information for cigarette or cigar smoking (e.g., Daisey et al., 1998 and Nelson et al., 1998).

A study conducted on two homes in the Boston metropolitan area (Abt et al., 2000a) showed that indoor PM sources predominate when air exchange rates were $< 1\ h^{-1}$, and outdoor sources predominate when air exchange rates were $\geq 2\ h^{-1}$. The authors attributed this to the fact that when air exchange rates were low (< 1 h--1), particles released from indoor sources tend to accumulate because particle deposition is the mechanism governing particle decay and not air exchange. Particle deposition rates are generally $< 1\ h^{-1}$, especially for accumulation-mode particles. When air exchange rates were higher ($\geq 2\ h^{-1}$), infiltration of ambient aerosols and exfiltration of indoor-generated aerosols occur more rapidly, reducing the effect of indoor sources on indoor particle levels. The study also confirmed previous findings that the major indoor sources of PM are cooking, cleaning, and human activity. They discuss the size characteristics of these ubiquitous sources and report the following.

> The size of the particles generated by these activities reflected their formation processes. Combustion processes (oven cooking, toasting, and barbecuing) produced fine particles and mechanical processes (sauteing, frying, cleaning, and movement of people) generated coarse particles. These activities increased particle concentrations by many orders of magnitude higher than outdoor levels and altered indoor size distributions. (Abt et al., 2000a; p. 43)

They also note that variability in indoor PM for all size fractions was greater than for outdoor PM, especially for short averaging times (2 to 33 times higher).

In a separate study conducted in nine nonsmoking homes in the Boston area, Long et al. (2000) concluded that the predominant source of indoor fine particles was infiltration of outdoor particles and that cooking activities were the only other significant source of fine particles. Coarse particles, however, had several indoor sources, such as cooking, cleaning, and various indoor activities. This study also concluded that more than 50% of the particles (by volume) generated during indoor events were ultrafine particles. Events that elevated indoor particle levels were found to be brief, intermittent, and highly variable, thus requiring the use of continuous instrumentation for their characterization. Because the concentration of ultrafine particles will be greater near the source (they will grow in size into the accumulation mode as they age), the personal cloud for ultrafine particles may be higher than for accumulation mode particles if the person is nearer the source than the indoor monitor. Table 5-11 provides information on the mean volume mean diameter (VMD) for various types of indoor particle sources. The differences in mean VMD confirm the clear separation of source types and suggest that there is very little resuspension of accumulation-mode PM. In addition, measurements of organic and elemental carbon indicated that organic carbon had significant indoor sources whereas elemental carbon was primarily of ambient origin.

Vette et al. (2001) found that resuspension was a significant indoor source of particles > 1 μm. Concentrations of fine particles were not affected by resuspension. Figure 5-12 shows the diurnal variability in the indoor/outdoor aerosol concentration ratio from an unoccupied residence in Fresno. The study was conducted in the absence of common indoor particle sources such as cooking and cleaning. The data in Figure 5-12 show the mean indoor/outdoor concentration ratio for particles > 1 μm increased dramatically during daytime hours. This pattern was consistent with indoor human activity levels. In contrast, the mean indoor/outdoor concentration ratio for particles < 1 μm (ultrafine and accumulation-mode particles) remain fairly constant during both day and night.

Wallace and Howard-Reed (2002) used three instruments (SMPS, APS, and Climet) to measure ultrafine, fine, and coarse particles in an inhabited residence for 18 months. They confirm the observations of Abt et al. (2000a) and Long et al. (2000) that indoor sources primarily generate ultrafine and coarse particles. Wallace and Howard-Reed report that, “Indoor

TABLE 5-11. VOLUME MEAN DIAMETER (VMD) AND MAXIMUM $PM_{2.5}$ CONCENTRATIONS OF INDOOR PARTICLE SOURCES [a,b]

		Size Statistics		$PM_{2.5}$	
Particle Source	N	Indoor Activity Mean VMD (µm)	Background[a,e] Mean VMD (µm)	Maximum Mean	Concentration[c,d] SD
Cooking					
Baking (Electric)	8	0.189[f]	0.221[f]	14.8	7.4
Baking (Gas)	24	0.107[f]	0.224[f]	101.2	184.9
Toasting	23	0.138[f]	0.222[f]	54.9	119.7
Broiling	4	0.114[f]	0.236[f]	29.3	43.4
Sautéing	13	0.184[f], 3.48[g]	0.223[f], 2.93[g]	65.6	95.4
Stir-Frying	3	0.135[f]	0.277[f]	37.2	31.4
Frying	20	0.173[f]	0.223[f]	40.5	43.2
Barbecuing	2	0.159[f]	0.205[f]	14.8	5.2
Cleaning					
Dusting	11	5.38[g]	3.53[g]	22.6	22.6
Vacuuming	10	3.86[g]	2.79[g]	6.5	3.9
Cleaning with Pine Sol	5	0.097[f]	0.238[f]	11.0	10.2
General Activities					
Walking Vigorously (w/Carpet)	15	3.96[g]	3.18[g]	12.0	9.1
Sampling w/Carpet	52	4.25[g]	2.63[g]	8.0	6.6
Sampling w/o Carpet	26	4.28[g]	2.93[g]	4.8	3.0
Burning Candles	7	0.311[f]	0.224[f]	28.0	18.0

Notes:
[a] All concentration data corrected for background particle levels.
[b] Includes only individual particle events that were unique for a given time period and could be detected above background particle levels.
[c] PM concentrations in $\mu g/m^3$.
[d] Maximum concentrations computed from 5-min data for each activity.
[e] Background data are for time periods immediately prior to the indoor event.
[f] Size statistics calculated for $PV_{0.02\text{-}0.5}$ using SMPS data.
[g] Size statistics calculated for $PV_{0.7\text{-}10}$ using APS data.

Source: Long et al. (2000).

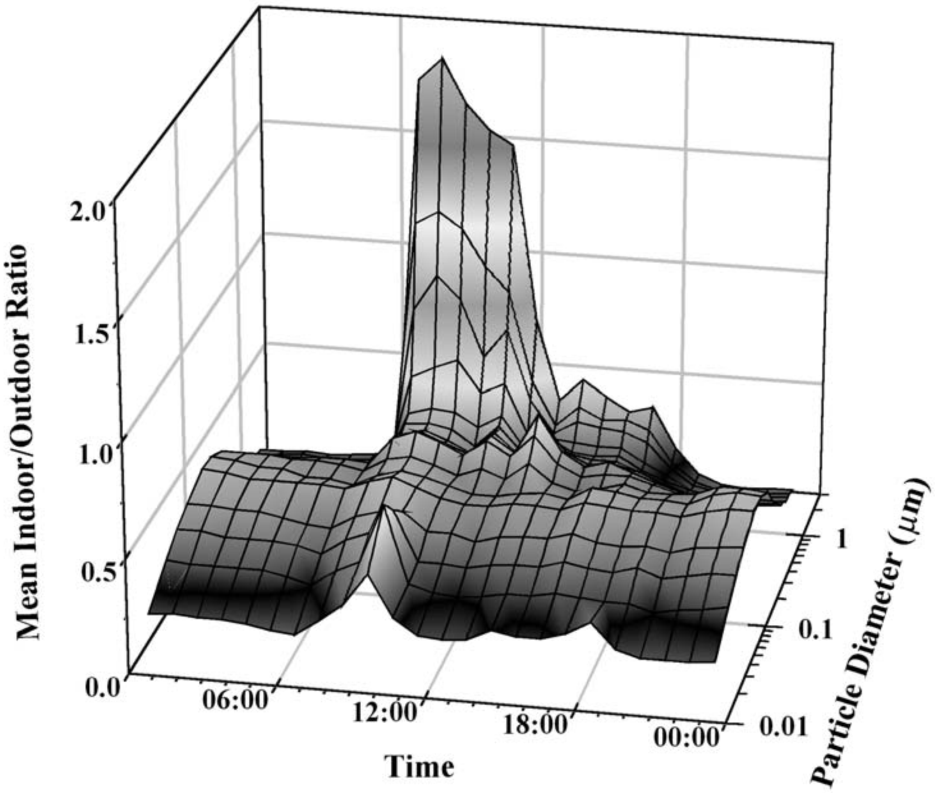


Figure 5-12. Mean hourly indoor/outdoor particle concentration ratio from an unoccupied residence in Fresno, CA, during spring 1999.

Source: Vette et al. (2001).

sources affecting ultrafine particle concentrations were observed 22% of the time, and sources affecting fine and coarse particle concentrations were observed 12 and 15% of the time, respectively . . . Indoor sources, such as cooking with natural gas, and simple physical activities, such as walking, accounted for a majority (50-90%) of the ultrafine and coarse particle concentrations, whereas outdoor sources were more important for accumulation-mode particles between 0.1 and 1 μm in diameter."

5.3.3.2.3 Time/Activity Patterns

Total exposure to PM is the sum of various microenvironmental exposures that an individual encounters during the day and will depend on the microenvironments occupied. As discussed previously, PM exposure in each microenvironment is the sum of exposures from ambient PM (in outdoor and indoor microenvironments), indoor-generated PM and indoor reaction PM. In addition, there is exposure to PM generated by personal activities that is determined by the personal activities that the individual conducts while in those microenvironments. As mentioned before, PM exposures and their components are variable across the population; thus, each are distributions rather than point estimates. A thorough analysis of these distributions would require a comprehensive sensitivity and uncertainty analysis.

Determining microenvironments and activities that contribute significantly to human exposure begins with establishing human activity pattern information for the general population, as well as subpopulations. Personal exposure and time-activity pattern studies have shown that different populations have varying time-activity patterns and, accordingly, different personal PM exposures. Both characteristics will vary greatly as a function of age, health status, ethnic group, socioeconomic status, season, and region of the country. Collecting detailed time activity data can be very burdensome on participants but is clearly valuable in assessing human exposure and microenvironments. For modeling purposes, human activity data frequently come from general databases that are discussed below.

The gathering of human activity information, often called “time-budget” data, started in the 1920s; however, their use for exposure assessment purposes only began to be emphasized in the 1980s. Many of the largest U.S. human activity databases have been consolidated by EPA’s National Exposure Research Laboratory’s (NERL) into one comprehensive database containing more than 22,000 person-days of 24-h activity known as the Consolidated Human Activity Database, or CHAD (Glen et al., 1997; McCurdy et al., 2000). The information in CHAD is accessible for constructing population cohorts of people with diverse characteristics that are useful for analysis and modeling (McCurdy, 2000). See Table 5-2 for a summary listing of human activity studies in CHAD. Most of the databases in CHAD are available elsewhere, including the National Human Activity Pattern Survey (NHAPS), California’s Air Resources Board (CARB), and the University of Michigan’s Institute for Survey Research data sets.

Although CHAD provides a very valuable resource for time and location data, there is little information on PM-generating personal activities. In addition, very few of the time-activity studies have collected longitudinal data within a season or over multiple seasons. Such longitudinal data are important in understanding potential variability in activities and how they affect correlations between PM exposure and ambient site measurements for both total PM and PM of ambient origin.

5.3.3.3 Effect of Ambient Sources on Exposures to Particulate Matter

Different sources may generate ambient PM with different aerodynamic and chemical characteristics, which may, in turn, result in different health responses. Thus, to fully understand the relationship between PM exposure and health outcomes, exposure from difference sources should be identified and quantified. Source apportionment techniques provide a method for determining personal exposure to PM from specific sources. Daily contributions from sources that have no indoor component can be used as tracers to generate exposure estimates for ambient PM of similar aerodynamic size or directly as exposure surrogates in epidemiological analyses. The most recent EPA PM Research Needs Document (U. S. Environmental Protection Agency, 1998) recommended use of source apportionment techniques to determine daily time-series of source categories for use in community, time-series epidemiology.

A number of epidemiologic studies (discussed more fully in Chapter 8) have evaluated relationships between health outcomes and sources of particulate matter determined from measurements at a community monitor. These studies suggest the importance of examining sources and constituents of indoor, outdoor, and personal PM. For example, Özkaynak and Thurston (1987) evaluated the relationship between PM sources and mortality in 36 Standard Metropolitan Statistical Areas (SMSAs). Particulate matter samples from EPA's Inhalable Particle (IP) Network were analyzed for SO_4^{-2} and NO_3^- by automated colorimetry, and elemental composition was determined with X-ray fluorescence (XRF). Mass concentrations from five PM source categories were determined from multiple regression of absolute factor scores on the mass concentration: (1) resuspended soil, (2) auto exhaust, (3) oil combustion, (4) metals, and (5) coal combustion.

In another study, Mar et al. (2000) applied factor analysis to evaluate the relationship between PM composition (and gaseous pollutants) in Phoenix. In addition to daily averages of $PM_{2.5}$ elements from XRF analysis, they included in their analyses organic and elemental carbon in $PM_{2.5}$ and gaseous species emitted by combustion sources (CO, NO_2, and SO_2). They identified five factors classified as (1) motor vehicles, (2) resuspended soil, (3) vegetative burning, (4) local SO_2, and (5) regional sulfate. Additionally, Laden et al. (2000) applied specific rotation factor analysis to particulate matter composition (XRF) data from six eastern cities (Ferris et al., 1979). Fine PM was regressed on the recentered scores to determine the daily source contributions. Three main sources were identified (1) resuspended soil (Si); (2) motor vehicle (Pb); and (3) coal combustion (Se).

Source apportionment or receptor modeling has been applied to the personal exposure data to understand the relationship between personal and ambient sources of particulate matter. Application of source apportionment to ambient, indoor, and personal PM composition data is especially useful in sorting out the effects of particle size and composition. If a sufficient number of samples are analyzed with sufficient compositional detail, it is possible to use statistical techniques to derive source category signatures, to identify indoor and outdoor source categories, and to estimate their contribution to indoor and personal PM.

Positive Matrix Factorization (PMF) has been applied to the PTEAM database by Yakovleva et al. (1999). The authors utilize mass and XRF elemental composition data from indoor and outdoor $PM_{2.5}$ and personal, indoor, and outdoor PM_{10} samples. PMF is an advance over ordinary factor analysis because it allows measurements below the quantifiable limit to be used by weighting them by their uncertainty. This effectively increases the number of species that can be used in the model. The factors used by the authors correspond to general source categories of PM, such as outdoor soil, resuspended indoor soil, indoor soil, personal activities, sea-salt, motor vehicles, nonferrous metal smelters, and secondary sulfates. PMF, by identifying the various source factors and apportioning them among the different monitor locations (personal, indoor, and outdoor), was able to estimate the contribution of resuspended indoor dust to the personal cloud (15% from indoor soil and 30% from resuspended indoor soil). Factor scores for these items then were used in a regression analysis to estimate personal exposures (Yakovleva et al., 1999).

The most important contributors to PM_{10} personal exposure were indoor soil, resuspended indoor soil, and personal activities; these accounted for approximately 60% of the mass (Yakovleva et al., 1999). Collectively, they include personal cloud PM, smoking, cooking, and vacuuming. For both $PM_{2.5}$ and PM_{10}, secondary sulfate and nonferrous metal operations accounted for another 25% of PM mass. Motor vehicle exhausts, especially from vehicles started inside attached garages, accounted for another 10% of PM mass. The PTEAM study was conducted in Riverside, CA in the fall of 1990. Yakovleva et al. (1999) caution that their results may not apply to other geographic areas, seasons of the year, or weather conditions.

Simultaneous measurement of personal (PM_{10}) and outdoor measurements ($PM_{2.5}$ and PM_{10}) were evaluated as a three-way problem with PMF, which allowed for differentiation of source categories based on their variation in time and type of sample, as well as their variation in composition. By use of this technique, it was possible to identify three sources of coarse-mode, soil-type PM. One was associated with ambient soil, one with indoor soil dispersed throughout the house, and one with soil resulting from the personal activity of the subject.

Two other source apportionment models have been applied to ambient measurement data and can be used for the personal exposure studies. The effective variance weighted Chemical Mass Balance (CMB) receptor model (Watson et al., 1984, 1990, 1991) solves a set of linear equations that incorporate the uncertainty in the sample and source composition. CMB requires the composition of each potential source of PM and the uncertainty for the sources and ambient measurements. Source apportionment with CMB can be conducted on individual samples; however, composition of each of the sources of PM must be known. An additional source apportionment model, UNMIX (Henry et al., 1994) is a multivariate source apportionment model. UNMIX is similar to PMF, but does not explicitly use the measurement uncertainties. Because measurement uncertainties are not used, only species above the detection limit are evaluated in the model. UNMIX provides the number of sources and source contributions and requires a similar number of observations as PMF.

The Yakovleva et al. (1999) study demonstrates that source apportionment techniques also could be very useful in determining parameters needed for exposure models and for determining exposure to ambient PM. Exposure information, similar to that obtained in the PTEAM study, but including other PM components useful for definition of other source categories (e.g., elemental [EC] and organic carbon [OC]; organic tracers for elemental carbon from diesel vehicle exhaust, gasoline vehicle exhaust, and wood combustion; nitrate; Na, Mg, and other metal tracers; and gas-phase pollutants) would be useful as demonstrated in the use of EC/OC and gas-phase pollutants by Mar et al. (2000).

5.3.3.4 Correlations of Particulate Matter with Other Pollutants

Correlations between ambient concentrations and between ambient concentrations and personal exposures for PM and other pollutants are of importance in understanding possible confounding in epidemiological studies as will be discussed more fully in Chapter 9. The available information from exposure studies is presented in this section. Several epidemiologic studies have included the gaseous pollutants CO, NO_2, SO_2, and O_3 along with PM_{10} or $PM_{2.5}$ in the analysis of the statistical association of health responses with pollutants. In a recent study, the personal exposure to O_3 and NO_2 was determined, as well as that to $PM_{2.5}$ and $PM_{2.5\text{-}10}$ for a cohort 15 elderly subjects in Baltimore, MD, although measured personal exposures to O_3, NO_2, and SO_2 were below their respective level of detection (LOD) for 70% of the samples. Spearman correlations for 14 subjects in summer and 14 subjects in winter are given in Table 5-12 for relationships between personal $PM_{2.5}$ and ambient concentrations of $PM_{2.5}$, $PM_{2.5\text{-}10}$, O_3, and NO_2. In contrast to ambient concentrations, neither personal exposure to total $PM_{2.5}$ nor $PM_{2.5}$ ambient origin was correlated significantly with personal exposures to the co-pollutants, $PM_{2.5\text{-}10}$, nonambient $PM_{2.5}$, O_3, NO_2, and SO_2. Personal-ambient associations for $PM_{2.5\text{-}10}$, O_3, NO_2, and SO_2 were similarly weak and insignificant. Based on these results, Sarnat et al. (2000) conclude that the potential for confounding of $PM_{2.5}$ by O_3, NO_2, or PM $_{10\text{-}2.5}$ appears to be limited, because, despite significant correlations observed among ambient pollutant concentrations, the correlations among personal exposures were low.

Sarnat et al. (2001) further evaluated the role of gaseous pollutants in particulate matter epidemiology by extending the measurements taken on the earlier adult cohort of 20 individuals in Baltimore by including additional PM and gaseous pollutant measurements that were collected during the same 1998-1999 period from 15 individuals with COPD and from 21 children, 24-h average personal exposures for $PM_{2.5}$, O_3, SO_2 and NO_2, and corresponding ambient concentrations for $PM_{2.5}$, O_3, SO_2, NO_2 and CO for all 56 subjects were collected over 12 consecutive days. Results from correlation and regression analysis of the personal and ambient data showed that personal $PM_{2.5}$ and personal gaseous pollutant exposures were generally not correlated. The analysis also showed that ambient $PM_{2.5}$ concentrations had significant associations with personal $PM_{2.5}$ exposures in both seasons. On the other hand, ambient gaseous pollutant concentrations were not correlated with their corresponding personal exposure concentrations. However, ambient gaseous concentrations were found to be strongly

TABLE 5-12. CORRELATIONS BETWEEN PERSONAL $PM_{2.5}$ AND AMBIENT POLLUTANT CONCENTRATIONS[1]

		Personal $PM_{2.5}$ vs. Ambient:				Personal $PM_{2.5}$ of Ambient Origin vs. Ambient:		
SUMMER	Subject	$PM_{2.5}$	O_3	NO_2	$PM_{2.5-10}$	O_3	NO_2	$PM_{2.5-10}$
	SA1	0.55	0.15	0.38	−0.12	0.27	*0.71*	0.15
	SA2	*0.85*	0.31	*0.66*	0.57	0.21	0.64	0.68
	SA5	*0.89*	0.18	*0.82*	0.64	0.33	*0.81*	0.79
	SB1	*0.65*	0.40	−0.15	0.38	*0.89*	*−0.74*	−0.03
	SB2	−0.21	−0.62	*0.81*	0.15	0.26	0.08	0.33
	SB3	*0.82*	0.55	−0.14	−0.04	0.52	−0.20	0.00
	SB4	*0.73*	*0.62*	−0.34	−0.12	0.45	−0.29	−0.14
	SB5	*0.73*	0.45	−0.42	0.23	0.36	−0.48	0.33
	SB6	0.53	0.15	−0.38	0.12	−0.03	−0.57	0.32
	SC1	*0.95*	*0.78*	*0.66*	*0.65*	*0.83*	*0.63*	0.57
	SC2	*0.78*	*0.68*	0.36	0.51	*0.66*	*0.65*	*0.76*
	SC3	*0.85*	*0.78*	*0.73*	*0.68*	*0.69*	*0.71*	*0.80*
	SC4	*0.78*	*0.66*	0.59	*0.70*	0.50	0.50	0.51
	SC5	0.55	0.51	0.32	0.43	0.34	0.33	0.27
WINTER	WA1	0.22	−0.18	−0.26	−0.05	*−0.78*	−0.04	−0.24
	WA2	−0.38	−0.07	−0.36	−0.70	−0.15	−0.15	0.02
	WA4	−0.18	*0.67*	−0.22	−0.29	−0.33	0.20	0.00
	WA5	0.22	−0.43	*0.61*	0.50	*−0.72*	−0.09	0.40
	WB1	*0.80*	−0.84	*0.77*	0.41	*−0.87*	0.53	*0.66*
	WB2	*0.62*	−0.32	*0.59*	0.09	*−0.76*	*0.59*	*0.59*
	WB3	0.55	−0.45	*0.62*	0.04	*−0.77*	0.56	0.60
	WB4	−0.12	−0.01	0.34	−0.10	*−0.80*	*0.68*	0.48
	WC1	*0.74*	−0.62	−0.15	0.44	*−0.64*	0.02	0.69
	WC2	*0.79*	−0.88	0.17	*0.77*	*−0.87*	0.25	*0.71*
	WC3	0.28	−0.42	0.03	0.57	*−0.77*	0.30	−0.45
	WC4	0.19	−0.84	0.50	0.45	*−0.72*	0.22	0.67
	WC5	*0.81*	−0.62	0.08	*0.81*	*−0.76*	0.05	0.42
	WC6	0.01	−0.03	*0.65*	0.37	*−0.75*	0.19	−0.45
Median	Summer	0.76	0.48	0.37	0.41	0.41	0.42	0.33
Median	Winter	0.25	−0.43	0.26	0.39	−0.76	0.21	0.45

[1] Correlations represent Spearman's r values; italicized values indicate significance at the $\alpha = 0.05$ level.

Source: Sarnat et al. (2000).

associated with personal $PM_{2.5}$ exposures, suggesting that ambient gaseous concentrations for O_3, NO_2, SO_2 are acting as surrogates, as opposed to confounders of $PM_{2.5}$ in the estimation of PM health effects based on multi-pollutant models. This study did not measure personal CO and did not find a significant association between summertime ambient CO and personal $PM_{2.5}$ (a significant winter-time association, however, was found).

Personal EC and SO_4^{-2} were also measured during the winter for the cohort of COPD patients only. The analysis of this subset of the data showed that personal SO_4^{-2} was significantly and negatively associated with ambient O_3 and SO_2, and personal EC was significantly associated with ambient O_3, NO_2, and CO. The authors interpret these findings as suggesting that O_3 is primarily a surrogate for secondary particle exposures whereas ambient CO and NO_2 are primarily surrogates for particles from traffic. Sarnat et al. (2001) caution that these findings were from only one location and various physical and personal factors, such as ventilation, time spent outdoors, and household characteristics could affect the strength of the reported associations for certain individuals and cohorts even though the qualitative results found are unlikely to change.

A newly developed Roll-Around System (RAS) was used to evaluate the hourly relationship between gaseous pollutants (CO, O_3, NO_2, SO_2, and VOCs) and PM (Chang et al., 2000). Exposures were characterized over a 15-day period for the summer and winter in Baltimore, based on scripted activities to simulate activities performed by older adults (65+ years of age). Spearman rank correlations were reported for $PM_{2.5}$, O_3, CO, and toluene for both the summer and winter. The correlations are given for each microenvironment in Table 5-13: indoor residence, indoor other, outdoor near roadway, outdoor away from road, and in vehicle. No significant relationships ($p < 0.05$) were found between hourly $PM_{2.5}$ and O_3. Significant relationships were found between hourly $PM_{2.5}$ and CO: indoor residence, winter; indoor other, summer and winter; and outdoor away from roadway, summer. Significant relationships also were found between hourly $PM_{2.5}$ and toluene: indoor residence, winter; indoor other, winter; and in vehicle, winter. The significant relationships between CO and $PM_{2.5}$ in the winter may be caused by reduced air exchange rates that could allow them to accumulate (Chang et al., 2000). Although no significant correlation was found between in vehicle $PM_{2.5}$ and CO, toluene, which is a significant component of vehicle exhaust (Conner et al., 1995), was significantly correlated to $PM_{2.5}$ in the winter.

TABLE 5-13. CORRELATIONS BETWEEN HOURLY PERSONAL $PM_{2.5}$ AND GASEOUS POLLUTANTS

	Indoor Residence		Indoor Other		Outdoor Near Roadway		Outdoor Away from road		In Vehicle	
	N	r_s	N	r_s	N	r_s	N	r_s	N	r_s
$PM_{2.5}$ vs. O_3										
Summer	35	0.29	16	−0.14	10	0.05	12	0.45	37	0.21
Winter	56	0.05	37	−0.06	11	-0.28	7	0.04	34	−0.10
$PM_{2.5}$ vs. CO										
Summer	41	0.25	19	0.59[a]	13	0.14	12	0.62	46	0.23
Winter	59	0.43[a]	39	0.62[a]	13	0.37	8	0.41	37	0.10
$PM_{2.5}$ vs. Toluene										
Summer	46	0.23	21	−0.14	14	0.26	14	0.02	48	0.12
Winter	66	0.38[a]	47	0.44[a]	17	0.40	8	0.48	42	0.43[a]

[a]Correlations represent Spearman's r values; italicized values indicate significance at the $\alpha = 0.05$ level.

Source: Chang et al. (2000).

emissions, there was no significant correlation between "commuting PM_{10}" and any of the substances (Carrer et al., 1998).

Carrer et al. (1998) present data on the correlations among microenvironmental and personal PM_{10} exposures and concentrations and selected environmental chemicals monitored simultaneously (using methods not described). These chemicals were nitrogen oxides (NO_x), carbon monoxide (CO), and total volatile organic compounds (TVOC), benzene, toluene, xylene, and formaldehyde. The Kendall τ correlation coefficient was used; only results significant at $p < 0.05$ are mentioned here. Significant associations were found only between the following pairs of substances (τ shown in parentheses): personal PM_{10} (24 h) and NO_x (0.34), CO (0.34), TVOC (0.18), toluene (0.19), and xylene (0.26); office PM_{10} and NO_x (0.31); home PM_{10} and NO_x (0.24), CO (0.24), toulene (0.17), and xylene (0.25). Even though most of these chemicals are associated with motor vehicular emissions, there was no significant correlation between commuting PM_{10} and any of the substances.

5.4 SUMMARY OF PARTICULATE MATTER CONSTITUENT DATA

5.4.1 Introduction

Atmospheric PM contains a number of chemical constituents that may be of significance to human exposure and health effects. These constituents may be either components of the ambient particles or bound to the surface of particles. They may be elements, inorganic species, or organic compounds. A limited number of studies have collected data on concentrations of elements, acidic aerosols, and PAHs in ambient, personal, and microenvironmental PM samples. However, there have not been extensive analyses of the constituents of PM in personal or microenvironmental samples. Data from relevant studies are summarized in this section. The summary does not address bacteria, bioaerosols, viruses, or fungi (e.g., Owen et al., 1992; Ren et al., 1999).

5.4.2 Monitoring Studies That Address Particulate Matter Constituents

Relevant studies published in recent years that have measured the constituents of PM in personal or microenvironmental samples are summarized in Tables 5-11 and 5-12 for personal exposure measurements of PM and microenvironmental samples, respectively. Studies that measured both personal and microenvironmental samples are included in Table 5-11.

The largest database on personal, microenvironmental, and outdoor measurements of PM elemental concentrations is the PTEAM study (Özkaynak et al., 1996b). The results are highlighted in the table and discussed below. The table shows that a number of studies have measured concentrations of elements (by XRF), organic carbon (OC), various indicators of elemental carbon (EC), aerosol acidity, sulfate, ammonia, and nitrate. Additionally, a number of studies have measured PAHs, both indoors and outdoors. Other than the PAHs, there are few data on organic constituents of PM.

5.4.3 Key Findings

5.4.3.1 Correlations of Personal and Indoor Concentrations with Ambient Concentrations of Particulate Matter Constituents

The elemental composition of PM_{10} in personal samples was measured in the PTEAM study, the first probability-based study of personal exposure to particles. A number of important observations made from the PTEAM data collected in Riverside, CA, are summarized by

Özkaynak et al. (1996b). Population-weighted daytime personal exposures averaged 150 ± 9 μg/m^3 compared to concurrent indoor and outdoor concentrations of 95 ± 6 μg/m^3. The personal exposure measurements suggested that there was a "personal cloud" of particles associated with personal activities. Daytime personal exposures to 14 of the 15 elements measured in the samples were considerably greater than concurrent indoor or outdoor concentrations; sulfur was the only exception.

The PTEAM data also showed good agreement between the concentrations of the elements measured outdoors in the backyard of the residences with the concentrations measured at the central site in the community. The agreement was excellent for sulfur. Although the particle and element mass concentrations were higher in personal samples than for indoor or outdoor samples, a nonlinear mass-balance method showed that the penetration factor was nearly 1 for all particles and elements.

Similarly to the PTEAM results, recent measurements of element concentrations in NHEXAS showed elevated concentrations of As and Pb in personal samples relative to indoor and outdoor samples (Clayton et al., 1999b). The elevated concentrations of As and Pb were consistent with elevated levels of PM_{50} in personal samples (median particle exposure of 101 μg/m^3) as compared to indoor concentrations (34.4 μg/m^3). There was a strong association between personal and indoor concentrations and indoor and outdoor concentrations for both As and Pb. However, there were no central site ambient measurements for comparison to the outdoor or indoor measurements at the residences.

Manganese (Mn) concentrations were measured in $PM_{2.5}$ samples collected in Toronto (Crump, 2000). The mean $PM_{2.5}$ Mn concentrations were higher outdoors than indoors. However, the outdoor concentrations measured at the participants' homes were lower than those measured at two fixed locations. Crump (2000) suggested that the difference in the concentrations may have been because the fixed locations were likely closer to high-traffic areas than were the participants' homes.

Studies of acidic aerosols and gases typically measure strong acidity (H^+), SO_4^{-2}, NH^{+4}, and NO^{-3}. The relationship between the concentrations of these ions and the relationship between indoor and outdoor concentrations have been addressed in a number of studies during which personal samples, microenvironmental, and outdoor samples have been collected, as shown in Tables 5-14 and 5-15. Key findings from these studies include the following:

TABLE 5-14. STUDIES THAT HAVE MEASURED PARTICULATE MATTER CONSTITUENTS IN PERSONAL EXPOSURE SAMPLES

PM Constituent	Study Name/Reference	Study Location	Population Size/No. of Samples	Summary of Results
Elements	PTEAM/Özkaynak et al. (1996b)	Riverside, CA	178 adults	Outdoor air was the major source for most elements indoors, providing 70 to 100% of the observed indoor concentrations for 12 of the 15 elements. Correlation coefficients for central monitoring site versus outdoor at the residences were 0.98 for sulfur and 0.5 to 0.9 for other elements (except copper).
As and Pb	NHEXAS/Clayton et al. (1999b)	EPA Region 5	167 samples	Personal As and Pb levels higher than indoor or outdoor levels. No community ambient site for comparison.
Mn	Pellizzari et al. (1998, 1999); Clayton et al. (1999a); Crump (2000)	Toronto	925 personal samples	Mean $PM_{2.5}$ Mn higher outdoors than indoors. But $PM_{2.5}$ Mn concentrations higher at two fixed locations than at participants' homes.
Acid Aerosol Constituents	Sarnat et al. (2000)	Baltimore, MD	20 adults	High correlations between personal and ambient sulfate measurements in summer and winter.
	Brauer et al. (1989)	Boston, MA	—	Personal exposures to aerosol strong acidity slightly lower than concentrations measured at stationary site.
	Suh et al. (1992)	Uniontown, PA	24 children for 2 days	Personal exposures to H^+ and SO_4^{-2} lower than outdoor levels, but higher than indoor microenvironmental levels; personal NH_4^+ and NO_3^- higher than indoor or outdoor levels.
	Suh et al. (1993a,b)	State College, PA	47 children	Results similar to Uniontown, PA, study.
	Suh et al. (1994)			Results indicate strong neutralization of acidity indoors.
	Waldman and Liang (1993); Waldman et al. (1990)	Georgia and New Jersey	Hospital, daycares	Indoor sulfate levels were 70 to 100% of outdoor levels. Indoor ammonia levels 5- to 50-times higher than outdoors. Indoors, acid aerosols were largely neutralized.
PAHs	Zmirou et al. (2000)	Grenoble, France	38 adults	Ambient air concentrations close to traffic emissions were 1.1- to 3.5-times higher than personal exposure concentrations.
Individual Particle Analyses by CCSEM	Conner et al. (2001)	Baltimore, MD Same study locations for both	3 sets of indoor-outdoor-personal filters, > 2000 particles/filter	CCSEM was used to identify individual particles and classify them by most likely sources.
Trace Elemental analyses by XRF	Landis et al. (2001)		19 days with P, I, A for 10 elderly retirees	P and A highly correlated for $PM_{2.5}$ and sulfates. P and A not significantly correlated for soil and trace element oxides.
Elemental analysis by HR-ICP-MS	Kinney et al. (2002)	New York City, NY	46 student volunteers, 1 week in summer and winter, $PM_{2.5}$	29 PM constituents were measured. Most were similar for P, I and O suggesting Outdoor sources dominant .

TABLE 5-15. STUDIES THAT HAVE MEASURED PARTICULATE MATTER CONSTITUENTS IN MICROENVIRONMENTAL SAMPLES

PM Constituent	Study Name/Reference	Study Location	Population Size/No. of Samples	Summary of Results
Acid Aerosol Constituents	Jones et al. (2000)	Birmingham, England	12 residences	Sulfate I/O ratios ranged from 0.7 to 0.9 for three PM size fractions.
	Patterson and Eatough (2000)	Lindon, UT	One school	Ambient sulfate, SO_2, nitrate, soot, and total particle number showed strong correlations with indoor exposure although ambient $PM_{2.5}$ mass was not a good indicator of total $PM_{2.5}$ exposure.
	Leaderer et al. (1999)	Virginia and Connecticut	232 homes	The regional ambient air monitoring site provided a reasonable estimate of indoor and outdoor sulfate at nonsmokers homes. I/O sulfate ratio of 0. 74 during summer. Ammonia concentrations were an order of magnitude higher indoors than outdoors. Nitrous acid levels higher indoors than outdoors.
	Brauer et al. (1990)	Boston, MA	11 homes	Outdoor levels of H^+, SO_2, HNO_3, and SO_4^{-2} exceeded indoor levels in winter and summer. I/O ratios of H^+ lower than I/O ratios of SO_4^{-2} indicated neutralization of the acidity by ammonia.
PAHs	Chuang et al. (1999)	Durham, NC	24 homes	Measurements with continuous monitor; PAH levels generally higher indoors than outdoors.
	Dubowsky et al. (1999)	Boston, MA	3 buildings	PAHs indoors attributable to traffic, cooking, and candle-burning.
	Sheldon et al. (1993a,b)	Placerville and Roseville, CA	280 homes	Mass balance model used to estimate source strengths for PAH sources such as smoking, wood-burning and cooking.
PAHs and phthalates	PTEAM/Özkaynak et al. (1996b), Sheldon et al. (1993c)	Riverside, CA	120 homes	12-h I/O ratios for particulate-phase PAHs ranged from 1.1 to 1.4 during the day and 0.64 to 0.85 during night. The concentrations of phthalates and the number of samples with detectable phthalates were higher indoors than outdoors.

- Acid aerosol concentrations measured at the residences in the Uniontown, PA, study were significantly different from those measured at a fixed ambient site located 16 km from the community. However, Leaderer et al. (1999) reported that the regional ambient air monitoring site in Vinton, VA, provided a reasonable estimate of indoor and outdoor sulfate measurements during the summer at homes without tobacco combustion.
- Approximately 75% of the fine aerosol indoors during the summer was associated with outdoor sources based on I/O sulfate ratios measured in the Leaderer et al. (1999) study.
- Personal exposures to strong acidity (H^+) were lower than corresponding outdoor levels measured in studies by Brauer et al. (1989, 1990) and Suh et al. (1992). However, the personal exposure levels measured by Suh et al. (1992) were higher than the indoor microenvironmental levels.
- Personal exposures to NH_4^+ and NO_3^- were reported by Suh et al. (1992) to be lower than either indoor or outdoor levels.

Personal exposures to SO_4^{-2} were also lower than corresponding outdoor levels, but higher than the indoor microenvironmental levels (Suh et al., 1992; 1993a,b) as shown in Table 5-16.

The fact that the personal and indoor H^+ concentrations were substantially lower than outdoor concentrations suggests that a large fraction of aerosol strong acidity is neutralized by ammonia. Ammonia is emitted in relatively high concentrations in exhaled breath and sweat. The difference between indoor and outdoor H^+ concentrations in the Suh et al. (1992, 1993a,b) studies was also much higher than the difference for indoor and outdoor SO_4^{-2}, indicative of neutralization of the H^+. Results of the Suh et al. (1992, 1993a,b) studies also showed substantial interpersonal variability of H^+ concentrations that could not be explained by variation in outdoor concentrations.

Similar results for ammonia were reported by Waldman and Liang (1993). They reported that levels of ammonia in monitored institutional settings were 10- to 50-times higher than outdoors and that acid aerosols were largely neutralized. Leaderer et al. (1999) reported that ammonia concentrations during both winter and summer in residences were an order of magnitude higher indoors than outdoors, consistent with results of other studies and the presence of sources of ammonia indoors.

Sulfate aerosols appear to penetrate indoors effectively. Waldman et al. (1990) reported I/O ratios of 0.7 to 0.9 in two nursing care facilities and a day-care center. Sulfate I/O ratios

TABLE 5-16. SUMMARY STATISTICS FOR PERSONAL, INDOOR, AND OUTDOOR CONCENTRATIONS OF SELECTED AEROSOL COMPONENTS IN TWO PENNSYLVANIA COMMUNITIES

			Concentration (nmol m^{-3})		
Aerosol	Home Type	Sample Site (In/Out)[a]	Indoor (12 h) GM ± GSD[b]	Outdoor (24 h) GM ± GSD[b]	Personal (12 h) GM ± GSD[b]
State College					
NO^{-3}	A/C Homes[c]	53/71	2.1 ± 2.7	1.4 ± 2.1	—
	Non-A/C	254/71	3.2 ± 2.3	1.4 ± 2.1	—
SO_4^{-2}	A/C Homes	56/75	61.8 ± 2.5	109.4 ± 2.4	—
	Non-A/C	259/75	96.7 ± 2.5	109.4 ± 2.4	—
	All Homes[d]	214/76	69.1 ± 2.6	91.0 ± 2.5	71.5 ± 2.4
NH_4^+	All Homes	314/155	154.7 ± 2.8	104.4 ± 2.3	—
H^+	A/C Homes	28/74	4.2 ± 4.3	82.5 ± 2.6	
	Non-A/C	230/74	11.2 ± 3.1	82.5 ± 2.6	
	All Homes[e]	163/75	9.1 ± 3.5	72.4 ± 2.9	18.4 ± 3.0
Uniontown					
SO_4^{-2}	All Homes[e]	91/46	87.8 ± 2.1	124.9 ± 1.9	110.3 ± 1.8
NH_4^+	All Homes[e]	91/44	157.2 ± 2.8	139.4 ± 2.1	167.0 ± 2.0
H^+	All Homes[e]	91/46	13.7 ± 2.5	76.6 ± 2.7	42.8 ± 2.2

[a] In/Out = Indoor sample site/outdoor sample site.
[b] GM ± GSD = Geometric mean ± geometric standard deviation.
[c] A/C Homes = Homes that had air-conditioning (A/C); this does not imply that it was on during the entire sampling period.
Non-A/C = Homes without air conditioning.
[d] The sample size (n) for the personal monitoring = 209.
[e] n = 174 for personal monitoring.

Source: Suh et al. (1992, 1993a,b).

were measured for three particle size fractions in 12 residences in Birmingham, England, by Jones et al. (2000). The sulfate I/O ratios were 0.7 to 0.9 for PM < 1.1 μm, 0.6 to 0.8 for PM 1.1 to 2.1 μm, and 0.7 to 0.8 for PM 2.1 to 10 μm. Suh et al. (1993b) reported that personal and outdoor sulfate concentrations were highly correlated as depicted in Figure 5-13.

Indoor/outdoor relationships for a number of $PM_{2.5}$ components and related species in Lindon, UT, during January and February of 1997 by Patterson and Eatough (2000). Outdoor samples were collected at the Utah State Air Quality monitoring site. Indoor samples were collected in the adjacent Lindon Elementary School. The infiltration factors, C_{ai}/C, given by the

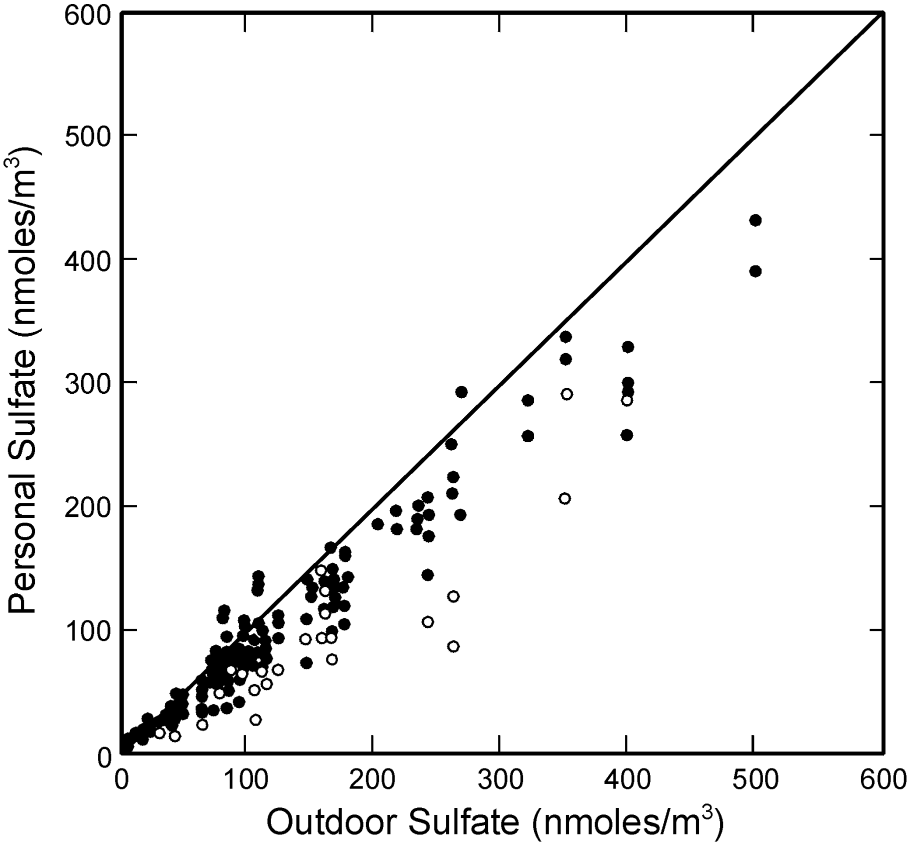


Figure 5-13. Personal versus outdoor SO_4^{-2} in State College, PA. Open circles represent children living in air conditioned homes; the solid line is the 1:1 line.

Source: Suh et al. (1993b).

slope of the regression lines (Table 5-17), were low (0.27 for sulfate and 0.12 for $PM_{2.5}$) possibly because of removal of particles in the air heating and ventilation system. The authors concluded that indoor $PM_{2.5}$ mass may not always be a good indicator of exposure to ambient combustion material due to the influence of indoor particle sources. Presumably this occurs because the concentrations of indoor-generated particles are not well correlated with the concentrations of ambient combustion particles. However, ambient sulfate, SO_2, nitrate, soot, and total particulate number displayed strong correlations with indoor exposure, presumably because these species have few indoor sources in the absence of indoor combustion. Ambient $PM_{2.5}$ mass was not a

TABLE 5-17. REGRESSION ANALYSIS OF INDOOR VERSUS OUTDOOR CONCENTRATIONS (units are nmol m^{-3}, except for soot and metals, which are $\mu g/m^3$ and absorption units m^{-3}, respectively.)[a]

Species	Slope = F_{INF}	Intercept = $\overline{C}_{ig}$	R^2	Average Outdoors, C_o
SO_2 All Samples	0.0272 ± 0.0023	0.34 ± 0.13	0.73	38
SO_2 Day Samples	0.0233 ± 0.0037	0.75 ± 0.26	0.62	56
SO_2 Night Samples	0.0297 ± 0.0029	0.099 ± 0.075	0.82	20
Sulfate All Samples	0.267 ± 0.024	−0.14 ± 0.48	0.70	16
Sulfate Day Samples	0.261 ± 0.034	0.40 ± 0.66	0.71	16
Sulfate Night Samples	0.282 ± 0.035	−0.84 ± 0.68	0.70	16
Nitrate All Samples	0.0639 ± 0.0096	0.9 ± 1.5	0.54	134
Nitrate Day Samples	0.097 ± 0.0096	−0.4 ± 1.4	0.88	126
Nitrate Night Samples	0.047 ± 0.011	1.5 ± 1.8	0.44	139
Soot Day Samples	0.43 ± 0.25	3.5 ± 1.7	0.43	6
Soot Night Samples	0.33 ± 0.13	0.00 ± 0.55	0.69	4
Total Acidity All Samples	0.04 ± 0.73	0.42 ± 0.23	0.00	0.2
Metals All Samples	0.10 ± 0.30	0.0014 ± 0.0042	0.01	0.0042

[a] Lindon Elementary School, Lindon, UT, January and February 1997.

Source: Patterson and Eatough (2000).

good indicator of indoor $PM_{2.5}$ mass exposure, presumably due to uncorrelated indoor sources of $PM_{2.5}$ mass.

Oglesby et al. (2000) conducted a study to evaluate the validity of fixed-site fine particle concentration measurements as exposure surrogates for air pollution epidemiology. Using 48-h EXPOLIS data from Basel, Switzerland, they investigated the personal exposure/outdoor concentration relationships for four indicator groups: (1) $PM_{2.5}$ mass, (2) sulfur and potassium for regional air pollution, (3) lead and bromine for traffic-related particles, and (4) calcium for crustal particles. The authors reported that personal exposures to $PM_{2.5}$ mass were not correlated to corresponding home outdoor levels (n = 44, r = 0.07). In the study group reporting neither relevant indoor sources nor relevant activities, personal exposures and home outdoor levels of sulfur were highly correlated (n = 40, r = 0.85). These results are consistent with spatially homogeneous regional pollution and higher spatial variability of traffic and crustal materials.

Indoor, outdoor, and personal concentrations of $PM_{2.5}$ mass and a variety of PM constituents were measured at an 18-story retirement facility in Towson, MD for 28, 24-hour monitoring periods during July and August 1998 (Landis et al., 2001). Indoor and outdoor measurements were made with a Versatile Air Pollutant Sampler (VAPS). Indoor, outdoor, and personal samples were made with a Personal Exposure Monitor (PEM). The VAPS (a dichotomous sampler) collected $PM_{2.5}$ (15 l min^{-1}) and $PM_{10\text{-}2.5}$ (2 l min^{-1}) while the PEM collected $PM_{2.5}$ (2 l min^{-1}). A comparison of the VAPS and the PEM indicated that the indoor PEM collected much higher mass and more soil components than the indoor VAPS although the differences between outdoor results were smaller and not significant. These differences were attributed to there being a larger coarse particle concentration inside (and perhaps larger diameter particles) and either more particle bounce or a higher 50% cut point for the PEM. In their analysis, Landis et al. (2001) compared indoor and outdoor VAPS data and outdoor and personal PEM data.

As shown in Table 5-18 (PEM) and Table 5-19 (VAPS), higher correlations were found for fine-particle components of $PM_{2.5}$ and lower correlations for coarse-particle components. Like Patterson and Eatough (2000), Landis et al. (2001) found low infiltration factors for nitrate but a reasonable correlation suggesting that fine-mode ammonium nitrate may be evaporating after it penetrates indoors. Neither sulfate nor nitrate had indoor sources.

Indoor and outdoor $PM_{2.5}$ and PM_{10} mass and chemical composition were measured in 13 homes (2-4 days for each home) in the Coachella Valley, a unique desert area in southern California during the winter and spring of 2000 (Geller et al., 2002). Maximum infiltration of ambient PM would be expected during this period because the mild climate minimizes the use of heating or air conditioning. Regression analysis was used to estimate $\overline{F}_{INF}$ and $\overline{C}_{ig}$. Results are shown in Table 5-20. The Coachella PM is generally considered to be rich in coarse PM and epidemiological studies have associated PM_{10} (Ostro et al., 1999) and estimated $PM_{10\text{-}2.5}$ (Ostro et al., 2000) with mortality. However, the results of Geller et al. (2002) indicate that even during periods of high air exchange rates indoor exposures would be dominated by $PM_{2.5}$. Geller et al. (2002) also report results for some chemical components of $PM_{2.5}$ and $PM_{10\text{-}2.5}$ and EC and OC in $PM_{2.5}$. For EC, $F_{INF}^{EC} = 0.74$, in good agreement with $F_{INF}^{2.5} = 0.74$. Indoor concentrations of OC

TABLE 5-18. MIXED MODEL ANALYSIS OF PERSONAL VERSUS OUTDOOR CONCENTRATIONS[a]

	$\overline{R}^2$	$\overline{\alpha}$	$\overline{C}$	$\overline{A}$	$\overline{N}$	$\overline{T}$	$\overline{A} + \overline{N}$
$PM_{2.5}$ (µg/m^3)	0.82	0.46 ± 0.04	21.0	9.66	3.57 ± 0.80	12.8	13.2
Sulfate[b] (µg/m^3)	0.95	0.40 ± 0.02	10.2	4.08	0.1 ± 0.04	4.5	4.2
Soil[c] (ng/m^3)	0.03	0.05 ± 0.12	458	93	544 ± 95	553	637
TEO[d] (ng/m^3)	0.39	0.43 ± 0.11	165	71	99 ± 23	170	170

[a] $\overline{\alpha}$ (slope) and $\overline{N}$ (intercept) taken from mixed model results. $\overline{A}$ calculated as $\overline{\alpha} \bullet \overline{C}$; $\overline{T}$ is measured value. Note good agreement between measured $\overline{T}$ and $\overline{T}$ estimated from $\overline{A} + \overline{N}$ except for soil.

[b] as $(NH_4)_2SO_4$.

[c] Soil = sum of oxides Si, Ca, Fe, and Ti (due to coarse PM in $PM_{2.5}$).

[d] TEO = trace element oxides (mostly fine PM components).

Source: Landis et al. (2001).

TABLE 5-19. REGRESSION ANALYSIS OF INDOOR VERSUS OUTDOOR CONCENTRATIONS[a]

	R^2	$\overline{F}_{INF}$	$\overline{C}$	$\overline{C}_{ai}$	$\overline{C}_{ig}$	$\overline{C}_i$	$\overline{C}_{ai} + \overline{C}_{ig}$
$PM_{2.5}$ (µg/m^3)	0.74	0.35	18.9	6.6	0.32	6.7	6.9
Sulfate[b] (µg/m^3)	0.98	0.41	10.4	4.4	-0.24	4.0	4.2
OC • 1.4 (µg/m^3)	0.44	0.30	5.4	1.6	8.0	9.7	9.6
EC[c] (µg/m^3)	0.58	0.32	0.50	0.16	0.09	0.4	0.25
NaCl (ng/m^3)	0.32	0.06	231	14	37	48	53
Soil[d] (ng/m^3)	0.30	0.07	363	25	51	74	76
TEO[e] (ng/m^3)	0.38	0.35	94	33	7	39	40
Nitrate (ng/m^3)	0.83	0.09	372	33	12	68	45

[a] $\overline{F}_{INF}$ (slope) and $\overline{C}_{ig}$ (intercept) taken from regression equation. C_{ai} calculated as $\overline{C} \bullet \overline{F}_{INF}$; $\overline{C}_i$ is measured value. Note reasonable agreement between measured $\overline{C}_i$ and $\overline{C}_i$ estimated from $\overline{C}_{ai} + \overline{C}_{ig}$ except for EC and nitrate.

[b] as $(NH_4)_2SO_4$.

[c] revised regression with outliers omitted.

[d] Soil = sum of oxides Si, Ca, Fe, and Ti (due to coarse PM in $PM_{2.5}$).

[e] TEO = trace element oxides (mostly fine PM components).

Source: Landis et al. (2001).

TABLE 5-20. REGRESSION ANALYSIS OF INDOOR VERSUS OUTDOOR CONCENTRATIONS[a]

	R^2	$\overline{F}_{INF}$	$\overline{C}$	$\overline{C}_{ai}$	$\overline{C}_{ig}$	$\overline{C}_i$
Fine	0.37	0.74	15.0	11.1	4.3	15.4
Coarse	0.35	0.30	8.6	2.6	3.0	5.6

[a] $\overline{F}_{INF}$ (slope) and $\overline{C}_{ig}$ (intercept) taken from regression equation. $\overline{C}_{ai}$ calculated as $\overline{C} \bullet \overline{F}_{INF}$. $\overline{C}_i$ is measured value. Note excellent agreement between measured $\overline{C}_i$ and $\overline{C}_i$ estimated from $\overline{C}_{ai} + \overline{C}_{ig}$.

Source: Geller et al. (2002).

were much higher than outdoor concentrations; the average indoor to outdoor ratio was 1.77. PAHs have been measured in studies by EPA and the California Air Resources Board. PAH results from a probability sample of 125 homes in Riverside are discussed in reports by Sheldon et al. (1992a,b) and Özkaynak et al. (1996b). Data for two sequential 12-h samples were reported for PAHs by ring size (3 to 7) and for individual phthalates. The results scan be summarized as follows.

- The particulate-phase 5- to 7-ring species had lower relative concentrations than the more volatile 3- to 4-ring species.
- The 12-h indoor/outdoor ratios for the 5- to 7-ring species ranged from 1.1 to 1.4 during the day and from 0.64 to 0.85 during the night (Sheldon et al., 1993a).
- An indoor air model used to calculate indoor "source strengths" for the PAHs showed that smoking had the strongest effect on indoor concentrations.

Results from a larger PAH probability study in 280 homes in Placerville and Roseville, CA (Sheldon et al., 1993a,b) were similar to the 125-home study. The higher-ring, particle-bound PAHs had lower indoor and outdoor concentrations than the lower-ring species. For most PAHs, the I/O ratio was greater than 1 for smoking and smoking/fireplace homes and less than 1 for fireplace-only, wood stove, wood stove/gas heat, gas heat, and "no source" homes.

A study of PAHs in indoor and outdoor air was conducted in 14 inner-city and 10 rural low-income homes near Durham, NC, in two seasons (winter and summer) in 1995 (Chuang et al., 1999). Fine-particle-bound PAH concentrations measured with a real-time monitor were usually higher indoors than outdoors (2.47 ± 1.90 versus 0.53 ± 0.58 $\mu g/m^3$). Higher indoor levels were seen in smokers' homes compared with nonsmokers' homes, and higher outdoor and indoor PAH levels were seen in urban areas compared with rural areas.

In a study reported by Dubowsky et al. (1999), the weekday indoor PAH concentrations attributable to traffic (indoor source contributions were removed) were 39 ± 25 ng/m^3 in a dormitory that had a high air exchange rate because of open windows and doors; 26 ± 25 ng/m^3 in an apartment; and 9 ± 6 ng/m^3 in a suburban home. The study showed that both indoor and outdoor sources (especially motor vehicular traffic) contributed to indoor PAH concentrations. BaP concentrations were measured in the THEES study (Waldman et al., 1991).
A comprehensive analysis of the data showed considerable seasonal variability of indoor and outdoor sources and resultant changes in personal exposures to BaP.

The indoor and outdoor concentrations of 30 PAHs were measured in 55 nonsmoking residences in Los Angeles, CA; Houston, TX; and Elizabeth, NJ (Naumova et al., 2002). A comparison of indoor/outdoor ratios of low molecular weight PAHs (3-4 rings) and higher molecular weight PAHs (5-7 rings) indicated that indoor sources had a significant effect on indoor concentrations of 3-ring PAHs and a smaller effect on 4-ring PAHs while outdoor sources dominated the indoor concentrations of 5-7 ring PAHs.

5.4.4 Factors Affecting Correlations Between Ambient Measurements and Personal or Microenvironmental Measurements of Particulate Matter Constituents

The primary factors affecting correlations between personal exposure and ambient air PM measurements have been discussed in Section 4.3.2. These include air exchange rates, particle penetration factors, decay rates, removal mechanisms, indoor air chemistry, indoor sources, and freshly-generated particles indoors. The importance of these factors varies for different PM constituents. For acid aerosols, indoor air chemistry is particularly important as indicated by the discussion of the neutralization of the acidity by ammonia which is present at higher concentrations indoors because of the presence of indoor sources. For SVOCs, including PAHs and phthalates, the presence of indoor sources will substantially affect the correlation between indoor and ambient concentrations (Özkaynak et al., 1996b; Sheldon et al., 1993b). Penetration factors for PM will affect correlations between indoors and outdoors for most elements, except Pb, which may have significant indoor sources in older homes. Indoor air chemistry, decay rates, and removal mechanisms may affect soot and organic carbon. Furthermore, reactions between indoor and outdoor gases and particles may produce freshly generated aerosols indoors. These factors must be fully evaluated when attempting to correlate concentrations of PM constituents in ambient, personal, or indoor samplers.

5.4.5 Limitations of Available Data

The previous discussion demonstrates that there is limited data available that can be used to compare personal, microenvironmental, and ambient air concentrations of PM constituents. Because of resource limitations, PM constituents have not been measured in many studies of PM exposure. There are little data on freshly generated aerosols indoors. Although there are some data on acid aerosols, the comparisons between the personal and indoor data generally have been with outdoor measurements at the participants' residences not with community ambient air measurement sites. The relationship between personal exposure and indoor levels of acid aerosols is not clear because of the limited database. The exception is sulfate, for which there appears to be a strong correlation between indoor and ambient concentrations.

With the exception of PAHs, there are practically no data available with which to relate personal or indoor concentrations with outdoor or ambient site concentrations of SVOCs that may be generated from a variety of combustion and industrial sources. The relationship between exposure and ambient concentrations of particles from specific sources, such as diesel engines, has not been determined.

Although there is an increasing amount of research being performed to measure PM constituents in different PM size fractions, the current data are inadequate to adequately assess the relationship between indoor and ambient concentrations of most PM constituents. Additional information is also needed on PM exposures that result from outdoor vapors reacting with indoor vapors. This is a source that could also vary with outdoor PM, for example, when the outdoor vapor is ozone.

5.5 IMPLICATIONS OF USING AMBIENT PARTICULATE MATTER CONCENTRATIONS IN TOXICOLOGICAL AND EPIDEMIOLOGICAL STUDIES OF PARTICULATE MATTER HEALTH EFFECTS

5.5.1 Toxicology

Most studies of PM toxicity have used either pure chemicals or ambient PM. Indoor-generated PM differs somewhat from ambient PM in terms of sources, size, and composition. It is possible, therefore, that indoor-generated PM could have different toxicological properties. Tobacco smoke has been studied extensively; however, there is little toxicological information on PM from other indoor sources. Long et al. (2001b) have assessed the in vitro toxicity of 14 paired indoor and outdoor $PM_{2.5}$ samples collected in 9 Boston-area homes. Bioasseys were conducted using rat alveolar macrophages (AMs) and tumor necrosis factor (TNF) was measured to assess particle-induced proinflammatory responses. TNF production was found to be significantly higher in AMs exposed to indoor PM than to those exposed to outdoor PM. This result held even after normalization for endotoxin concentrations which were higher in indoor samples. The authors feel that their results "suggest that indoor-generated particles may be more bioactive than ambient particles." PM, in its various forms, produces many types of biological effects. It seems possible that indoor PM could be more active than ambient PM for some effects and less for others.

5.5.2 Potential Sources of Error Resulting from Using Ambient Particulate Matter Concentrations in Epidemiological Analyses

In this section, the exposure issues that relate to the interpretation of the findings from epidemiological studies of PM health effects are examined. This section examines the errors that may be associated with using ambient PM concentrations in epidemiological analyses of PM health effects. First, implications of associations found between personal exposure and ambient PM concentrations are reviewed. This is discussed separately in the context of either community time-series studies or long-term, cross-sectional studies of chronic effects. Next, the role of compositional and spatial differences in PM concentrations are discussed and how these may influence the interpretation of findings from PM epidemiology. Finally, using statistical methods, an evaluation of the influence of exposure measurement errors on PM epidemiological studies is presented.

Measurement studies of personal exposures to PM are still few and limited in spatial, temporal, and demographic coverage. Consequently, with the exception of a few longitudinal panel studies, most epidemiological studies of PM health effects rely on ambient community monitoring data giving 24-h average PM concentration measurements. Moreover, because of limited sampling for $PM_{2.5}$, many of these epidemiological studies had to use available PM_{10} or in some instances had to rely on historic data on other PM measures or indicators, such as TSP, SO_4^{-2}, IP_{15} (inhalable particles with an upper cut of 15 μm), RSP (respirable particles), COH (coefficient of haze), etc. A critical question often raised in the interpretation of results from acute or chronic epidemiological community-based studies of PM is whether the use of ambient stationary site PM concentration data influences or biases the findings from these studies.

If it is assumed that total personal PM exposure is responsible for observed effects, use of ambient concentrations could lead to misclassification of individual exposures and to errors in the epidemiological analysis of pollution and health data depending on the pollutant and on the mobility and lifestyles of the population studied. Ambient monitoring stations can be some distance away from the individuals and can represent only a fraction of all likely outdoor microenvironments that individuals come in contact with during the course of their daily lives. Furthermore, most individuals are quite mobile and move through multiple microenvironments (e.g., home, school, office, commuting, shopping, etc.) and engage in diverse personal activities at home (e.g., cooking, gardening, cleaning, smoking). Some of these microenvironments and activities may have different sources of PM and result in distinctly different concentrations of PM than that monitored by the fixed-site ambient monitors. Consequently, exposures of some individuals could be classified incorrectly if only ambient monitoring data are used to estimate individual level total personal PM exposures. Thus, improper assessment of exposures using data routinely collected by the neighborhood monitoring stations could conceivably lead to a bias or increase in the standard error in epidemiological analysis. Except for extremely unlikely situations, however, the bias would be expected to reduce the estimated health risk coefficient.

Because many individuals are typically exposed to particles in a multitude of indoor and outdoor microenvironments during the course of a day, concern about possible error introduced in the estimation of PM risk coefficients using ambient, as opposed to personal, PM measurements has received considerable attention recently from exposure analysts, epidemiologists, and biostatisticians. Some exposure analysts contend that, for community time-series epidemiology to yield information on the statistical association of a pollutant with a health response, there must be an association between personal exposure to a pollutant and the ambient concentration of that pollutant because people tend to spend around 90% time indoors and are exposed to both indoor-generated and ambient-infiltrated PM (cf. Wallace, 2000b; Brown and Paxton, 1998; Ebelt et al., 2000). Consequently, numerous findings reported in the epidemiological literature on significant associations between ambient PM concentrations and various morbidity and mortality health indices, in spite of the low correlations between ambient PM and concentrations and measures of personal exposure, have been described by some exposure analysts as an exposure paradox (Lachenmyer and Hidy, 2000; Wilson et al., 2000).

To resolve the so-called exposure paradox, several types of analyses need to be considered. The first type of analysis has to examine the correlations between ambient PM concentrations and personal exposures that are relevant to most of the existing PM epidemiological studies using either pooled, daily-average, or longitudinal exposure data. The second approach has to study the degree of correlations between the two key components of personal PM exposures (i.e., exposures caused by ambient PM and exposures caused by nonambient PM) with ambient or outdoor PM concentrations, for each of the three types of exposure study designs. Yet, even with these two approaches, it may still be difficult to examine complex synergisms which, in some situations, may preclude simple decoupling of indoor and outdoor particles either in terms of exposure or total dose delivered to the lung. In addition, several factors that influence either the exposure or health response characterization of the subjects have to be addressed. These include such factors as

- spatial variability of PM components,
- health or sensitivity status of subjects,
- variations of PM with other co-pollutants,
- co-generation of fine and ultrafine particles from outdoor air and indoor gaseous pollutants,
- formal evaluation of exposure errors in the analysis of health data, and
- how the results may depend on the variations in the design of the epidemiological study.

To facilitate the discussion of these topics, a brief review of concepts pertinent to exposure analysis issues in epidemiology is presented.

5.5.2.1 Associations Between Personal Exposures and Ambient Particulate Matter Concentrations

As defined in Sections 5.3 and 5.4, personal exposures to PM result from an individual's exposures to PM in many different types of microenvironments (e.g., outdoors near home, outdoors away from home, indoors at home, indoors at office or school, commuting, restaurants, malls, other public places, etc.). Total personal exposures that occur in these indoor and outdoor microenvironments can be classified as those resulting from ambient PM (ambient PM exposure includes exposure to ambient PM while outdoors and exposure while indoors to ambient PM that has infiltrated indoors) and those primarily generated by indoor sources, indoor reaction, and personal activities (nonambient PM exposure). The associations between personal exposures and ambient PM concentrations that have been reported from various personal exposure monitoring studies under three broad categories of study design, (1) longitudinal, (2) daily-average, or (3) pooled exposure studies, are summarized below.

In Sections 5.4.3.1.2 and 5.4.3.1.3, recent studies mainly conducted in the United States and involving children, the elderly, and subjects with COPD were reviewed, and they indicated that both intra- and inter-individual variability in the relationships between personal exposures and ambient PM concentrations were observed. A variety of different physical, chemical, and personal or behavioral factors were identified by the original investigators that seem to influence the magnitude and the strength of the associations reported.

For cohort studies in which individual daily health responses are obtained, individual longitudinal PM personal exposure data (including ambient and nonambient components) may provide the appropriate indicators. In this case, health responses of each individual can be associated with the total personal exposure, the ambient exposure, or the nonambient exposure of each individual. Additionally, the relationships of personal exposure indicators with ambient concentration can be investigated. In the case of community time-series epidemiology, however, it is not feasible to obtain experimental measurements of personal exposure for the millions of people over time periods of years that are needed to investigate the relationship between air pollution and infrequent health responses such as deaths or even hospital admissions. The epidemiologist must work with the aggregate number of health responses occurring each day and a measure of the ambient concentration that is presumed to be representative of the entire community. The relationship of PM exposures of the potentially susceptible groups to monitored ambient PM concentrations depends on their activity pattern and level, residential building and HVAC factors (which influence the infiltration factor), status of exposure to ETS, amount of cooking or cleaning indoors, and seasonal factors, among others. For these special subgroups, average personal exposures to ambient PM are correlated well with ambient PM concentrations regardless of individual variation in the absence of major microenvironmental sources.

Even though both ambient and nonambient PM exposure contribute to daily baseline PM dose received by the lung, there seem to be clear differences in the relationships of ambient and nonambient PM exposure with ambient PM concentration. Various researchers have shown that nonambient PM exposure is independent of ambient PM concentration, but that ambient PM exposure is a function of ambient PM concentration. Wilson et al. (2000) explain the difference based on different temporal patterns that affect PM concentrations. "Concentrations of ambient PM are driven by meteorology and by changes in the emission rates and locations of emission sources, while concentrations of nonambient PM are driven by the daily activities of people." Still, although nonambient PM exposure may not correlate with ambient PM concentration or ambient PM exposure, it will nevertheless add to the daily baseline dose received by the lung. An important concern, for which there is little information, is the relative biological activity of ambient and indoor generated PM both in terms of the type of toxic effect and the relative potency for a given effect.

Ott et al. (2000) also discuss the reasons for assuming that nonambient PM exposure is independent of ambient PM exposure and ambient PM concentration. They show that the nonambient component of total personal exposure is uncorrelated with the outdoor concentration data. Ott et al. (2000) show the ambient PM exposure is similar for three population-based exposure studies: two large probability-based studies (the PTEAM study conducted in Riverside [Clayton et al., 1993; Thomas et al., 1993; Özkaynak et al., 1996a,b] and a study in Toronto [Pelizzarri et al., 1999; Clayton et al., 1999a]), and a nonprobability-based study conducted in Phillipsburg (Lioy et al., 1990). Based on these three studies, they conclude that the average nonambient PM exposure and the distribution of individual, daily values of nonambient PM exposure can be treated as constant from city to city.

Dominici et al. (2000) examined a larger database consisting of five different PM exposure studies and concluded that nonambient PM exposure can be treated as relatively constant from city to city although their data show greater variability than the data reported by Ott (2000). The constancy of nonambient PM exposure remains an open question. If daily values of nonambient PM exposure were constant, this would imply a zero correlation with ambient PM concentration. However, this hypothesis of constant individual, daily nonambient PM exposure has not been established fully because only a few studies have obtained the data needed to estimate daily, individual values of nonambient PM exposure. Although nonambient PM exposure is independent of ambient PM concentration, it may not be independent of the attenuation factor (ambient PM exposure/ambient PM concentration). Sarnat et al. (2000) show that nonambient PM exposure goes up as the ventilation rate (and attenuation factor) goes down. By comparing winter and summer regression equations Lachenmeyer and Hidy (2000) also show that as the slope, which gives the attenuation factor, decreases, the intercept, which gives the nonambient PM exposure, increases.

Mage et al. (1999) assume that the PM_{10} concentration component from indoor sources (such as smoking, cooking, cleaning, burning candles, and so on) is not correlated with the outdoor concentration. They indicate that this lack of correlation is expected because people are unaware of ambient concentrations and do not necessarily change their smoking or cooking activities as outdoor PM_{10} concentrations vary, an assumption supported by other empirical analyses of personal exposure data. For the PTEAM data set, Mage et al. (1999) have shown that individual, daily exposures to indoor-generated PM and daily ambient PM concentrations have a correlation coefficient near zero ($R^2 = 0.005$). Wilson et al. (2000) have shown that individual, daily values of concentration of ambient PM which has infiltrated indoors and indoor-generated PM concentrations also have a near zero correlation ($R^2 = 0.03$). Figure 5-14 shows the relationship of estimated values of nonambient PM exposure with ambient PM concentrations (calculated by EPA, daily, individual values from PTEAM and daily average values for the cohort from THEES).

Based on these results it is reasonable to assume that ordinarily nonambient PM exposure will have little correlation with ambient PM concentration. A possible exception could be caused by indoor-reaction PM, PM formed when an ambient gas infiltrates indoors and reacts with an indoor-generated gas, i.e., the reaction of O_3 with terpenes from air cleaners. However, ambient O_3 does not appear to be highly correlated with ambient or personal $PM_{2.5}$ (See Table 5-12, Sarnat et al., [2000]). Additionally, not every home will use air fresheners or have the same level of terpene emissions. Hence, indoor-reaction PM concentrations would not be

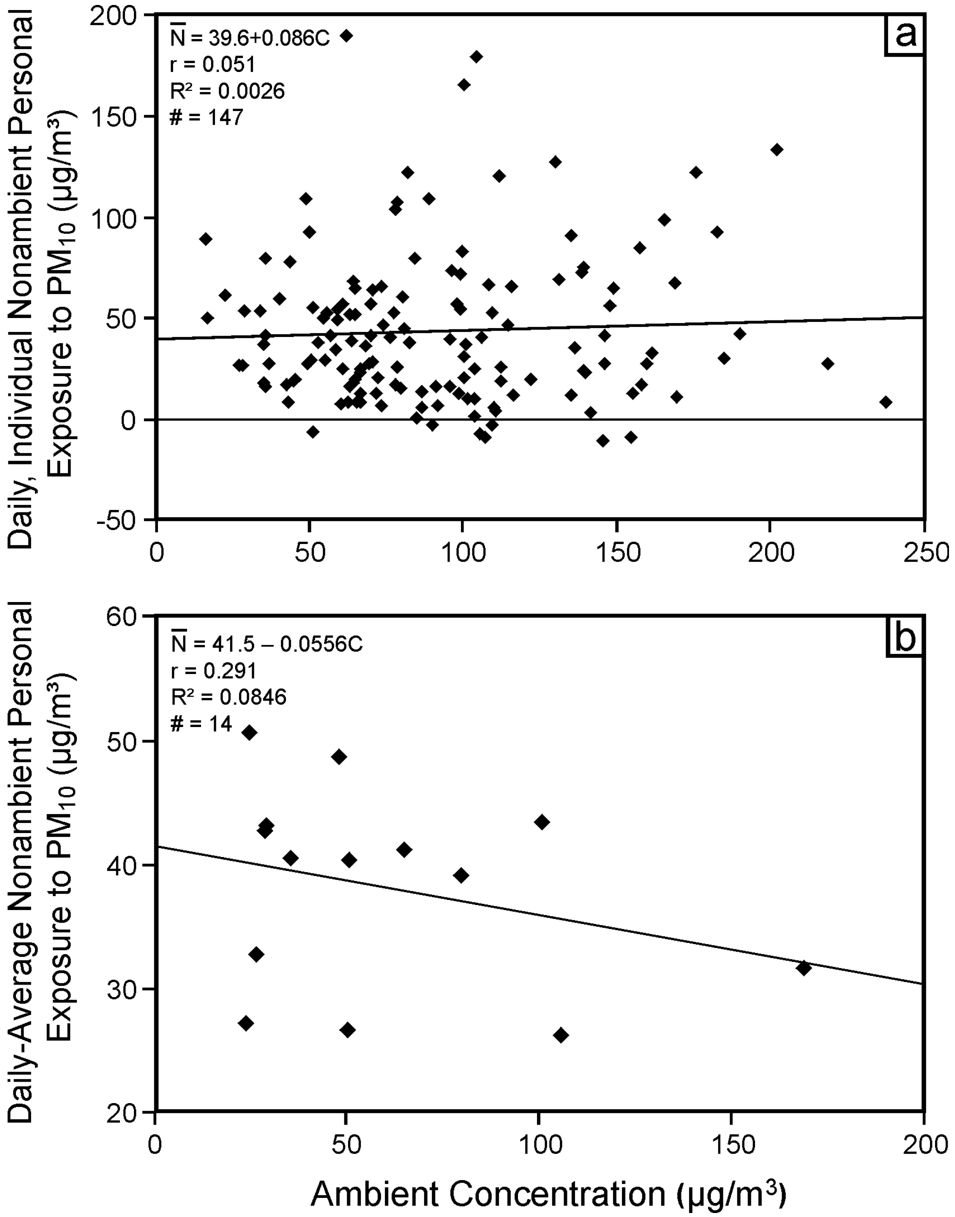


Figure 5-14. Plots of nonambient exposure to PM_{10}, (a) daily individual daytime values from PTEAM data and (b) daily-average values from THEES data.

Source: Data taken from (a) Clayton et al. (1993) and (b) Lioy et al. (1990).

expected to correlate with ambient PM concentrations on a community basis. Therefore, in linear nonthreshold models of PM health effects, nonambient PM exposure is not expected to contribute to the relative risk determined in a regression of health responses on ambient PM concentration. Furthermore, in time-series analysis of pooled or daily health data, it is expected that ambient PM exposure rather than total personal PM exposure will have the stronger association with ambient PM concentration.

5.5.2.2 Role of Compositional Differences in Exposure Characterization for Epidemiology

The majority of the available data on PM exposures and relationships with ambient PM have come from a few large-scale studies, such as PTEAM, or longitudinal studies on selected populations. Consequently, for most analyses, exposure scientists and statisticians had to rely on PM_{10} or $PM_{2.5}$ mass data, instead of elemental or chemical compositional information on individual or microenvironmental samples. In a few cases, researchers have examined the factors influencing indoor outdoor ratios or penetration and deposition coefficients using elemental mass data on personal, indoor, and outdoor PM data (e.g., Özkaynak et al., 1996a,b; Yakovleva et al., 1999). These results have been informative in terms of understanding relative infiltration of different classes of particle sizes and sources into residences (e.g., fossil fuel combustion, mobile source emissions, soil-derived, etc.). Clearly, in the accumulation-mode, particles associated with stationary or mobile combustion sources have greater potential for penetration into homes and other microenvironments than does crustal material. There will be variability in the chemical composition of these broad categories of source classes and also probably variations in relative toxicity. Moreover, when particles and reactive gases are present indoors in the presence of other pollutants or household chemicals, they may react to form additional or different compounds and particles with yet unknown physical, chemical, and toxic composition (Wainman et al., 2000). Thus, if indoor-generated and ambient PM were responsible for different types of health effects or had significantly different toxicities on a per unit mass basis, it would then be important that ambient and nonambient exposure should be separated and treated as different components, much like the current separation of PM_{10} into $PM_{2.5}$ and $PM_{10-2.5}$. These complexities in personal exposure profiles may introduce nonlinearities and other statistical challenges in the selection and fitting of concentration-response models. Unfortunately, PM health effects models have not yet been able to meaningfully consider such complexities.

It is important also to note that individuals spend time in places other than their homes and outdoors. Many of the interpretations reported in the published literature on factors influencing personal PM_{10} exposures, as well as in this chapter, come from the PTEAM study. The PTEAM study was conducted 10 years ago in one geographic location in California, during one season, and most residences had very high and relatively uniform air exchange rates. Non-home indoor microenvironments were not monitored directly during the PTEAM study. Commuting exposures from traffic or exposures in a variety of different public places or office buildings could not be assessed directly. Nonresidential buildings may have lower or higher ambient infiltration rates depending on the use and type of the mechanical ventilation systems employed. Because the source and chemical composition of particulate matter affecting personal exposures in different microenvironments vary by season, day-of-the-week, and time of day, it is conceivable that some degree of misclassification of exposures to PM toxic agents of concern could be introduced when health-effects models use only daily-average mass measures such as PM_{10} or $PM_{2.5}$. However, because of the paucity of currently available data on many of these factors, it is not now possible to ascertain the potential magnitude or severity of any such complex exposure missclassification problems or their potential implications for interpretation of results from PM epidemiology at this point.

5.5.2.3 Role of Spatial Variability in Exposure Characterization for Epidemiology

Chapter 3, Section 3.2.3 and Chapter 5, Section 5.3 present information on the spatial variability of PM mass and chemical components at fixed-site ambient monitors; for purposes of this chapter, this spatial variability is called an “ambient gradient.” Any gradient that may exist between a fixed-site monitor and the outdoor microenvironments near where people live, work, and play obviously affects the concentration profile actually experienced by people as they go about their daily lives.

However, the evidence so far indicates that PM concentrations, especially fine PM (mass and sulfate), generally are distributed uniformly in most metropolitan areas. This reduces the potential for exposure misclassification because of outdoor spatial gradients when a limited number of ambient PM monitors are used to represent population average ambient exposures in time-series or cross-sectional epidemiological studies of PM. This topic is further discussed in Section 5.6.5. However, as discussed earlier, the same assumption is not necessarily true for different components of PM such as $PM_{10-2.5}$ because source-specific and other spatially nonuniform pollutant emissions could alter the spatial profile of individual PM components in a community. For example, particulate and gaseous pollutants emitted from motor vehicles tend to be higher near roadways and inside cars. Likewise, acidic and organic PM species may be location- and time-dependent. Furthermore, human activities are complex. If outdoor PM constituent concentration profiles are either spatially or temporally variable, it is likely that exposure misclassification errors could be introduced in the analysis of PM air pollution and health data.

5.5.3 Analysis of Exposure Measurement Error Issues in Particulate Matter Epidemiology

The effects of exposure misclassification on relative risk estimates of disease using classical 2 by 2 contingency design (i.e., exposed/nonexposed versus diseased/nondiseased) have been studied extensively in the epidemiological literature. It has been shown that the magnitude of the exposure-disease association (e.g., relative risk) because of either misclassification of exposure or disease alone (i.e., nondifferential misclassification) biases the effect results toward the null; and differential misclassification (i.e., different magnitudes of disease misclassification in exposed and nonexposed populations) can bias the effect measure toward or away from the null value relative to the true measure of association (Shy et al., 1978; Gladen and Rogan, 1979; Copeland et al., 1977; Özkaynak et al., 1986). However, the extension of these results from contingency analysis design to multivariate models (e.g., log-linear regression, Poissson, logit) typically used in recent PM epidemiology has been more complicated.

5.5.3.1 Time-Series Analyses

Researchers have investigated the appropriateness of using ambient PM concentration as an exposure metric and have developed a framework for analyzing measurement errors typically encountered in the analysis of time-series mortality and morbidity effects from exposures to ambient PM (cf. Zeger et al., 2000; Dominici et al., 2000; Samet et al., 2000). Use of this framework, discussed more extensively in Chapters 8 and 9, leads to the following conclusions: the deviation of an individual's personal exposure from the risk-weighted average exposure due to variations in ambient concentrations, infiltration rates, and indoor-generated PM concentrations is a Berkson error and will not bias the estimated regression coefficient (β, the increase in risk per unit increase in PM) in a time-series analysis of mortality as a function of ambient PM concentrations. However, the difference between the average personal exposure and the true ambient concentration will bias β. If the daily, individual values of ambient PM exposure and nonambient PM exposure are poorly correlated and the attenuation coefficient, α, equal to the ambient PM concentration/ambient PM exposure were constant, the bias would be given by $\beta_c = \alpha\beta_A$ where β_C is calculated using the ambient PM concentration, C, and β_A is calculated using the ambient PM exposure, A; i.e., the risk determined from an analysis using the daily ambient PM concentrations would be lower than the risk obtained using ambient PM exposure by the factor α. However, β_C provides the correct information on the change in health risks that would be produced by a change in ambient concentrations. However, if the daily, individual values of ambient PM exposure and nonambient PM exposure are highly correlated and the nonambient PM is toxic for the effect being studied, nonambient PM exposure will act as a confounder and could introduce substantial bias into β_c. Only one study has reported the association between the daily, individual values of ambient PM exposure and nonambient PM exposure. Wilson et al. (2000), in a further analysis of the PTEAM data set, found a coefficient of determination (R^2) of 0.03 suggesting that the daily, individual values of ambient PM exposure and nonambient PM exposure are independent so that nonambient PM exposure will not confound β_c.

5.5.3.2 Studies of Chronic Effects

The Six Cities (Dockery et al., 1993) and American Cancer Society (ACS) (Pope et al., 1995) studies have played an important role in assessing the health effects from long-term exposures to particulate pollution. Even though these studies often have been considered as chronic epidemiological studies, it is not easy to differentiate the role of historic exposures from those of recent exposures on chronic disease mortality. In the Six Cities study, fine particles and sulfates were measured at the community level, and the final analysis of the database used six city-wide average ambient concentration measurements. This limitation also applies to the ACS study but has less impact because of the larger number of cities considered in that study. In a HEI-sponsored reanalysis of the Six Cities and the ACS data sets, Krewski et al. (2000) attempted to examine some of the exposure misclassification issues either analytically or through sensitivity analysis of the aerometric and health data. The HEI reanalysis project also addressed exposure measurement error issues related to the Six Cities study. For example, the inability to account for exposures prior to the enrollment of the cohort hampered accurate interpretation of the relative risk estimates in terms of acute versus chronic causes. Although the results seem to suggest that past exposures are more strongly associated with mortality than recent exposures, the measurement error for long-term averages could be higher and influence these interpretations. For example, Krewski et al. (2000), using the individual mobility data available for the Six Cities cohort, analyzed the mover and nonmover groups separately. The relative risk of fine particle effects on all-cause mortality was shown to be higher for the nonmover group than for the mover group, suggesting the possibility of higher exposure misclassification biases for the movers. The issue of using selected ambient monitors in the epidemiological analyses also was investigated by the ACS and Six Cities studies reanalysis team. Krewski et al. (2000) presented the sensitivity of results to choices made in selecting stationary or mobile-source-oriented monitors. For the ACS study, reanalysis of the sulfate data using only those monitors designated as residential or urban and excluding sites designated as industrial, agricultural, or mobile did not change the risk estimates appreciably. On the other hand, application of spatial analytic methods designed to control confounding at larger geographic scales (i.e., between cities) caused changes in the particle and sulfate risk coefficients. Spatial adjustment may account for differences in pollution mix or PM composition, but many other cohort-dependent risk factors will vary across regions or cities in the United States. Therefore, it is difficult to interpret these findings solely in terms of spatial differences in pollution composition or relative PM toxicity until further research is concluded.

The influence of measurement errors in air pollution exposure and health effects assessments has also been examined by Navidi et al. (1999). This study developed techniques to incorporate exposure measurement errors encountered in long-term air pollution health- effects studies and tested them on the data from the University of Southern California Children’s Health Study conducted in 12 communities in California. These investigators developed separate error analysis models for direct (i.e., personal sampling) and indirect (i.e., microenvironmental) personal exposure assessment methods. These models were generic to most air pollutants, but a specific application was performed using a simulated data set for studying ozone health effects on lung function decline in children. Because the assumptions made in their microenvironmental simulation modeling framework were similar to those made in estimating personal PM exposures, it is useful to consider the conclusions from Navidi et al. (1999). According to Navidi et al. (1999), neither the microenvironmental nor the personal sampler method produces reliable estimates of the exposure-response slope for O_3 when measurement error is uncorrected. Because of nondifferential measurement error, the bias was toward zero under the assumptions made in Navidi et al. (1999) but could be away from zero if the measurement error was correlated with the health response. A simulation analysis indicated that the standard error of the estimate of a health effect increases as the errors in exposure assessment increase (Navidi et al., 1999). According to Navidi et al. (1999), when a fraction of the ambient level in a microenvironment is estimated with a standard error of 30%, the standard error of the estimate is 50% higher than it would be if the true exposures were known. It appears that errors in estimating ambient PM indoor/ambient PM outdoor ratios have much more influence on the accuracy of the microenvironmental approach than do errors in estimating time spent in these microenvironments.

Epidemiological studies of chronic effects, that use long-term average ambient PM concentrations as the exposure metric, generally do not address the nonambient component of personal exposure (N). However, if N contributes to the health effect being studied and the average N is different in different cities, the correlation between the average ambient PM concentration and the health effect could be reduced. In an analysis of the effect of nonambient exposure on time-series epidemiology, Dominici et al. examine nonambient exposure data from several cities and conclude that the average nonambient PM exposure varies little among cities in developed countries. Ott et al. (2000) examined estimated average and daily, individual values of nonambient exposure from three studies and concluded that both the average and the distribution of daily, individual values were similar for the three studies.

5.5.4 Conclusions from Analysis of Exposure Measurement Errors on Particulate Matter Epidemiology

Personal exposures to PM are influenced by a number of factors and sources of PM located in both indoor and outdoor microenvironments. However, PM resulting from ambient sources does penetrate into indoor environments such as residences, offices, public buildings, etc., in which individuals spend a large portion of their daily lives. The correlations between total personal exposures and ambient or outdoor PM concentrations can vary depending on the relative contributions of indoor PM sources to total personal exposures. Panel studies of both adult and young subjects have shown that, in fact, individual correlations of personal exposures with ambient PM concentrations could vary person to person, and even day to day, depending on the specific activities of each person. Separation of PM exposures into two components, ambient PM and nonambient PM, would reduce uncertainties in the analysis and interpretation of PM health effects data. Nevertheless, because ambient PM is an integral component of total personal exposures to PM, statistical analyses of cohort-average exposures are strongly correlated with ambient PM concentrations when the size of the underlying population studied is large. Using the PTEAM study data, analysis of exposure measurement errors, in the context of time-series epidemiology, also has shown that errors or uncertainties introduced by using surrogate exposure variables, such as ambient PM concentrations, could lead to biases in the estimation of health risk coefficients. These then would need to be corrected by suitable calibration of the PM health risk coefficients. Correlations between the PM exposure variables and other covariates (e.g., gaseous co-pollutants, weather variables, etc.) also could influence the degree of bias in the estimated PM regression coefficients. However, most time-series regression models employ seasonal or temporal detrending of the variables, thus reducing the magnitude of this cross-correlation problem (Özkaynak and Spengler 1996).

Ordinarily, exposure measurement errors are not expected to influence the interpretation of findings from either the chronic or time-series epidemiological studies that have used ambient concentration data if they include sufficient adjustments for seasonality and key confounders. Clearly, there is no question that better estimates of exposures to components of PM of health concern are beneficial. Composition of PM may vary in different geographic locations and different exposure microenvironments. Compositional and spatial variations could lead to further errors in using ambient PM measures as surrogates for exposures to PM. Even though the spatial variability of PM ($PM_{2.5}$ in particular) mass concentrations in urban environments seems to be small, the same conclusions drawn above regarding the influence of measurement errors may not necessarily hold for all of the toxic PM components. Again, the expectation based on statistical modeling considerations is that these exposure measurement errors or uncertainties will most likely reduce the statistical power of the PM health effects analysis, making it difficult to detect a true underlying association between the correct exposure metric and the health outcome studied. However, until more data on exposures to toxic agents of PM become available, existing studies on PM exposure measurement errors must be relied on; thus, at this time the use of ambient PM concentrations as a surrogate for exposures is not expected to change the principal conclusions from PM epidemiological studies that use community average health and pollution data.

5.6 SUMMARY OF OBSERVATIONS AND LIMITATIONS

Exposure Definitions and Components

- Personal exposure to PM mass or its constituents results when individuals come in contact with particulate pollutant concentrations in locations or microenvironments that they frequent during a specific period of time. Various PM exposure metrics can be defined according to its source (i.e., ambient, nonambient) and the microenvironment where exposure occurs.
- Personal exposure to PM results from an individual's exposure to PM in many different types of microenvironments (e.g., outdoors near home, outdoors away from home, indoors at home, indoors at office or school, commuting, restaurants, malls, other public places, etc.). Thus, total daily exposure to PM for a single individual can be expressed as the sum of various microenvironmental exposures that the person encounters during the course of a day.
- In a given microenvironment, particles may originate from a wide variety of sources. In an indoor microenvironment, PM may be generated from within as a result of PM-generating activities (e.g., cooking, cleaning, smoking, resuspending PM from PM resulting from both indoor and outdoor sources that had settled out), from outside (outdoor PM entering through cracks and openings in the structure), and from the chemical interaction of pollutants from outdoor air with indoor-generated pollutants.
- The total daily exposure to PM for a single individual also can be expressed as the sum of contributions of ambient and nonambient PM. Nonambient PM exposure is due to PM generated by indoor sources, personal activities, and chemical reactions in indoor air. Ambient PM exposure includes exposure to ambient PM while outdoors, and ambient PM that has infiltrated indoors while indoors. However, within a large population, there will be distributions of total personal exposure and its components due to variations in human activities and microenvironmental concentrations and sources each individual encounters.
- Exposure models are useful tools for examining the importance of sources, microenvironments, and physical and behavioral factors that influence personal exposures to

PM. However, development and evaluation of population exposure models for PM and its components have been limited. Improved modeling methodologies and new model input data are needed.

Factors Affecting Concentrations and Exposures to Particulate Matter

- Concentrations of PM indoors are affected by several factors and mechanisms: ambient concentrations outdoors; air exchange rates; particle penetration factors; particle production from indoor sources and indoor air chemistry; and indoor particle decay rates and removal mechanisms caused by physical processes or resulting from mechanical filtration, ventilation or air-conditioning devices.
- Average personal exposures to PM mass and its constituents are influenced by microenvironmental PM concentrations and by how much time is spent by each individual in these various indoor and outdoor microenvironments. Nationwide, individuals, on average, spend nearly 90% of their time indoors (at home and in other indoor locations) and about 6% of their time outdoors.
- Personal exposures are associated with both indoor as well as outdoor sources. The personal exposure/outdoor concentration ratios present substantial intra- and inter-personal variability. This variability is due to both the presence of personal and microenvironmental sources and the varying effect of the outdoor particles on indoor environments.
- Home characteristics may be the most important factor that affects the relationship between the average population exposures and ambient concentrations. Air exchange rate seems to be an important home characteristic surrogate that can explain a large fraction of the observe inter- and intra-personal variability. One reason why longitudinal studies (many repeated measurements per person) provide stronger correlations between personal exposure and outdoor concentrations than cross-sectional studies (few repeated measurements per individual) may be because home characteristics remain the same.
- Because home characteristics constitute the most important factor affecting personal exposures, one would expect that correlations between average population exposures and outdoor concentrations will vary by season and geography.

- The relative size of personal exposure to ambient PM relative to nonambient PM depends on the ambient concentration, the infiltration rate of outdoor PM into indoor microenvironments, the amount of PM generated indoors (e.g., ETS, cooking and cleaning emissions), and the amount of PM generated by personal activity sources. Infiltration rates primarily depend on air exchange rate, size-dependent particle penetration across the building membrane, and size-dependent removal rates. All of these factors vary over time and across subjects and building types.
- The relationship between PM exposure, dose, and health outcome could depend on the concentration, composition, and toxicity of PM or PM components originating from different sources. Application of source apportionment techniques to indoor and outdoor $PM_{2.5}$ and personal, indoor, and outdoor PM_{10} composition data have identified the following general source categories: outside soil, resuspended indoor soil, indoor soil, personal activities, sea-salt, motor vehicles, nonferrous metal smelters, and secondary sulfates.
- There have been only a limited number of studies that have measured the physical and chemical constituents of PM in personal or microenvironmental samples. Available data on PM constituents indicate the following:
    - personal and indoor sulfate measurements often are correlated highly with outdoor and ambient sulfate concentration measurements;
    - for acid aerosols, indoor air chemistry is particularly important because of the neutralization of the acidity by ammonia, which is present at higher concentrations indoors because of the presence of indoor sources of ammonia;
    - for SVOCs, including PAHs and phthalates, the presence of indoor sources will substantially affect the relation between indoor and ambient concentrations;
    - penetration and decay rates are functions of size and will cause variations in the attenuation factors as a function of particle size; infiltration rates will be higher for PM_1 and $PM_{2.5}$ than for PM_{10}, $PM_{10-2.5}$ or ultrafine particles; and
    - indoor air chemistry may increase indoor concentrations of organic PM.
- Even though there is an increasing amount of research being performed to measure PM constituents in different PM size fractions, with few exceptions (i.e., sulfur or sulfates) the current data are inadequate to adequately assess the relationship between personal, indoor, and ambient concentrations of most PM constituents.

Correlations Between Personal Exposures, Indoor, Outdoor, and Ambient Measurements

- Most of the available personal data on PM measurements and information on the relationships between personal and ambient PM come from a few large-scale studies (e.g., the PTEAM study) or the longitudinal panel studies that have been conducted on selected populations, such as the elderly.
- Panel and cohort studies that have measured PM exposures and concentrations typically have reported their results in terms of three types of correlations: (1) longitudinal, (2) pooled, and (3) daily-average correlations between personal and ambient or outdoor PM.
- The type of correlation analysis performed can have a substantial effect on the resulting correlation coefficient. Low correlations with ambient concentrations could result when people with very different nonambient exposures are pooled even though their individual personal exposures may temporally be correlated highly with ambient concentrations.
- Longitudinal and pooled correlations between personal exposure and ambient or outdoor PM concentrations reported by various investigators varied considerably among the different studies and in each study between the study subjects. Most studies report longitudinal correlation coefficients that range from close to zero to near one, indicating that individual's activities and residence type may have a significant effect on total personal exposures to PM.
- Longitudinal studies that measured sulfate found high correlations between personal and ambient sulfate.
- In general, probability-based population studies tend to show low pooled correlations because of the high differences in levels of nonambient PM-generating activities from one subject to another. In contrast, the absence of indoor sources for the populations in several of the longitudinal panel studies resulted in high correlations between personal exposure and ambient PM within subjects over time for these populations. However, even for these studies, correlations varied by individual depending on their activities and the microenvironments that they occupied.

Potential Sources of Error Resulting from Using Ambient Particulate Matter Concentrations in Epidemiological Analyses

As yet, there is no clear consensus among exposure analysts as to how well community monitor measurements of ambient air PM concentrations represent a surrogate for personal exposure to total PM or to ambient PM.

- Measurement studies of personal exposures to PM are still few and limited in spatial, temporal, and demographic coverage. Consequently, with the exception of a few longitudinal panel studies, most epidemiological studies on PM health effects have relied on daily-average PM concentration measurements obtained from ambient community monitoring data as a surrogate for the exposure variable.
- Because individuals are exposed to particles in a multitude of indoor and outdoor microenvironments during the course of a day, concerns about error introduced in the estimation of PM risk coefficients using ambient, as opposed to personal PM measurements, have been raised.
- Total personal exposures to PM could vary from person to person, and even day to day, depending on the specific activities of each person. Separation of PM exposures into two components, ambient and nonambient PM, would reduce potential uncertainties in the analysis and interpretation of PM health effects data.
- Available data indicate that PM mass concentrations, especially fine PM, typically are distributed relatively uniformly in most metropolitan areas, thus reducing the potential for exposure misclassification because of spatial variability when a limited number of ambient PM monitors are used to represent population average ambient exposures in community time-series or long-term, cross-sectional epidemiological studies of PM.
- Even though the spatial variability of PM (in particular, $PM_{2.5}$) mass concentrations in urban environments seems to be small, the same conclusions drawn above regarding the influence of measurement errors may not necessarily hold for all PM components.
- There are important differences in the relationship of ambient PM concentrations with ambient PM exposures and with nonambient PM exposures. Various researchers have shown that ambient PM exposure is a function of ambient PM concentration and that concentrations of ambient PM are driven by meteorology, by changes in source emission rates, and in locations of emission sources relative to the measurement site. However,

nonambient PM exposure is independent of ambient PM concentration because concentrations of nonambient PM are driven by the daily activities of people.

- Because personal exposures also include a contribution from ambient concentrations, the correlation between daily-average personal exposure and the daily-average ambient concentration increases as the number of subjects measured daily increases. An application of a Random Component Superposition model has shown that the contributions of ambient PM_{10} and indoor-generated PM_{10} to community mean exposure can be decoupled in modeling urban population exposure distributions.
- If linear nonthreshold models are assumed in time-series analysis of daily-average ambient PM concentrations and community health data, nonambient PM exposure is not expected to contribute to the relative risk estimates determined by regression of health responses on ambient PM concentration.
- Using the PTEAM study data, analysis of exposure measurement errors in the context of time-series epidemiology has shown that the error introduced by using ambient PM concentrations as a surrogate for ambient PM exposure biases the estimation of health risk coefficients low by the ratio of ambient PM exposure to ambient PM concentration (called the attenuation factor). However, the health risk coefficient determined using ambient PM concentrations provides the correct information on the change in health risks that would be produced by a change in ambient concentrations.
- Because sources and chemical composition of particulate matter affecting personal exposures in different microenvironments vary by season, day-of-the-week, and time of day, it is likely that some degree of misclassification of exposures to PM toxic agents of concern will be introduced when health-effects models use only daily-average mass measures such as PM_{10} or $PM_{2.5}$. Because of the paucity of currently available data on many of these factors, at this point it is impossible to ascertain the significance of these more complex exposure misclassification problems in the interpretation of results from PM epidemiology.
- Exposure measurement errors may depend on particle size and composition. $PM_{2.5}$ better reflects personal exposure to PM of outdoor origin than PM_{10}. Various indicators of ultrafine particle concentrations or other components of PM may also be useful exposure indicators for epidemiological studies.

- Seasonal or temporal variations in the measurement errors and their correlations between different PM concentration measures and co-pollutants (e.g., SO_2, CO, NO_2, O_3) could influence the error analysis results but not likely the interpretation of current findings.
- Multipollutant personal exposure studies have suggested that ambient concentrations of gaseous co-pollutants serve as surrogates of personal exposures to particles rather than as confounders. The implications for epidemiology are discussed in Chapters 8 and 9.
- Ordinarily, PM exposure measurement errors are not expected to influence the interpretation of findings from either the community time-series or long-term epidemiological studies that have used ambient concentration data if they include sufficient adjustments for seasonality and key personal and geographic confounders.
- In the context of long-term epidemiological studies, it appears that the errors introduced in estimating ambient PM indoor/ambient PM outdoor ratios have much more influence on the accuracy of the microenvironmental exposure estimation approach than do errors in estimating time spent in these microenvironments.
- To reduce exposure misclassification errors in PM epidemiology, conducting new cohort studies of sensitive populations with better real-time techniques for exposure monitoring and further speciation of indoor-generated, ambient, and personal PM mass are essential.
- Based on statistical modeling considerations, it is expected that existing PM exposure measurement errors or uncertainties most likely will reduce the statistical power of the PM health effects analysis, thus making it difficult to detect a true underlying association between the correct exposure metric and the health outcome studied.
- Although exposure measurement errors for fine particles are not expected to influence the interpretation of findings from either the community time-series or the long-term, cross-sectional epidemiological studies that have used ambient concentration data, they may underestimate the strength of the effect. Sufficient data are not available to evaluate the effect of exposure measurement error for other PM species or size fractions.

Key Findings

- Most people spend most of their time indoors where they are exposed to indoor-generated PM and ambient PM that has infiltrated indoors.
- Indoor-generated and ambient PM differ in sources, sizes, chemical composition, and toxicity.
- The ambient PM concentration and the indoor PM concentration can be measured by outdoor and indoor monitors. The total personal exposure can be measured by a personal exposure monitor carried by the person. However, the concentrations of indoor-generated PM and ambient PM that has infiltrated indoors and the related values of ambient and nonambient PM exposures must be estimated.
- From a regression of individual, daily values of total personal exposure on daily PM concentrations, the intercept gives the average nonambient PM exposure and the slope gives the average attenuation factor (the ratio of ambient PM exposure to ambient PM concentration).
- Similarly, from a regression of individual, daily values of indoor PM concentration on daily ambient concentrations, the intercept gives the average concentration of indoor-generated PM and the slope gives the average infiltration factor (concentrations of ambient PM that has infiltrated indoors/ambient PM concentration).
- The attenuation factor and the infiltration factor depend on the penetration coefficient, the fraction of ambient PM that penetrates through the walls, doors, windows, etc.; the deposition or removal rate, a measure of how rapidly PM within the indoor microenvironment is removed by deposition to surfaces or by filtration in a heating/cooling system; and the air exchange rate, a measure of how rapidly indoor air is replaced by outdoor air. The attenuation factor also depends on the fraction of time spent outdoors.
- The air exchange rate is an important variable for determining the concentration of ambient PM found indoors. It can be measured by release and measurement of an inert tracer gas indoors. The air exchange rate increases with opening of windows or doors or operation of window or attic fans. It also increases as the indoor/outdoor temperature difference increases. For closed homes, i.e., no open windows or doors, the air exchange rate does not appear to be a function of wind speed or direction.

1 - The penetration coefficient and the deposition rate can be estimated from measurements of outdoor and indoor concentrations under conditions when there are no indoor sources (night time or unoccupied home). These parameters are functions of particle size. The penetration coefficient is high and the deposition rate is low for accumulation mode particles (0.1 to 1.0 µm). The penetration coefficient is lower and the deposition rate is higher for ultrafine particles (< 0.1 µm) and coarse mode particles (> 1.0 µm). The attenuation factor and the infiltration factor are higher for particles in the accumulation mode than for ultrafine or coarse particles.

2 - The attenuation factor and the infiltration factor will vary as the air exchange rate and therefore will vary with season and housing characteristics. These factors will increase with increased opening of windows and doors. For closed homes, these factors will increase with an increase of the indoor/outdoor temperature difference but they do not appear to be affected by wind speed or direction.

3 - The regression technique is useful for finding average values of the attenuation factor and the nonambient exposure and possibly for estimating the distribution of individual, daily values of the nonambient PM exposure.

4 - However, individual, daily values of the ambient PM exposure, the nonambient PM exposure, and the attenuation factor are needed. These may be determined from individual, daily values of the total PM personal exposure and daily ambient PM concentrations by several techniques:

5 (1) *Mass balance technique.* Direct measurement of the air exchange rate, measurement of the fraction of time spent outdoors by a diary of the subject's activity pattern, and use of the equilibrium mass balance equation for the attenuation factor with estimated values of the penetration coefficient and the deposition rate.

6 (2) *Sulfate ratio technique.* Individual, daily values of the attenuation factor (for $PM_{2.5}$) will be given by individual, daily values of personal exposure to sulfate / the daily ambient sulfate concentration provided there are no indoor sources of sulfate and sulfate and $PM_{2.5}$ have similar particle size distributions.

(3) *Recursive technique.* Indoor-generated emissions, which tend to be episodic, can be removed from a continuous record of indoor PM concentration, allowing separation of indoor-generated PM and ambient PM that has infiltrated indoors.

- In pooled studies (different subjects measured on different days), individual, daily values of the total PM exposure are usually not well correlated with the daily ambient PM concentrations. In longitudinal studies (each subject measured for multiple days), individual, daily values of the total PM personal exposure and the daily ambient PM concentrations are found to be highly correlated for some, but not all subjects.
- Only one study has reported estimated individual, daily values of ambient and nonambient PM exposure. Individual, daily values of the total PM personal exposure and the daily ambient PM concentrations were poorly correlated. However, individual, daily values of ambient PM exposure and the daily ambient PM concentrations were highly correlated. Individual daily values of ambient and nonambient PM exposure were not well correlated. Individual daily values of nonambient PM exposure and daily ambient PM concentrations were also not well correlated.
- These key findings will be used in examining the implications of using the ambient PM concentration instead of the total PM personal exposure (or the ambient PM exposure) in epidemiological studies.

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