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Second External Review Draft

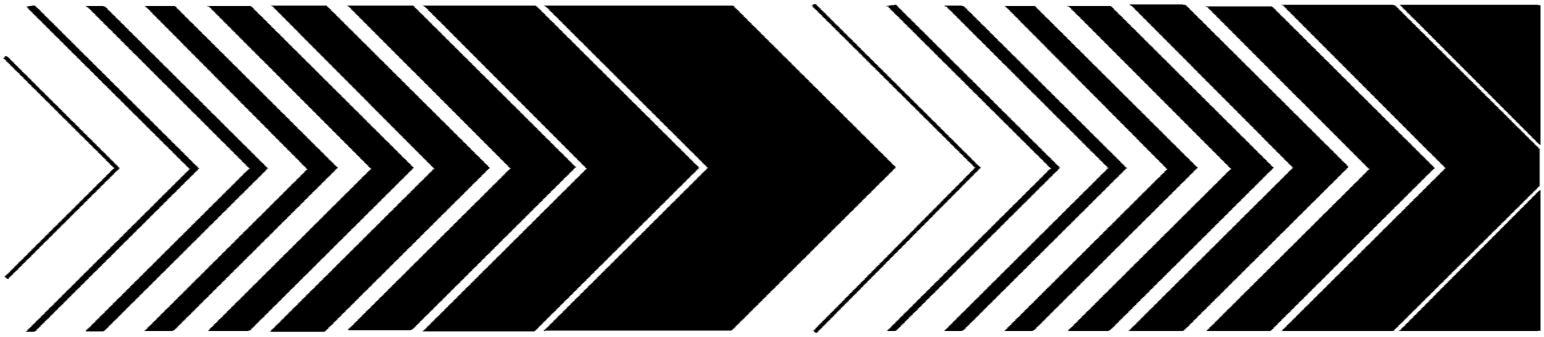
EPA

Air Quality Criteria for Particulate Matter

Volume I

Notice

This document is a preliminary draft. It has not been formally released by EPA and should not at this stage be construed to represent Agency policy. It is being circulated for comment on its technical accuracy and policy implications.



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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 ($\leq 10\ \mu$m) 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 $\leq 2.5\ \mu$m ($PM_{2.5}$) were promulgated in July 1997.

This Second External Review Draft of revised Air Quality Criteria for Particulate Matter assesses new scientific information that has become available mainly between early 1996 through December 2000. 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. Extensive additional pertinent information is expected to be published during the next 6 to 9 mo (including results from a vastly expanded EPA PM Research program and from other federal and state agencies, as well as other partners in the general scientific community) and, as such, the findings and conclusions presented in this draft document must be considered only provisional at this time. Public comments and CASAC review recommendations will be taken into account, along with any pertinent newly available information published or accepted for peer-reviewed publication by May/June 2001, in making any appropriate further revisions to this document for incorporation into a Third External Review Draft. That draft is expected to be released in September/October, 2001 for further public comment and CASAC review (December 2001) in time for a final version to be completed by early 2002. 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 options 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 NGO's 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).

The NCEA of EPA acknowledges the contributions provided by authors, contributors, and reviewers and the diligence of its staff and contractors in the preparation of this document.

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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 exposure to various concentrations of PM in ambient air. The document is not intended as a complete and detailed literature review, but rather focuses on assessment and integration of information most relevant to PM NAAQS criteria development, based on pertinent literature mainly available through December 2000. This introductory chapter presents a brief summary of the 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 this document.

1.1 LEGISLATIVE REQUIREMENTS

Sections 108 and 109 of the U.S. Clean Air Act (CAA) (U.S. Code, 1991) govern the establishment, review, and revision of National Ambient Air Quality Standards (NAAQS). Section 108 directs the 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 exposure-related effects on public health and welfare that may be expected from the presence of the pollutant in ambient air.

Section 109(a,b) 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 judgment of the Administrator, based on the criteria and allowing for an adequate margin of safety, is requisite to protect the public health. Under Section 109(b) of the CAA, the EPA

Administrator must consider available information to set secondary NAAQS that are based on the criteria and are requisite to protect public welfare from any known or anticipated adverse effects associated with the presence of such pollutants. Welfare effects include effects on vegetation, crops, soils, water, animals, manufactured materials, visibility, weather, and climate, as well as damage to and deterioration of property, hazards to transportation, and effects on economic value and personal comfort and well-being. Section 109(d) also requires periodic review and, if appropriate, revision of existing criteria and standards, and it requires an independent committee of non-EPA experts, the Clean Air Scientific Advisory Committee (CASAC), to provide the EPA Administrator advice and recommendations regarding the scientific soundness and appropriateness of criteria and NAAQS for PM and other “criteria air pollutants” (e.g., ozone, nitrogen oxides, sulfate dioxide, carbon monoxide, lead) regulated under CAA Sections 108-109.

1.2 HISTORY OF PREVIOUS PARTICULATE MATTER CRITERIA AND NATIONAL AMBIENT AIR QUALITY STANDARDS REVIEWS

On April 30, 1971 (Federal Register, 1971), EPA promulgated the original primary and secondary NAAQS for PM under Section 109 of the CAA. The reference method for measuring attainment of these standards was the “high-volume” sampler (Code of Federal Regulations, 1977), which collects ambient PM up to a nominal size of 25 to 45 micrometers (μm) (i.e., so-called “total suspended particulate” or “TSP”). Thus, TSP was the original indicator for the PM NAAQS. 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. The next review of PM air quality criteria and standards was completed in July 1987, when the original TSP NAAQS set in 1971 were revised to protect against adverse health effects of inhalable airborne particles with an upper 50% cut-point of 10-μm aerodynamic diameter (PM_{10}), which can be deposited in the lower (thoracic) regions of the human respiratory tract (Federal Register, 1987). Identical primary and secondary PM_{10} standards were set 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 3 years.

1.2.1 The 1997 Particulate Matter National Ambient Air Quality Standards Revision

The EPA initiated the last previous review of the air quality criteria and standards for PM in April 1994 by announcing its intention to develop revised Air Quality Criteria for Particulate Matter (henceforth, the “PM Air Quality Criteria Document” or PM AQCD). Thereafter, the EPA presented its plans for review of the criteria and standards for PM under a highly accelerated, court-ordered schedule 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 workshops were held by EPA’s National Center for Environmental Assessment RTP Division (NCEA-RTP) in November 1994 and January 1995 to discuss important new health effects information useful in preparing initial PM AQCD draft materials. External review drafts of the PM AQCD then were made available for public comment and were reviewed by CASAC at public meetings held in August 1995, December 1995, and February 1996. The CASAC came to closure in its review of the PM AQCD, 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 in response to public and CASAC comments were incorporated as appropriate in the final 1996 PM AQCD (U.S. Environmental Protection Agency, 1996a). A PM Staff Paper (SP), prepared by EPA’s Office of Air Quality Planning and Standards (OAQPS) and drawing on the 1996 PM AQCD and other exposure and risk assessments to pose options for PM NAAQS decisions, also underwent similar CASAC review and public comment, with consequent revision to its July 1996 final form (U.S. Environmental Protection Agency, 1996b).

The SP analyses served as key inputs to subsequently published proposals for revision of the primary PM NAAQS. Taking into account information and assessments presented in the PM AQCD and the SP, advice and recommendations of CASAC, and public comments received on the proposal, the EPA Administrator revised the PM NAAQS by adding new $PM_{2.5}$ standards and by revising the form of the 24-h PM_{10} standard. Specifically, in July 1997, the Administrator made the following revisions to the PM NAAQS:

(1) The suite of PM standards was revised to include an annual primary $PM_{2.5}$ standard and a 24-h $PM_{2.5}$ standard.

(2) The 24-h $PM_{2.5}$ standard is met when the 3-year average of the 98th percentile of 24-h $PM_{2.5}$ concentrations at each population-oriented monitor within an area is less than or equal to 65 μg/m^3, with fractional parts of 0.5 or greater rounding up.

(3) The annual $PM_{2.5}$ standard is met when the 3-year average of the annual arithmetic mean $PM_{2.5}$ concentrations, from single or multiple community-oriented monitors is less than or equal to 15 μg/m^3, with fractional parts of 0.05 or greater rounding up.

(4) The form of the 24-h PM_{10} (150 μg/m^3) standard was revised to be based on the 3-year average of the 99th percentile of 24-h PM_{10} concentrations at each monitor within an area.

(5) In addition, the Administrator retained the annual PM_{10} standard at the level of 50 μg/m^3, which is met when the 3-year average of the annual arithmetic mean PM_{10} concentrations at each monitor within an area is less than or equal to 50 μg/m^3, with fractional parts of 0.5 or greater rounding up.

The principal focus of the last review of the air quality criteria and standards for PM was on recent epidemiological evidence reporting associations between ambient concentrations of PM and a range of serious health effects. Particular 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 particles with an upper 50% cutpoint of 2.5-μm aerodynamic diameter. $PM_{10-2.5}$ refers to those particles with an upper 50% cutpoint 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. Detailed discussions of 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, can be found in the 1996 PM AQCD and in the 1996 OAQPS SP (U.S. Environmental Protection Agency, 1996b).

1.2.2 Presidential Memorandum: Next Particulate Matter Review and Research

On July 18, 1997, the EPA published a final rule revising the NAAQS for PM (Federal Register, 1997a) and, on the same day, a final rule revising the Ozone NAAQS (Federal Register, 1997b). A Presidential Memorandum (Federal Register, 1997c) also was published outlining the Administration's goals for implementing the revised PM and Ozone NAAQS. The Memorandum directed EPA to provide to CASAC within 90 days and to publish a notice outlining its schedule for the next periodic review of PM and to complete the next review, including review by CASAC, within 5 years after issuance of the revised standards (i.e., by July 2002). Such a schedule would ensure that EPA's review of newly emerging scientific information, which forms the criteria on which the standards are based, and of the standards themselves will have been completed prior to any areas being designated as "nonattainment" under the newly established standards for fine particles (i.e., $PM_{2.5}$ standards) and prior to the imposition of any new controls related to the revised standards. The Presidential Memorandum also directed EPA and other relevant Federal agencies to develop and implement a greatly expanded, coordinated research program. To facilitate timely scientific research within this review period, EPA initiated certain activities immediately, as noted below in the discussion of the PM Research Program.

Particulate Matter Research Program

The EPA broadened 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 further coordination with other research organizations, including the Health Effects Institute and other state-, university-, and industry-sponsored research groups. Beginning in the fall of 1997, public participation has been and continues to be encouraged through workshops and review of program documentation.

To aid identification of needed research efforts, EPA published a particulate matter health risk research needs document (U.S. Environmental Protection Agency, 1998a). That document identifies research needed to improve scientific information supporting future health risk assessment and review of the PM NAAQS. The document aimed to provide a foundation for PM research coordination among Federal agencies and other research organizations and served as one useful input to National Research Council PM research deliberations. In January 1998, the National Research Council (NRC) established its Committee on Research Priorities for Airborne Particulate Matter in response to a request from Congress in the Fiscal 1998 appropriation to EPA. This Committee is charged to identify the most important research priorities relevant to setting particulate matter standards, to develop a conceptual plan for particulate matter research, and to monitor research progress toward improved understanding of the relationship between particulate matter and public health. The Committee issued its first report in early 1998 (National Research Council, 1998) and a second one in 1999 (National Research Council, 1999).

The EPA's PM Research Program includes studies to improve understanding of the formation and composition of fine PM, the characteristics or components of PM that are responsible for its health effects, the mechanisms by which these effects are produced, and improved measurements and estimation of population exposures to PM. Specific EPA research efforts include controlled human exposure studies, in vivo and in vitro toxicology, epidemiology, atmospheric sciences including monitoring and modeling studies, development of data on emissions of fine particles from stationary and mobile sources, and identification and evaluation of risk management options. The results from these efforts, as well as related efforts by other Federal agencies and the general scientific community, are expected to enhance substantially the scientific and technical bases for future decisions on the PM NAAQS and for the implementation of PM monitoring and control efforts.

1.3 CURRENT PARTICULATE MATTER CRITERIA AND NATIONAL AMBIENT AIR QUALITY STANDARDS REVIEW

1.3.1 Criteria Review

As with all NAAQS reviews, the purpose is to update the criteria and to determine whether it is appropriate to revise existing standards in light of new scientific and technical information.

Although the EPA concluded in its most recent final rule on the PM standards (Federal Register, 1997a) that the current scientific knowledge provides a strong basis for the revised PM standards, including the establishment of $PM_{2.5}$ standards, there remain scientific uncertainties associated with the health effects of PM and with the means of reducing such effects. Recognizing the importance of developing a better understanding of the effects of fine particles on human health, including their causes and mechanisms, as well as the species and sources of $PM_{2.5}$, EPA has and will continue to sponsor research to address these uncertainties even as this criteria review progresses.

As with other NAAQS reviews, a rigorous assessment of relevant scientific information is to be presented in this updated, revised PM AQCD being prepared by EPA's NCEA-RTP. Development of the document has and will continue to involve 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 sound 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. This Second External Review Draft takes into account the earlier public comments and CASAC review recommendations and includes consideration of relevant new peer-reviewed scientific studies published or accepted for publication from January 1996 through December 2000.

Following CASAC review of the First External Review Draft of this revised PM AQCD in December 1999, EPA's OAQPS started to prepare an SP for the EPA Administrator. Drawing on information in this newly revised PM AQCD, the SP will evaluate policy implications of the key studies and scientific information contained in the AQCD and identify critical elements that EPA staff believes should be considered in reviewing the PM standards. The SP is intended to bridge the gap between the scientific review in the AQCD and the public health and welfare policy judgments required of the Administrator in reviewing the PM NAAQS. For that purpose, the SP will present technical analyses, including air quality analyses and a quantitative health risk assessment, and other factors relevant to the evaluation of the PM NAAQS, as well as staff conclusions and recommendations of options for the EPA Administrator's consideration. The SP also will be reviewed by CASAC and the public, and the final SP will reflect the input received through these reviews.

Following completion of the final SP, the Administrator will then announce in the Federal Register proposals for retaining or revising the current PM NAAQS, and opportunities will be provided for public comment and CASAC review of those proposals. Taking into account public comments and CASAC recommendations, final decisions regarding the current PM NAAQS review are scheduled to be promulgated by July 2002.

1.3.2 Methods and Procedures for Document Preparation

The procedures followed for developing this revised PM AQCD build on the knowledge 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 to be 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 then discussed with CASAC (May 1998) and appropriately revised. An ongoing literature search has continued to be conducted to identify, to the extent possible, all PM literature published since early 1996. Additionally, EPA published (1) a request for information in the Federal Register 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). 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.

The main focus of this revised criteria document is the evaluation and interpretation of 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 PM NAAQS. Initial draft versions of AQCD chapters were evaluated via expert workshops and/or expert written peer reviews, which 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 the 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 was released for public comment and reviewed at a December 1999 CASAC public meeting. Necessary revisions, based on public comments and the recommendations derived from the December 1999 CASAC review, as well as evaluation of newly emerging research results, have been incorporated into this Second External Review Draft. The final version of the newly revised PM AQCD will incorporate changes made in response to public comments and CASAC review of this Second External Review Draft.

New research results are being incorporated into this document as they become available. 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”, which was held in Charleston, SC, in January 2000. 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 into this revised draft EPA PM AQCD so as to allow for its release for public comment and CASAC review by December 2000. 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 this Second External Review Draft of the revised PM AQCD include consideration of such PM 2000 papers and extensive additional information published elsewhere since completion of the previous First External Review Draft.

1.3.3 Approach

The approach to organization and content of this revised PM AQCD is somewhat different from those used for previous criteria documents. Because the most recent prior document (U.S. Environmental Protection Agency, 1996a) provides an extensive discussion of most topic areas, this new document focuses more specifically on critical issues that have been identified as areas needed to improve the scientific basis (criteria) for PM NAAQS, particularly for those areas in which the information database has continued to evolve rapidly.

An initial step was to review the available scientific literature and to focus on the selection of pertinent issues to include in the document as the basis for the development of PM NAAQS criteria. Preliminary issues were identified by the NCEA PM Team and through input from other EPA program and policy offices. Identification of issue topics was derived from the 1996 PM AQCD and SP, their CASAC and public reviews, from the standard promulgation process, and from EPA's PM Research Needs Document. Further identification and clarification of issues resulted from the NRC review and reports on PM research priorities. The CASAC review of the PM AQCD Development Plan and public comments on draft AQCD materials at various stages of their development also has played an important role in 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) the concise summary of key findings derived from previous PM criteria reviews and (2) evaluation of the most pertinent new key information, with greater emphasis on more interpretive assessment. This approach reflects recommendations made by CASAC.

Building on the previous PM AQCD, most of the scientific information selected for review and discussion in the text is from literature published since completion of the previous PM AQCD (U.S. Environmental Protection Agency, 1996a). To aid in development of a concise document, compilation of summary tables of the relevant published literature and selective discussion of the literature has been undertaken, and increased emphasis has been placed in text discussions on interpretive evaluation and integration of key points derived from the newly summarized research results.

1.3.4 Key Issues of Concern

Several broad topics related to the main issues of concern addressed by this revised PM AQCD are summarized below. The document reviews and assesses available data bearing on each of the issues identified below.

1. *Causality*. Evaluation of the evidence for or against a causal relationship between health outcomes and ambient PM and/or specific physical-chemical components.
    - Specific components of interest include size classes such as PM_{10}, $PM_{10-2.5}$, $PM_{2.5}$, and ultrafine particles. Chemical components include transition metals, acidity, sulfates, nitrates, and organics.
    - Expand review of foundations of causal inference for associated PM air pollution health effects.
    - Access new long-term PM exposure and health data to broaden interpretation of long-term exposure findings.
    - Review data exploring potential mechanisms of response to PM physical-chemical characteristics, response pathway, and exposure-dose-response relationships (laboratory and clinical research).
2. *Uncertainties.* In carrying out overall assessment, address the following types of uncertainty.
    - Uncertainties between stationary PM monitoring instruments and personal exposure to PM of ambient origin, especially for susceptible groups and their related activity patterns. Specific topics include measurement error in outdoor monitors themselves, use of central monitors for estimates of community concentrations, and the use of community concentrations as a surrogate for personal exposure to particles of ambient origin.
    - Uncertainties related to particulate matter size fraction, particle number, surface area, and content of semi-volatile components.
    - Uncertainties about the effects of long-term PM exposure, such as life shortening, and development and progression of disease.
    - Uncertainties because of coexposure to other pollutants such as O_3, SO_2, CO, and NO_2, and because of meterological factors.
    - Uncertainties because of potential confounding in epidemiologic studies (e.g., economic factors, demographic and lifestyle attributes, genetic susceptibility factors, occupational exposure, medical care).

- Uncertainty about shape of concentration-response (CR) relationships and associated community risks (linear and threshold models for CR).
- Uncertainty about methods for synthesis of health outcome studies and evaluation of sensitivity and confounding aspects, including but not limited to meta-analyses.

3. *Biological Mechanisms of Action.* Evaluate data examining mechanisms underlying health outcomes of PM. Mechanistic information aids judgment about causality.
    - New studies have examined mechanisms of action of PM constituents, including transition metals, airborne allergens, and the generation of reactive oxygen species. Different cell types have differing responses to PM components.
    - Newly published studies also have identified potential mechanisms for the production of cardiac arrhythmias by PM constituents, especially in animal models of disease and suggest that particular attention should be accorded to PM metal constituents.
    - Although many new animal toxicology studies involve instillation of previously collected particles and this technique is appropriate to study mechanisms of action, extrapolation to human equivalent exposure/doses is uncertain.
    - Ongoing work on the effects of lung inflammation and PM phagocytosis on subsequent systemic effects, especially cardiac or vascular effects, is needed to provide further information on the relationship between inhaled pollutants and cardiac events.
    - Interpretation of concentrated ambient particles studies. Newly available information is examined from toxicology studies using devices that concentrate (to variable extents) ambient PM to determine PM concentration-response relationships. Again, difficulties are encountered regarding extrapolation to comparable human exposures to ambient PM levels.
4. *Susceptible Populations.* Examine health outcome data to determine specific risk groups that are more susceptible than normal healthy adults to adverse effects from PM exposure.
    - Preexisting respiratory or cardiovascular disease in conjunction with advanced age appear to be important factors in PM mortality susceptibility.
    - For morbidity health endpoints, children and asthmatics potentially may display increased sensitivity to PM exposure. Data will be examined for coherence.
    - Patterns of respiratory tract deposition, clearance, and retention in susceptible populations have been studied recently and provide evidence of differences in respiratory tract PM deposition for children and small-sized adults and for those with lung diseases.

- Animal models of lung disease exposed to PM constituents suggest a role for PM in cardiac death.

5. *Environmental Effects.* Evaluate several types of PM welfare effects.
   - Vegetation and ecosystem effects.
   - Visibility effects.
   - Materials damage.
   - Role of PM in atmospheric radiative transfer and potential consequences for penetration of biologically harmful UVB to the earth's surface and for climate change.
6. *Background Information Topics Useful in Evaluating Health Risks.* Topics include the following.
   - New monitoring methods, especially methods used in epidemiology studies.
   - Indicator topics such as $PM_{2.5}$ versus $PM_{1.0}$; ultrafine; and $PM_{2.5}$ versus $PM_{10\text{-}2.5}$.
   - New data patterns of daily and annual concentrations for $PM_{2.5}$, $PM_{10\text{-}2.5}$, and PM_{10}.

1.4 DOCUMENT CONTENT AND ORGANIZATION

The present draft document attempts to critically review and assess relevant scientific literature on PM through December 2000. The material selected for review and comment in the text generally comes from the more recent literature published since early 1996, with emphasis on studies conducted at or near PM pollutant concentrations found in ambient air. Literature discussed in detail in the previous 1996 EPA PM AQCD (U.S. Environmental Protection Agency, 1996a) generally is not discussed in depth in this document. However, some limited treatment is included of the earlier studies judged to be potentially useful in deriving PM NAAQS. Key literature is presented mainly in tables and overall interpretive points are discussed mainly in the text.

The primary emphasis is on consideration of published material that has undergone scientific peer review. However, in the interest of admitting new and important information expected to become available shortly, some material not yet fully published in the open literature but meeting other standards of scientific reporting (i.e., peer review, quality assurance) are now provisionally included. As noted earlier, emphasis has been placed on studies in the range of current ambient levels. However, studies examining effects of higher concentrations have been included if they contain unique data or documentation of a previously unreported effect or mechanism. In reviewing and summarizing the literature, an attempt has been made to present alternative points of view where scientific controversy exists.

The present document includes nine chapters presented in two volumes. Volume 1 contains this general introduction (Chapter 1). It also includes Chapters 2 and 3, which 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 ambient air concentrations. Next, Chapter 4 describes PM environmental effects on vegetation and ecosystems, visibility, man-made materials, and climate, as well as economic impacts of such welfare effects. Chapter 5, which discusses factors affecting exposure of the general population to ambient PM, is also included in Volume 1. The second volume contains Chapters 6 through 9 and the Executive Summary for the entire document. Chapters 6 through 8 evaluate information concerning the health effects of PM (Chapter 6 discusses epidemiological studies; Chapter 7, dosimetry of inhaled particles in the respiratory tract, and Chapter 8, the toxicology of specific types of PM constituents, including laboratory animal studies and controlled human exposure studies). Chapter 9 integrates key information on exposure, dosimetry, and critical health risk issues derived from studies reviewed in the prior chapters.

Neither control techniques nor control strategies for abatement of PM are discussed in this document, although some topics covered may be incidentally relevant to control strategies. Issues germane to the scientific basis for control strategies, but not pertinent to the development of NAAQS criteria, are addressed in numerous other documents issued by EPA’s OAQPS. Technologies for controlling PM emissions also are discussed in other documents issued by OAQPS. Also, certain issues of direct relevance to standard setting are not addressed explicitly in this document, but instead are analyzed in documentation prepared by OAQPS as part of its regulatory analyses materials. Such analyses include (1) delineation of particular adverse effects that the primary and secondary NAAQS are intended to protect against, (2) exposure analyses and assessment of consequent risk, and (3) discussion of factors to be considered in determining an adequate margin of safety. Key points and conclusions from such analyses will be presented in the PM SP prepared by OAQPS for review by CASAC. Although scientific data contribute significantly to decisions regarding the above issues, their resolution cannot be achieved solely on the basis of experimentally acquired information. Final decisions on items (1) and (3) are made by the EPA Administrator, as mandated by the CAA.

A fourth issue directly pertinent to standard setting is identification of populations at risk, which is basically a selection by EPA of the subpopulation(s) to be protected by the promulgation of a given standard. This issue is addressed only partially in this document. For example, information is presented on factors, such as preexisting disease, that may biologically predispose individuals and subpopulations to adverse effects from exposures to PM. The characterization of population risk, however, requires information above and beyond data on biological predisposition (e.g., information on estimated exposure, activity patterns, and personal habits). Such information is typically addressed in the SP developed by OAQPS.

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2. PHYSICS, CHEMISTRY, AND MEASUREMENT OF PARTICULATE MATTER

An extensive review of the physics and chemistry of particulate matter (PM) was included in Chapter 3 of the 1996 EPA document Air Quality Criteria for Particulate Matter (U.S. Environmental Protection Agency, 1996). Chapter 2 of this new version of the PM Air Quality Criteria Document (PM AQCD) provides background information on the physics and chemistry of atmospheric particles that may be useful in reading subsequent sections and chapters. New information needed to understand risk assessment is discussed, with emphasis placed on differences between fine and coarse particles and differences between the nuclei mode and the accumulation mode within fine particles.

Chapter 4 of the 1996 PM AQCD (U.S. Environmental Protection Agency, 1996) 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 some progress in developing new and improved measurement techniques. Therefore, a more extensive survey on measurement problems and on newly developed measurement techniques is included below in Section 2.2. For more detail and older references, the reader is referred to Chapter 3 and 4 of the 1996 PM AQCD (U.S. Environmental Protection Agency, 1996).

2.1 PHYSICS AND CHEMISTRY OF PARTICULATE MATTER

2.1.1 Definitions

Atmospheric particles originate from a variety of sources and possess a range of morphological, chemical, physical, and thermodynamic properties. Examples 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 of organic compounds. Primary particles are emitted directly from sources. Secondary particles are formed in the atmosphere from products of chemical reactions of gases from natural and anthropogenic sources such as SO_2, NO_X, and certain organic compounds. 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.

The composition and behavior of airborne particles are fundamentally linked with those of the surrounding gas. 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 often used to refer to the suspended particles only. “Particulate” is an adjective and should only be used as a modifier, 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, most often the physical and chemical characteristics of particles are measured separately. Size distributions by particle number, from which surface area and volume distributions are calculated, often are determined by physical means, such as electrical mobility or light scattering of suspended particles. Chemical composition usually is determined by analysis of collected samples, although sulfate 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 suspended particles passing through a sensing volume, provide elemental composition of individual particles by particle size and, thus, are bringing the description envisioned by Friedlander (1970) 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 often described by an "equivalent" diameter (i.e., that of a unit density sphere that would have the same physical behavior). The aerodynamic diameter is important for particle transport, collection, and respiratory tract deposition. The aerodynamic diameter (D_a) depends on the density of the particle. It is defined as the diameter of a spherical particle with a settling velocity equal to that of the particle in question, but with a density of 1 g/cm^3. Particles with the same physical size and shape but different densities will have different aerodynamic diameters. Detailed definitions of the various sizes and their relationships are given in standard aerosol textbooks (e.g., Friedlander [1977], Reist [1984, 1993], Seinfeld and Pandis [1998], Hinds [1999], Vincent [1989, 1995], Willeke and Baron [1993], 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 aerodynamic diameters. The aerodynamic diameter also influences deposition patterns of particles within the lung. Light scattering is strongly dependent on the optical particle size. Particle size distributions, therefore, have a strong influence on atmospheric visibility and, through their effect on radiative balance, on climate. Studies using impactors or cyclones measure the particle-size distribution directly in aerodynamic diameter. The diameters of atmospheric particles range from 1 nm to 100 μm, thus 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 diameters rather than aerodynamic diameters. In recent years, aerodynamic particle sizers, which give a direct measurement of the aerodynamic diameter in the range of approximately 0.7 to 10 μm diameter, have been used with electrical mobility analyzers, which measure the mobility diameter from approximately 0.5 μm to very small particles of the order of 0.005 μm, to cover the range of regulatory interest. 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 must be careful to determine exactly which equivalent diameter is reported. Aerodynamic diameter is the most widely used equivalent diameter. Therefore, particle diameters, unless otherwise indicated, refer to the aerodynamic diameter in the discussions which follow below.

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. It has been found that atmospheric aerosol size distributions frequently may be approximated by a sum of log-normal distributions corresponding to the various modes or fractions. 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

Averaged atmospheric size distributions are shown in Figures 2-1 through 2-3 (Whitby, 1978; Whitby and Sverdrup, 1980). Figure 2-1 describes 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 distribution is shown in Figure 2-2. Figure 2-3

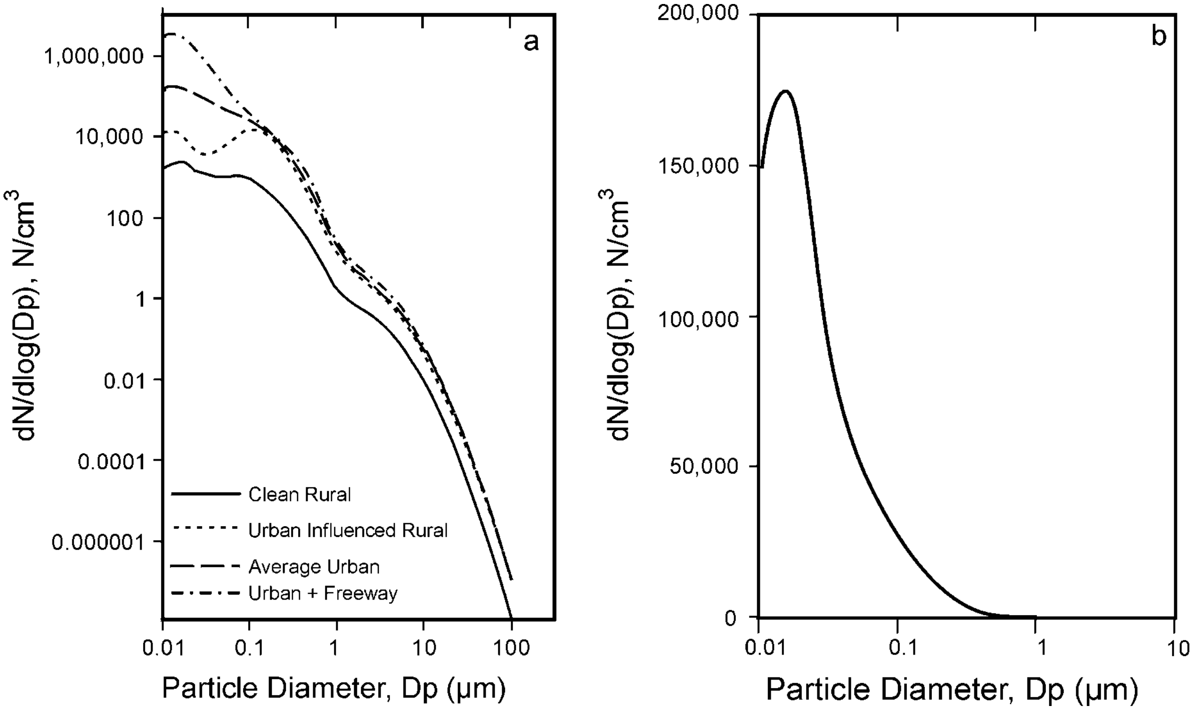

Figure 2-1. Number of particles as a function of particle diameter: (a) number concentrations are shown on a logarithmic scale to display the wide range by site and size; (b) number concentrations for the average urban distribution are shown on a linear scale for which the area under any part of the curve is proportional to particle number in that size range.

Source: Whitby and Sverdrup (1980).

shows the number, surface, and volume distribution for the grand average continental size distribution. Note that the particle diameter is always shown on a logarithmic scale. The particle number is frequently shown on a logarithmic scale in order to display the wide range in number concentration for different particle sizes and different sites. Volume and surface area, and sometimes number, are shown on an arithmetic scale with the distributions plotted 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.

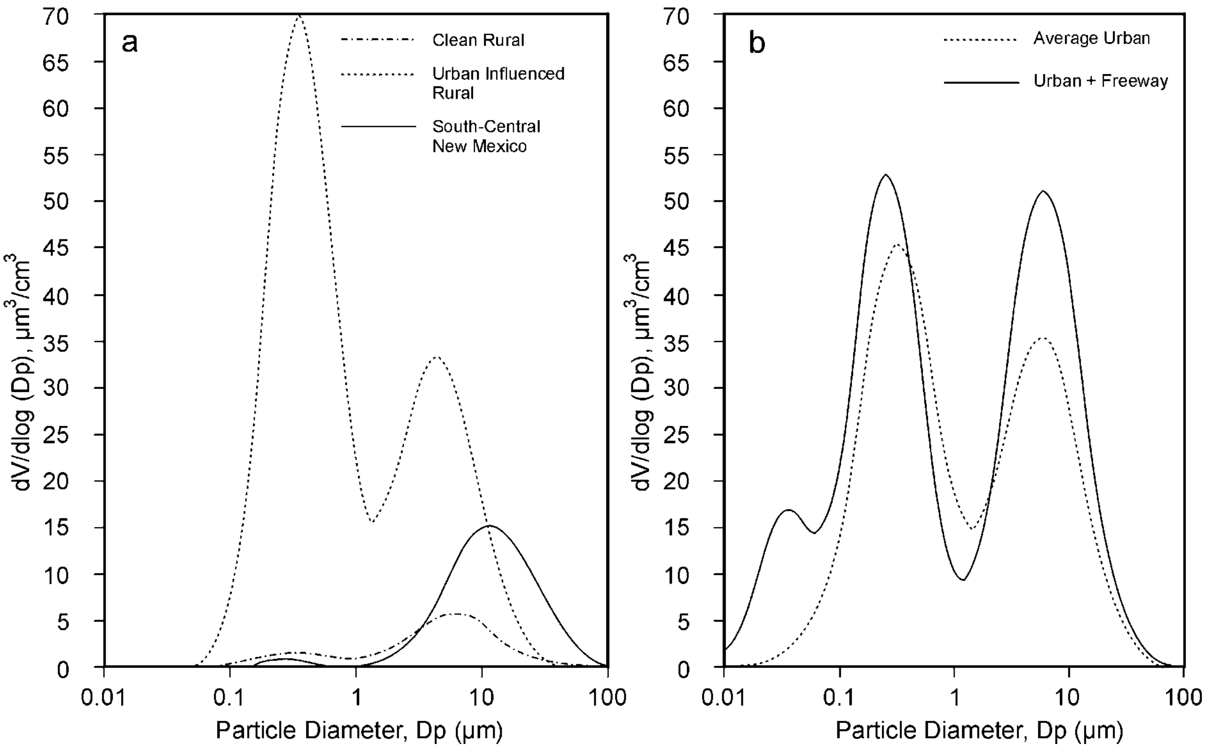

Figure 2-2. Particle volume distribution as a function of particle diameter: (a) for the averaged rural and urban-influenced rural number distributions shown in Figure 2-1 and a distribution from south central New Mexico, and (b) for the averaged urban and freeway-influenced urban number distributions shown in Figure 2-1.

Source: Whitby and Sverdrup (1980) and Kim et al. (1993).

An important feature of the mass or volume size distributions of atmospheric aerosols is their multimodal nature. Volume distributions, measured in ambient air in the United States, are almost always found to be bimodal, with a minimum between 1 and 3 μm. The distribution of particles that are mostly larger than the minimum is termed “coarse.” The distribution of particles that are mostly smaller than the minimum is termed “fine.” Whitby and Sverdrup (1980), Whitby (1978), and Willeke and Whitby (1975) identified three modes: (1) nuclei, (2) accumulation, and (3) coarse. The three modes are most apparent in the freeway-influenced size distribution of Figure 2-2b, in the surface area distribution of Figure 2-3b, and in the in-traffic volume distribution of Figure 2-4. However, the nuclei mode, corresponding to

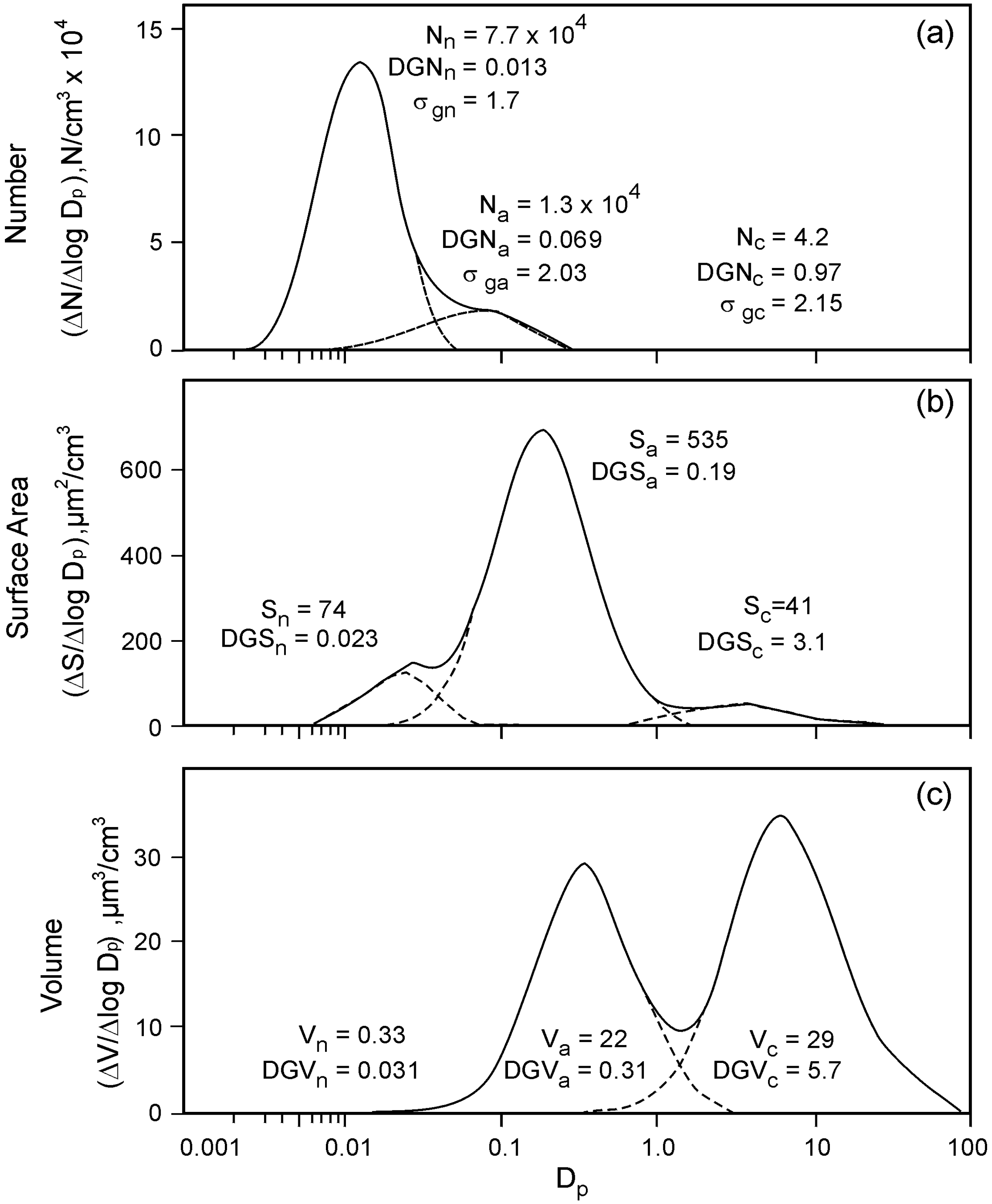

Figure 2-3. Distribution of coarse (c), accumulation (a), and nuclei- or ultrafine (n) -mode particles by three characteristics, a) number (N), b) surface area (S) and c) volume (V) for the grand average continental size distribution. DGV = geometric mean diameter by volume; DGS = geometric mean diameter by surface area; DGN = geometric mean diameter by number; D_p = geometric diameter.

Source: Whitby (1978).

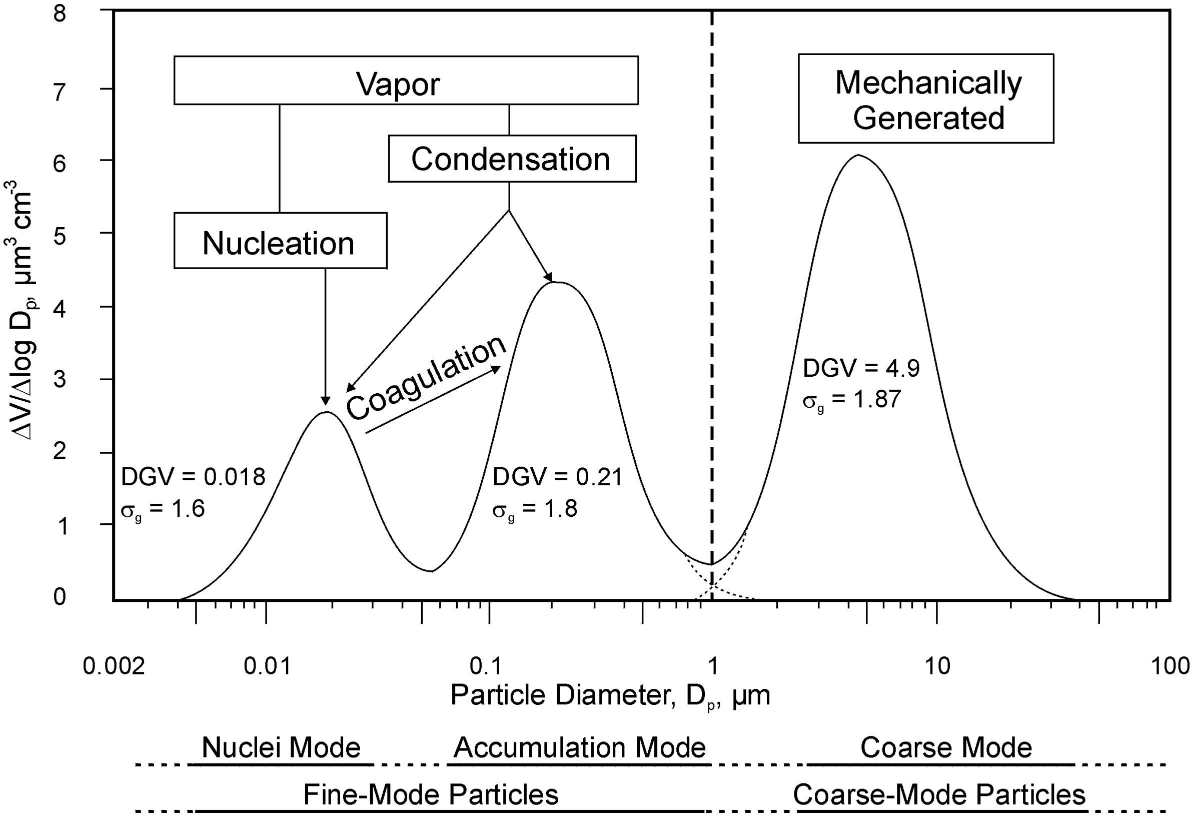

Figure 2-4. Volume size distribution, measured in traffic, showing fine-mode and coarse-mode particles and the nuclei and accumulation modes within the fine-particle mode. DGV (geometric mean diameter by volume, equivalent to volume median diameter) and σ_g (geometric standard deviation) are shown for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

Source: Adapted from Wilson and Suh (1997).

particles below about 0.1 μm, may not be noticeable in volume or mass distributions. The middle mode, from 0.1 to 1 or 2 μm, is the accumulation mode. Fine particles include both the accumulation and the nuclei modes. The third mode, containing particles larger than 1 or 2 μm, is known as the coarse particle mode. The number concentrations of coarse particles are usually too small to be seen in arithmetic plots (Figures 2-1b and 2-3a) but can be seen in a logarithmic plot (Figure 2-1b). Whitby and Sverdrup (1980) observed that rural aerosols, not influenced by sources, have a small accumulation mode and no observable nuclei mode. For urban aerosols, the accumulation and coarse particle modes are comparable in volume. The nuclei mode is small in volume but it dominates the number distributions of urban aerosols. Whitby's conclusions were based on extensive studies of size distributions in a number of western and midwestern locations during the 1970s (Whitby, 1978; Whitby and Sverdrup, 1980). No size-distribution studies of similar scope have been published since then. Newer results from particle counting and impactor techniques, including data from Europe (U.S. Environmental Protection Agency, 1996) and Australia (Keywood et al., 1999, 2000), show similar results.

Definitions of Particle Size Fractions

In the preceding discussion several subdivisions of the aerosol size distribution were identified. Aerosol scientists use four 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; (3) dosimetry or occupational health sizes, based on the entrance into various compartments of the respiratory system; and (4) legally specified, regulatory sizes for air quality standards.

Modal. The modal classification, first proposed by Whitby (1978), is shown in Figure 2-3. The nuclei mode can be seen clearly in the volume distribution only in traffic or near traffic or other sources of nuclei mode particles (Figure 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.

> *Coarse Mode:* The distribution of 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 mechanically generated (e.g., from wind erosion of crustal material).
>
> *Fine Mode:* The distribution of particles with diameters mostly smaller than the minimum in the particle mass or volume distributions, which generally occurs between 1 and 3 μm. These particles are generated in combustion or formed from gases. The fine mode includes the accumulation mode and the nuclei mode.

Nuclei Mode: That portion of the fine particle mode with diameters below about 0.1 μm. The nuclei 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. Toxicologists and epidemiologists use ultrafine to refer to particles in the nuclei-mode size range. Aerosol physicists and material scientists tend to use nanoparticles to refer to particles in this size range generated in the laboratory.

Accumulation Mode: That portion of the fine particle mode with diameters above about 0.1 μm. Accumulation-mode particles normally do not grow into the coarse mode. Nuclei-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.

Over the years, the terms fine and coarse, as applied to particle sizes, 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 particular, $PM_{2.5}$ and fine-mode particles are not equivalent. In this document, the term mode is used with fine and coarse when it is desired to specify the distribution of fine-mode particles or coarse-mode particles as shown in Figures 2-4 and 2-5.

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, usually defined by the upper 50% cut point size, and has arisen in an effort to measure particle size fractions with some special significance (e.g., health, visibility, source apportionment, etc.). Dichotomous samplers split the particles into smaller and larger fractions, which 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 also have been used.

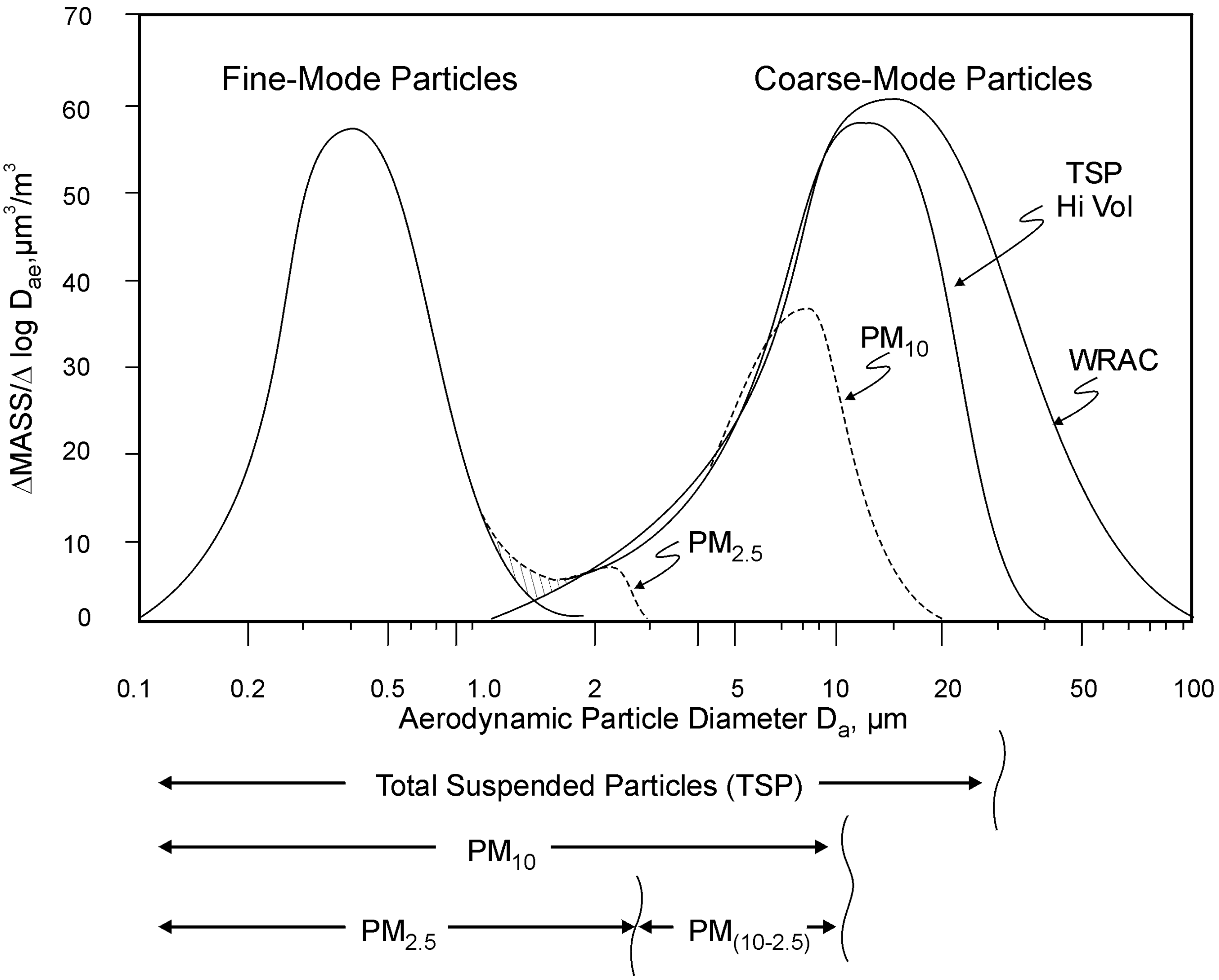

Figure 2-5. An idealized distribution of ambient particulate matter showing fine-mode particles and coarse-mode particles and the fractions collected by size-selective samplers. (WRAC is the Wide Range Aerosol Classifier which collects the entire coarse mode [Lundgren and Burton, 1995].)

Source: Adapted from Wilson and Suh (1997).

Occupational Health or Dosimetric Size Cuts. The occupational health community has defined size fractions for use in the protection of human health. This convention classifies particles into inhalable, thoracic, and respirable particles according to their upper size cuts. However, these size fractions may also be characterized in terms of their entrance into various compartments of the respiratory system. Thus, 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 which 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.

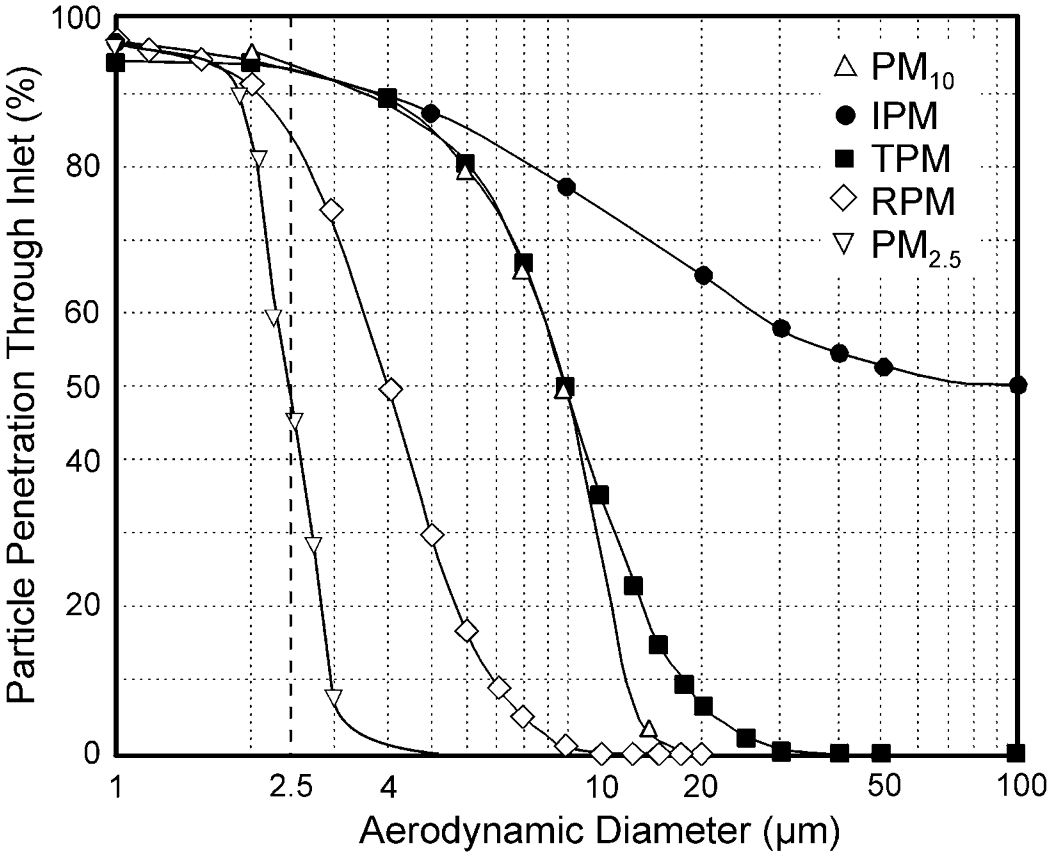

Figure 2-6. Specified particle penetration (size-cut curves) through an ideal (no-particle-loss) inlet for five different size-selective sampling criteria. PM_{10} is defined in the Code of Federal Regulations (1991a). $PM_{2.5}$ is also defined in the Federal Register (1997). Size-cut curves for inhalable 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).

Regulatory Size Cuts. 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 epidemiological studies using concentrations measured with $PM_{2.5}$ samplers as an exposure index. However, the $PM_{2.5}$ sampler was not designed to collect respirable particles. It was designed to collect fine-mode particles because of their different sources (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-mode particles.

Prior to 1997, the indicator for the NAAQS for PM was TSP. TSP is defined by the design of the High Volume Sampler (hivol), which collects all of the fine particles but only part of the coarse particles. 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 (Lundgren and Burton, 1995).

An idealized distribution, showing 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 $PM_{(10-2.5)}$ samplers, is shown in Figure 2-5. PM_{10} samplers, as defined in Appendix J to 40 Code of Federal Regulations (CFR) Part 50 (Code of Federal Regulations, 1991a; Federal Register, 1987), collect all of the fine particles and part of the coarse 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, 1991b). 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 Sampler. The basic design of the FRM is given in the Federal Register (1997, 1998) and as 40 CFR Part 50, Appendix L in the Code of Federal Regulations (Code of Federal Regulations, 1999a). Additional performance specifications are given in 40 CFR Parts 53 and 58 (Code of Federal

Regulations, 1999b). Each actual $PM_{2.5}$ reference method, as represented by a specific sampler design and associated manual operational procedures, must be designated as a reference method under Part 53 (see Section 1.2 of Appendix L). Thus there may be many somewhat different $PM_{2.5}$ FRMs (currently, 6 have been designated).

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). Although these explanations may seem to be easier than (upper 50% cut point of x μm aerodynamic diameter), they are incorrect and misleading because they suggest an upper 100% cut point of x μm. This is illustrated in Figure 2-7, which shows the penetration curve of a PM_{10} sampler where PM_{10} does mean particles less than 10 μm (i.e., a penetration of zero or an exclusion of 100% for particles of 10 μm aerodynamic diameter). PM_x, as defined by EPA, refers to a sampler with a penetration curve that collects 50% of x μm particles and excludes 50% of x μm particles. It also means that some particles >x are collected and not all particles <x 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, they recommended 2.5 μm 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 contains all of the fine particles it may, especially in dry areas or during dry conditions, collect a small fraction of the coarse particles. A PM_{10}-$PM_{2.5}$ 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}-$PM_{2.5}$ mass, or $PM_{(10-2.5)}$, is sometimes called “coarse” particles. However, it would be more correct to call $PM_{2.5}$ an indicator of fine-mode particles (because it contains some coarse-mode particles), $PM_{(10-2.5)}$ an indicator of the thoracic component of coarse-mode particles (because it excludes some coarse-mode particles below 2.5 μm and above 10 μm). 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; so, thoracic PM contains some particles between 10 and 30 μm diameter that are excluded from PM_{10}.

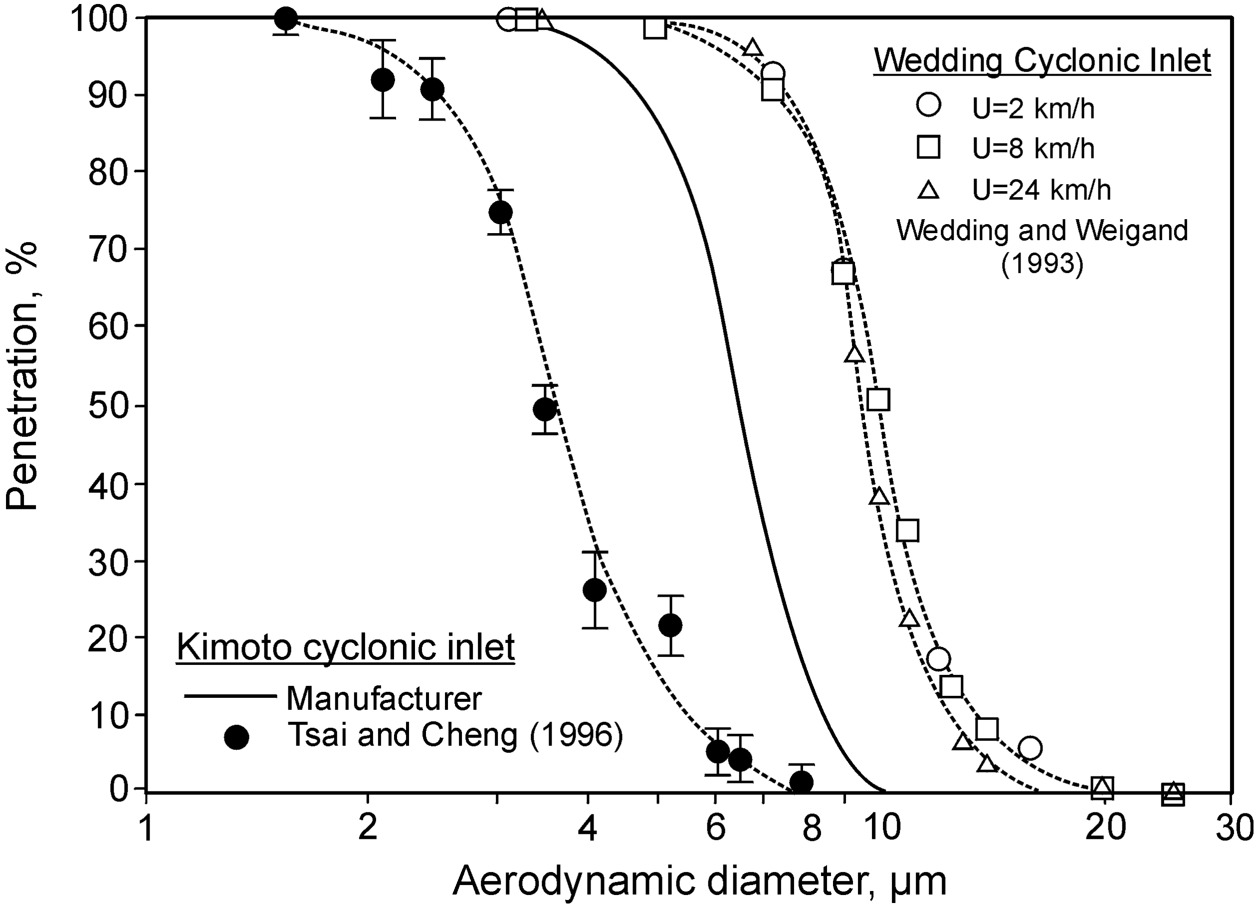

Figure 2-7. Comparison of penetration curves for two PM_{10} beta gauge samplers using cyclone inlets. The Wedding PM_{10} sampler uses the U.S. EPA definition of PM_x as x = 50% cut point. The Kimoto PM_{10} defines PM_x as x = the 100% cut point (or zero penetration).

Source: Tsai and Cheng (1996).

2.1.2.3 Nuclei-Mode Particles

As discussed in Section 8.5.5 of Chapter 8, Toxicology of Particulate Matter, and in Chapter 6, Epidemiology of Human Health Effects from Ambient Particulate Matter, some scientists argue that ultrafine (nuclei-mode) particles pose potential health problems and that some health effects may be more closely associated with particle number or particle surface area than particle mass. Because nuclei-mode particles contribute the major portion of particle number and a significant portion of particle surface area, some further attention to nuclei-mode particles is justified.

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. 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, nuclei mode particles grow into the accumulation mode, but accumulation mode particles do not grow into the coarse mode (see Figure 2-4). More information and references on formation and growth of fine particles may be found in the AQC PM 1996 (U.S. Environmental Protection Agency, 1996).

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, 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; thus 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 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 sufficient to rapidly scavenge the newly formed condensable species. Formation of new particles (nuclei mode) is usually not important except near sources of condensable species. Wilson et al. (1977) report observations of the nuclei mode in traffic. 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 Nuclei-Mode Particles

Nuclei mode 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 sources 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. Nuclei-mode metallic particles were discussed in Section 6.9 of the 1996 PM AQCD (U.S. Environmental Protection Agency, 1996).

(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., 1998a).

(3) *Sulfates and nitrates.* Sulfuric acid (H_2SO_4), or its neutralization products with ammonia (NH_3), ammonium sulfate ($(NH_4)_2SO_4$) or ammonium acid sulfate (NH_4HSO_4), 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 nuclei mode or accumulation mode particles (Clark and Whitby, 1975; Whitby, 1978). The possible formation of ultrafine NH_4NO_3 by reaction of NH_3 and HNO_3 apparently has not been investigated.

(4) *Organic carbon.* 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).

Concentration of Nuclei-Mode 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 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 concentration of SO_2 and OH, which is generated primarily by the photolysis of O_3. Thus, the reductions in SO_2 and O_3 that are expected to form a major basis for attaining $PM_{2.5}$ and O_3 standards and the implementation of Title II and Title IV Clean Air Act programs should 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, 1977) or by aerosol dynamics modules in newer air quality models (Binkowski and Shanker, 1995; Binkowski and Ching, 1995).

Further research is important due to the possibility of enhanced toxicity of ultrafine particles. It is possible that freshly generated ultrafine particles relatively near significant sources could present an additional risk to health, above those associated with particle mass per se. It will, therefore, be important to monitor particle number and surface as well as mass to further delineate the relative effectiveness of strategies for reducing particle mass, surface, and number.

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, 1996). The composition and concentrations of PM are discussed in Chapter 3 of this document.

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 some primary organic compounds; 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 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., which 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 preexisting 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; 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. 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.

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 a result of atmospheric reactions. Such reactions involve 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 (catalyzed by Fe and Mn). These heterogeneous reactions may occur in cloud and fog droplets or in films on atmospheric particles. The NO_2 portion of NO_x can be converted to HNO_3 by reaction with OH radicals during the day. At night, NO_x also is oxidized to nitric acid by a sequence of reactions initiated by O_3, that include nitrate radicals (NO_3) and dinitrogenpentoxide (N_2O_5). 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 in $SO_4^=$ in $(NH_4)_2SO_4$. In addition, acid gases such as SO_2 and HNO_3 may react with coarse particles to form coarse secondary PM containing sulfate and nitrate. Examples include reactions with basic compounds resulting in neutralization (e.g., $CaCo_3 + 2NHO_3 \rightarrow Ca\ (NO_3)_2 + H_2CO_3\uparrow$) 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 is usually 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 may be higher than that of sulfate. 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^+, $SO_4^=$, 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, the gas-phase rate in such plumes during summer midday conditions in the eastern United States 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 $SO_4^=$ can be several times larger than the gas-phase rates given above. Overall, it appears that SO_2 oxidation rates to $SO_4^=$ by gas-phase and aqueous-phase mechanisms may be comparable in summer, but aqueous phase chemistry may dominate in winter.

In the western United States, markedly higher SO_2 conversion rates have been reported in smelter plumes than in power plant plumes. The conversion is 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 and competes with SO_2 for OH.

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.

Organic Aerosol

Organic compounds contribute from 20 to 60% of the dry fine particle mass in the atmosphere (Gray et al., 1984; Shah et al., 1986; U.S. Environmental Protection Agency, 1996). However, organic PM concentrations, composition, and 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 (positive artifact). Semivolatile compounds, originally present in the condensed phase, may evaporate from particles collected on glass, quartz, or Teflon filters (negative artifact). In addition, no single analytical technique is currently capable of analyzing the entire range of organic compounds present in the atmosphere in PM. Even rigorous analytical methods are able to identify only 10 to 20% of the organic PM mass on the molecular level (Rogge et al., 1993a). Even in smog chamber studies of specific compounds, only about 50% of the condensed phase compounds could be identified (Forstner et al., 1997a,b). Measurement techniques are discussed in Section 2.2.3.2. Information on the identification and concentration of the many different organic compounds identified in atmospheric samples is given in Chapter 3.

Formation of Secondary Organic Particulate Matter

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 ambient temperature, saturation vapor pressures. 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. Organic compounds with two double bounds 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 secondary organic PM are not as well understood. Ozone and the hydroxyl radical 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). Understanding the mechanisms of formation of secondary organic PM is important because secondary organic PM 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 secondary organic PM: (1) condensation of oxidized end-products of photochemical reactions (e.g., ketones, aldehydes, organic acids, hydroperoxides), (2) adsorption of organic gases 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 summertime 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 secondary organic PM 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 product.

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 data from Pandis et al. (1991) for β-pinene and 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 given in the above studies. Estimates of the production rate of secondary organic PM in the Los Angeles airshed are provided in the previous 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 were generally between 3 and 4% within a range of existing organic carbon levels between 13 and 100 $\mu g/m^{-3}$. This grouping is consistent with those found by Izumi and Fukuyama (1990). Reasons for the differences in secondary organic PM yields found between the two classes of compounds are not clear.

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., $SO_4^=$, 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 1σ (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. Further studies are needed to determine if these relations are valid at other locations and to what extent the results might be influenced by the evaporation of volatile constituents during or after sampling. It must be emphasized that the inferences drawn from field studies in the Los Angeles Basin are unique to that area and cannot be extrapolated to other areas of the country.

Secondary Organic Aerosol Formation from Oxidation Products of Biogenic Hydrocarbons

The formation of atmospheric aerosols from biogenic emissions has been of interest for many years. Recently, more quantitative results have been reported. Hoffmann et al. (1997) found secondary organic PM yields of ≈5% for open-chain biogenic hydrocarbons such as ocimene and linalool, 5 to 25% for monounsaturated cyclic monoterpenes such as α-pinene, d-3 carene and terpinene-4-ol, and ≈40% for a cyclic monoterpene with two double bonds 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.

Kamens et al. (1999) observed secondary organic PM 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 $\mu gm^{-3}\ ppb^{-1}$ and varied by almost a factor of two depending on the initial mixture.

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. A number of multifunctional oxidation products have been identified in laboratory studies (Yu et al., 1998; Glasius et al., 2000; Christoffersen et al., 1998; Koch et al., 2000; 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; Casimiro et al., 2001; Castro et al., 1999). However, further investigations are needed to accurately access their overall contributions to $PM_{2.5}$ concentrations.

Sampling and characterization of 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 compliance issues related to reducing PM mass concentrations that affect 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. 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. They offered two explanations: (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. If the former consideration is correct, then the production of aerosol carbon from terpene emissions could be substantial; if the latter is correct, then terpene emissions could have been overestimated by the techniques used.

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, which cause gas-particle partitioning to be dynamic on a time scale of a few hours, can cause semivolatile compounds to evaporate during the sampling process. The pressure drop across the filter can also contribute to 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 3.2.3.

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 aerodynamic properties (important for deposition to surfaces, to airways following inhalation, and in sampling instrumentation) and their light scattering properties. 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 in the gas phase (Friedlander and Yeh, 1998; Kao and Friedlander, 1995; Wilson, 1995). An extensive review of this equilibrium as it pertains to ambient aerosols was given in Chapter 3 of the 1996 PM AQCD (U.S. Environmental Protection, Agency, 1996).

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 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), returning typically 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 completely worked out. Mixed anion systems containing nitrate are more difficult because of the equilibrium between particulate NH_4NO_3 and gaseous NH_3 and HNO_3. 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 (H_2SO_4), are hygroscopic (i.e., they form water 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 2-8). A particle can grow to five times its dry diameter as the RH approaches 100% (Figure 2-9). The Federal Reference Methods, for filter measurements of $PM_{2.5}$ and PM_{10} mass, require, after collection, equilibration at a specified, low relative humidity (≈40% RH). This equilibration removes much of the particle-bound water and provides a stable PM mass (see Section 2.2 for details and references). Otherwise, particle mass would be a function of relative humidity and, at higher relative humidities, the particle mass would be largely particle-bound water.

Continuous monitoring techniques must remove particle-bound water before measurement, either by heating or dehumidification. Semivolatile material may be lost during sampling or equilibration. It is certainly lost when the collected sample is heated above ambient. In addition to problems due to the loss of semivolatile species, 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). Large increases in mass with increasing relative humidity were observed for the accumulation mode. The change in particle size with relative humidity also means that particle measurements such as surface area or volume, or composition as a function of size, all must be made at the same RH if the results are to be comparable. These problems are addressed below in more detail, in Section 2.2 on Measurement of Particulate Matter.

2.1.3.4 Removal Processes

The lifetimes of particles vary with size. Coarse particles can settle rapidly from the atmosphere within 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 distances. 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-mode particles of less than ≈10 μm diameter, as well as accumulation-mode and

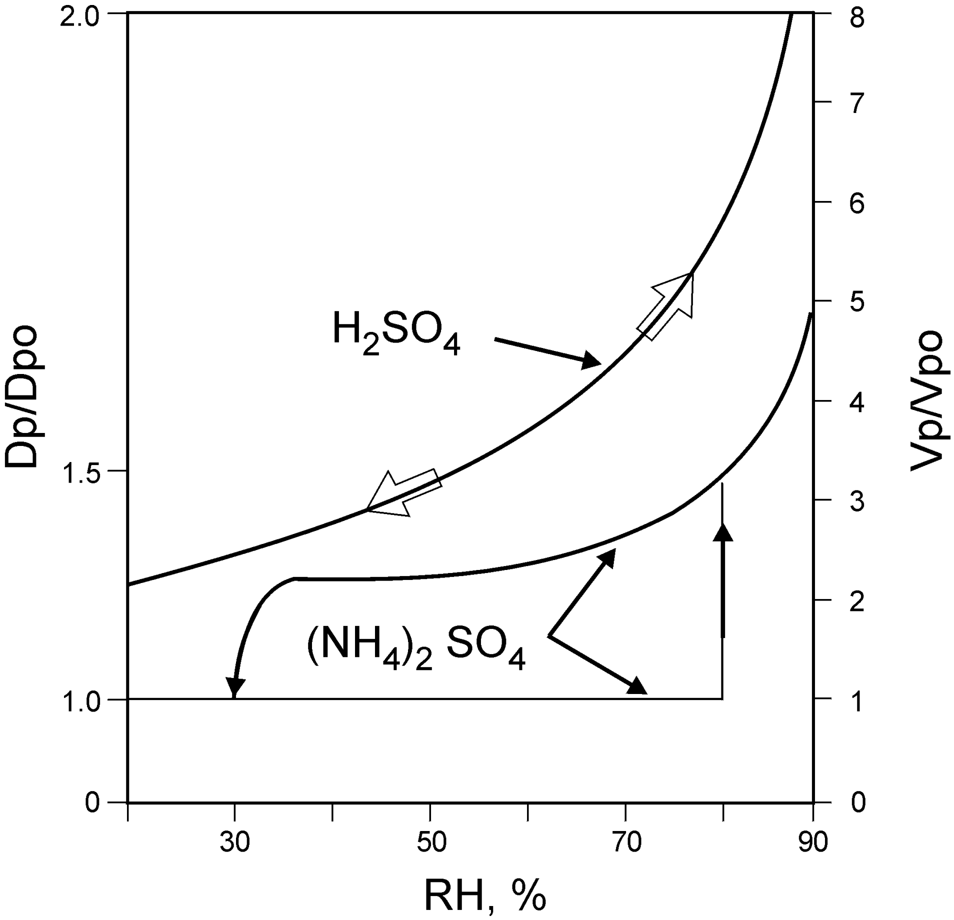

Figure 2-8. Particle growth curves showing fully reversible hygroscopic growth of sulfuric acid (H_2SO_4) particles, deliquescent growth of ammonium sulfate [$(NH_4)_2\ SO_4$] particles at about 80% relative humidity (RH), hygroscopic growth of ammonium sulfate solution droplets at RH greater than 80%, and hysteresis (the droplet remains supersaturated as the RH decreases below 80%) until the crystallization point is reached.

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

nuclei-mode (or ultrafine) particles, all have the ability to penetrate deep into the lungs and to be removed by deposition in the lungs. 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. Accumulation-mode particles are removed from the atmosphere primarily by cloud processes. Fine particles, especially particles with a hygroscopic component, grow as the relative

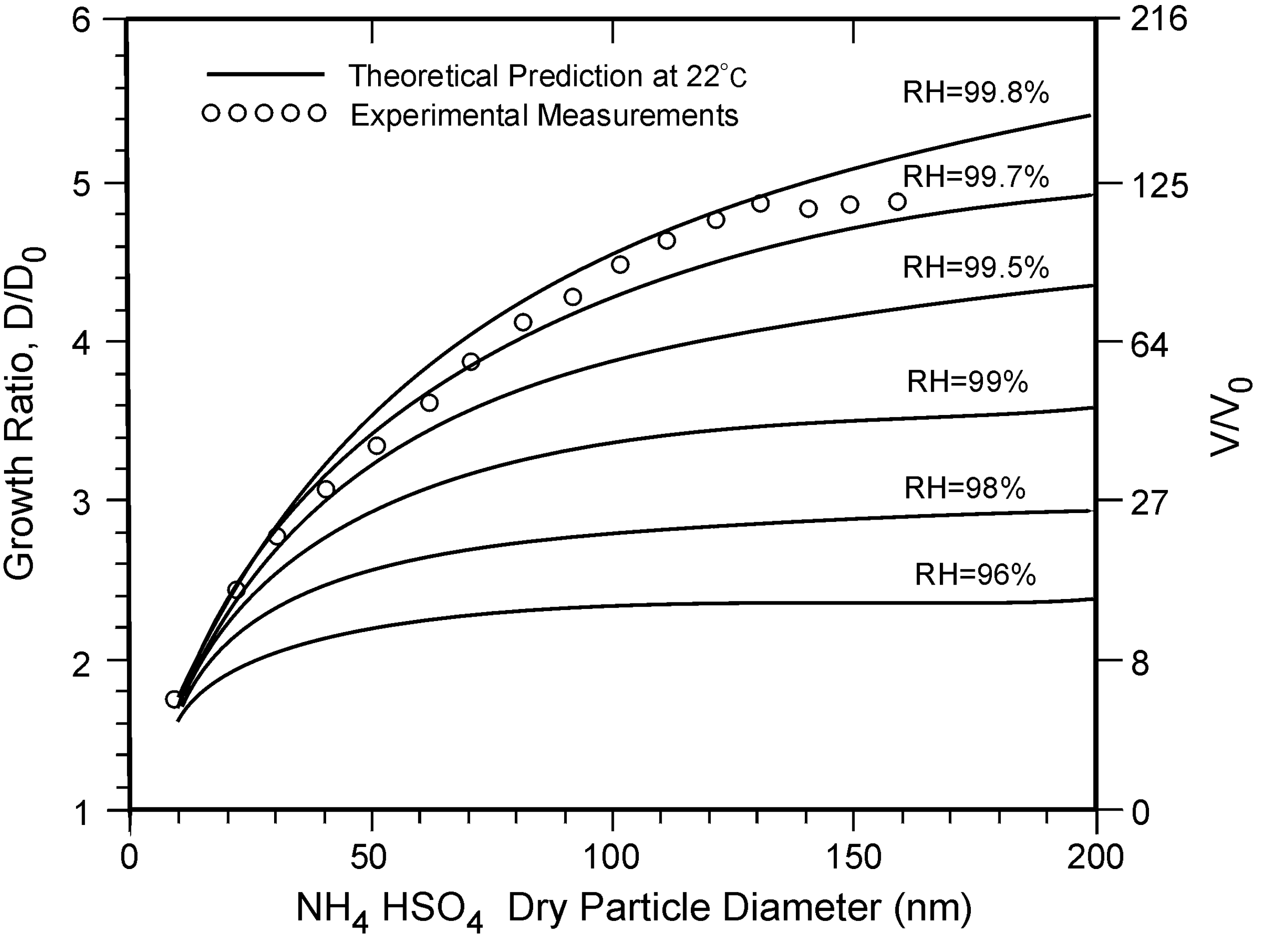

Figure 2-9. Theoretical predictions and experimental measurements of growth of NH_4HSO_4 particles at relative humidity between 95 and 100%.

Source: Li et al. (1992).

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 effective in removing accumulation-mode particles.

2.1.3.5 Particulate Matter and Welfare Effects

The EPA is required by law to set primary standards to protect human health and secondary standards to mitigate welfare effects. The role of particles in reducing visibility and affecting radiative balance through scattering and absorption of light is evident, as are the effects of particles in soiling and damaging materials. Visibility effects are addressed through regional haze regulations and are considered in establishing secondary NAAQS. The direct effects of particles in scattering and absorbing light and the indirect effects of particles on clouds are being addressed in climate change programs in several government agencies with the lead role assigned to the Department of Energy. These welfare effects are discussed briefly in Chapter 4. The effects on vegetation resulting from the direct and indirect effects of particles on light flux also are discussed in Chapter 4.

Concerns over the possible ecological effects of acid deposition in the United States led to the creation of a major research program in 1980 under the new National Acid Precipitation Assessment Program (NAPAP). However, the role of PM in acid deposition has not always been recognized. Acid deposition and PM are intimately related, however, first because particles contribute significantly 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 do not take place in the gas phase but only in solution in water. 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 PNA organic compounds that may add to the toxicity of the rain. Thus, the adverse effects of acid deposition on soils, plants, and trees as well as lakes, streams and fish must be taken into account in setting secondary PM standards. These effects are discussed in Chapter 4.

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 damages caused by acid deposition.

2.1.4 Summary

The physical and chemical properties of ultrafine mode, accumulation mode, and coarse mode particles are summarized in Table 2-1.

2.2 MEASUREMENT OF PARTICULATE MATTER

The 1996 PM AQCD (U.S. Environmental Protection Agency, 1996) 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 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; the current EPA monitoring program (including measurements with Federal Reference Methods, speciation monitors, and continuous monitors); and the importance of intercomparison studies in the absence of any reference standard for suspended atmospheric particles.

2.2.1 Problems in Measuring 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. Unfortunately, it is very difficult to measure and characterize particles suspended in the atmosphere.

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

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

	Fine		Coarse
	Nuclei	Accumulation	
Formed from:	Combustion, high-temperature processes, and atmospheric reactions		Break-up of large solids/droplets
Formed by:	Nucleation Condensation Coagulation	Condensation Coagulation 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:	Sulfates Elemental carbon Metal compounds Organic compounds with very low, saturation vapor pressure at ambient temperature	Sulfate, $SO_4^=$ Nitrate, NO_3^- Ammonium, NH_4^+ Hydrogen ion, H^+ 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	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).

equilibration. However, numerous uncertainties remain 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 existed in the atmosphere as suspended PM. The goal of a PM indicator might be to measure accurately what exists as a particle in the atmosphere. However, this is not currently possible, in part because of the difficulty of creating a reference standard for particles suspended in the atmosphere. 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.

There are five general areas where choices must be made in designing an aerosol indicator. These include (1) treatment of semivolatile components; (2) selection of an upper cut point; (3) separation of fine-mode and coarse-mode PM; (4) treatment of pressure, temperature, and relative humidity; and (5) assessment of the reliability of the measurement technique. In many cases, choices have been made without adequate knowledge or understanding 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 identical.

2.2.1.1 Treatment of Semivolatile Components of Particulate Matter

Current filtration-based mass measurements lead to 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 2-10.

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, Harvard pressure drop monitor. Both require preconcentration of the accumulation mode and reduction of ambient humidity.)

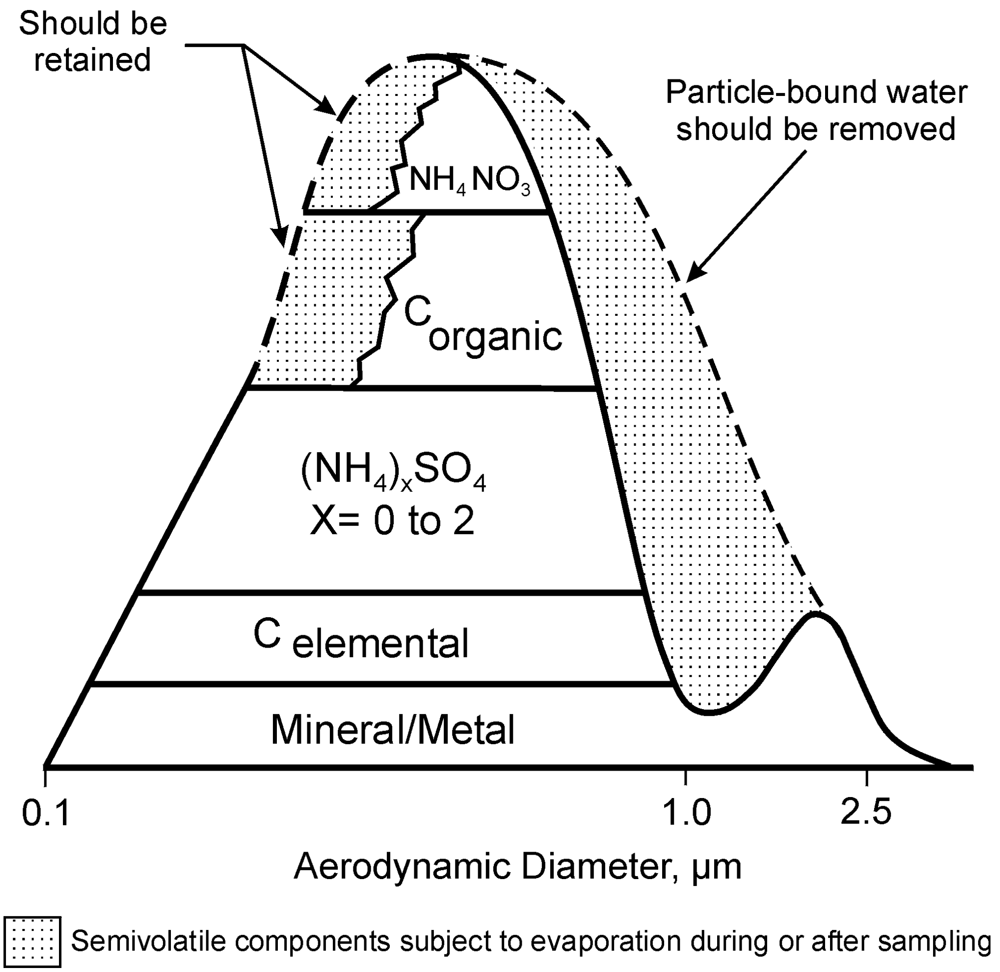

Figure 2-10. Schematic showing major nonvolatile and semivolatile components of $PM_{2.5}$. Semivolatile components are subject to partial to complete loss during equilibration or heating. The optimal technique would be to remove all particle-bound water but no ammonium nitrate or semivolatile organic PM.

2. Stabilize PM at a specified temperature high enough to remove all particle-bound water. This results in loss of most of the semivolatile PM. (Examples: TEOM operated at 50 ºC beta gauge with heated inlet.)
3. Equilibrate collected material at fixed, near-room temperature and moderate relative humidity (RH) to remove most 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.) (Note: Equilibration originally was designed to remove adsorbed

water vapor from glass fiber filters in order to maintain a stable filter weight. The designated RH (40%) 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.

The amount of semivolatile material lost is dependent on the concentration and composition of the semivolatile components and is, therefore, also dependent on season and location. The amount of semivolatile material lost has been found to be significant in air sheds with high nitrate, wood smoke, or secondary organic aerosols.

2.2.1.2 Upper Cut Point

A technique must be used that gives an upper cut-point, and its standard deviation, that is independent of wind speed and direction (the classical high volume sampler head was unsatisfactory because of radial asymmetry). A separation that simulates the removal of particles by the upper part of the human respiratory system would appear to be a good choice (i.e., measure what gets into the lungs). The ACGIH-ISO-CEN penetration curve for thoracic particles, with a 50% cut-point at 10 μm aerodynamic diameter (AD), would be an appropriate choice. (Thoracic particles are able to pass the larynx and penetrate into the bronchial and alveolar regions of the lung.) Some countries, however, use PM_{10} to refer not to samplers with a 50% cut at 10 μm AD but samplers with 100% rejection of all particles greater than 10 μm AD. Such samplers miss too much of the thoracic PM. The U.S. PM_{10} separation curve, while sharper than the thoracic curve, is probably satisfactory both for regulatory and health risk monitoring. It 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 AD. (See Figure 2-6 and Section 2.1.2.2.)

2.2.1.3 Cut Point for Separation of Fine-Mode and Coarse-Mode Particulate Matter

Fine-mode and coarse-mode particles differ not only in size and morphology (e.g., smooth droplets versus rough solid particles) but also in formation mechanisms; sources; and chemical, physical, and biological properties. They also differ in terms of dosimetry (deposition in the respiratory system), toxicity, and health effects as observed by epidemiologic studies. The many reasons for wanting to collect fine and coarse particles separately and considerations as to the appropriate cutpoint for separating fine and coarse particles were discussed in Chapter 3 of the 1996 PM AQCD (U.S. Environmental Protection Agency, 1996). A review of atmospheric particle-size-distribution data did not provide a clear or obvious rationale for selection of an appropriate cutpoint. Depending on conditions, a significant amount of either fine- or coarse-mode material may be found in the intermodal region between 1 and 3 μm. However, the analysis of the existing data did demonstrate the important role of relative humidity in influencing the size of particles in the accumulation mode.

At high relative humidity, such as that found in fog and clouds, hygroscopic fine-mode particles will increase in size due to accumulation of particle-bound water. Under such conditions, some, originally submicrometer, fine-mode PM may be found with an AD above 1 μm. At very low relative humidity, coarse-mode particles may be fragmented into smaller sizes, and small amounts of coarse-mode PM may be found with an AD below 1 μm (Lundgren et al., 1984). Thus, a $PM_{2.5}$ sample will contain most of the fine-mode material, except during periods of RH near 100 %. However, especially under conditions of low RH, it may contain 5 to 20% of the coarse-mode material below 10 μm in diameter. A cut point of 1.0 μm would reduce the misclassification of coarse-mode material as fine, but under high RH conditions could result in some fine-mode material being misclassified as coarse. A reduction in RH, either intentionally or inadvertently, will reduce the size of the fine mode. A sufficient reduction in RH will yield a dry fine-particle 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 μm in diameter at RH below 60% but a substantial fraction will grow above 1 μm for RH above 80% (Hitzenberger et al., 1997; McMurry and Stolzenburg, 1989; U.S. Environmental Protection Agency, 1996).

It is desirable to separate fine-mode PM and coarse-mode PM as cleanly as possible in order to properly allocate health effects to either fine-mode PM or coarse-mode PM and to correctly determine sources by factor analysis and/or chemical mass balance. For example, sulfate in the fine-mode is associated with hydrogen or ammonium ions; sulfate in the coarse mode is associated with basic metal ions. The sources are different and the health effects may be different. Transition metals in the coarse mode are likely to be associated with soil and tend to be less soluble than transition metals in the fine mode, which may be found in fresh combustion particles.

In areas where winds cause high concentrations of wind blown soil, the current practice of separating fine-mode and coarse-mode particles at 2.5 μm AD may not provide the best separation for exposure or epidemiologic studies. An example, taken from data collected during the August 1996 dust storm in Spokane, WA, is shown in Figure 2-11. 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, $PM_{(2.5-1)}$ 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 biased by the intrusion of coarse-mode particles.

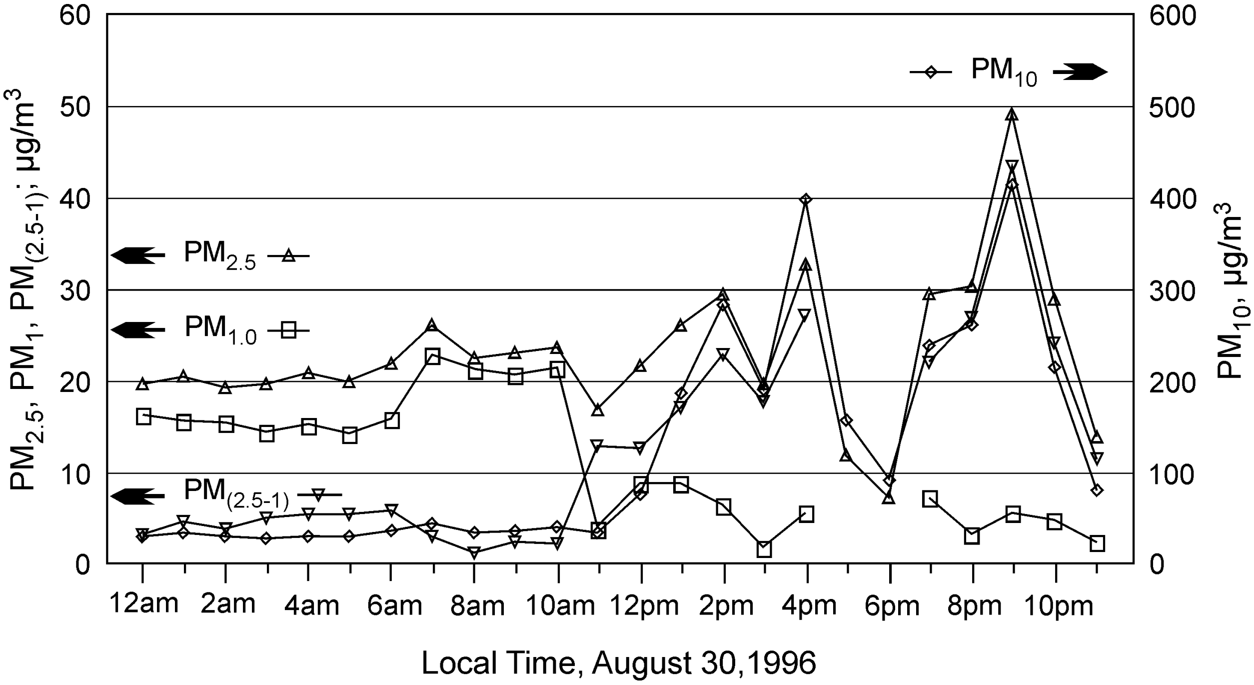

Figure 2-11. Particulate matter concentrations in Spokane, WA, during the August 30, 1996 dust storm.

Source: Claiborn et al. (2000).

Under conditions of high relative humidity, a cut point near 1 μm AD may reject some fine-mode material. Under these circumstances, a monitor using a 1.0 μm AD 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 have been developed for both integrated and continuous measurement of fine particulate matter minus particle-bound water, but including semivolatile nitrate and organic compounds. These techniques (see Section 2.2.5) require reduction of RH prior to collection. With such techniques, PM_1 would be a good indicator of fine-mode particles.

2.2.1.4 Treatment of Pressure, Temperature, and Relative Humidity

There are a variety of techniques for defining (or ignoring) the pressure, temperature, and relative humidity during or after sampling.

Temperature and Pressure

(a) Sample volume based on mass or volumetric flow corrected to standard temperature and pressure (273 K and 1 atm.).
(b) Sample volume based on volumetric flow at ambient conditions of temperature and pressure.

Temperature During Collection

(a) Heat enough to remove all particle-bound water (i.e., TEOM at 50 °C).
(b) Heat several degrees to prevent condensation of water in sampling system.
(c) Try to maintain sampler near ambient temperature.
(d) Maintain sampler at constant temperature inside heated/air conditioned shelter.

Temperature After Collection

(a) No control
(b) Constant Temperature (room temperature)
(c) Store at cool temperature (4 °C)

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 the following items.

(a) Particle number, particle surface area and particle size distribution
(b) Amount of overlap of fine-mode and coarse-mode particles

Changing relative humidity by intentional or inadvertent changes in temperature affects above measurements plus the following.

(c) Amount of loss of ammonium nitrate and semivolatile organic compounds.

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 concentrations, the modeling of personal exposure to all particles, and exposure apportionment by the disaggregation of personal exposure into exposure to particles of ambient origin and exposure to particles of indoor origin.

2.2.1.5 No Way To Determine Accuracy for Ambient Particulate Matter Mass Measurement

Precision is typically determined by comparison of collocated samplers or through replicate analyses, while 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, to establish the precision of identical monitors and the extent of agreement between different types of monitors, are essential 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, 1996). 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, because of the inclusion in $PM_{2.5}$ of a small amount of coarse particles, and because of problems associated with the definition of $PM_{2.5}$ as what remains after collection on a filter and equilibration rather than the mass of particles as they exist in the air. However, it is possible to measure PM indicators with high precision.

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 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 (FRM) for $PM_{2.5}$ is discussed below in Section 2.2.3.3. As mentioned earlier, volatilization losses, during sampling or post-sampling handling, of some organics as well as ammonium nitrate can lead to significant underestimation of the true fine particulate mass concentration in some locations. Sources of error in the measurement of true $PM_{2.5}$ mass 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 NIST Standard Reference Material 1649 (Urban Dust) in air for collection on up to 320 filters simultaneously, using SRI, International's dust generation and collection system. However, the fine component is not resuspended and the semivolatile component has evaporated so this material is not a suitable standard for suspended PM. Little additional work in this area has been reported.

Methods validation was discussed in the 1996 PM AQCD (U.S. Environmental Protection Agency, 1996), 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 analysis (PESA) analysis 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 semi-volatile 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.

2.2.2 Why Measure Particles

2.2.2.1 Attainment of a Standard

A critical need for particle measurements is to determine if a location is in compliance with an existing standard and to determine if trends show improvements in air quality. For this purpose, precision of the measurement by the variety of indicators in use is the most important consideration. Therefore, intercomparisons of various potential indicators, under a variety of atmospheric and air quality conditions, are essential.

2.2.2.2 Implementation of a Standard

In order to reduce pollution to attain a standard, local 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.

2.2.2.3 Determination of Health Effects

PM measurements are needed to determine exposure for use in epidemiological studies, to assess exposure for risk assessment, and to determine components of PM to guide planning and interpretation of toxicologic experiments. For these purposes, size and chemical composition may be needed. For exposure assessment, different measurement time intervals may be needed. For epidemiologic studies of acute (short-term PM exposures), 1-h or continuous measurements may be needed as well as 24-h measurements. However, for epidemiologic studies of chronic PM exposures, measurements that integrate over longer intervals (e.g., a week to a month) may be more cost effective. 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 are increased to those in the respiratory system.

2.2.2.4 Determination of Ecological Effects

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. Information on chemical composition is also needed to understand materials damage and ecological damage.

2.2.2.5 Determination of Radiative Effects

Particles reduce visibility by scattering and absorbing light. They also have a direct effect on the climate by scattering visible and ultraviolet light back into space and, indirectly, as cloud condensation nuclei, by changing the albedo and stability of clouds. For understanding these effects, information is needed on refractive index (including ratio of scattering to absorption), size distribution, and change in particle size with change in relative humidity.

2.2.2.6 Particulate Matter Components/Parameters That Need To Be Measured

PM parameters and components of PM that need to be measured for various purposes are summarized in Table 2-2.

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

Particle number
Particle surface area
Particle size distribution
PM mass (fine-mode [$PM_{1.0}$] and coarse-mode [PM_{10-1}] mass as well as $PM_{2.5}$ and PM_{10}); nonvolatile mass, Federal Reference mass, and 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

2.2.3 Problems Associated with Semivolatile Particulate Matter

It is becoming increasingly apparent that the semivolatile component of PM may impact significantly the quality of the measurement and can lead to both positive and negative sampling artifacts. Losses of semivolatile species, like ammonium nitrate and many organic species, 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 (McMurry, 1999). Gas phase organic species, both volatile and semivolatile, may adsorb onto or react with filter media or collected PM, leading to a positive sampling artifact. Quartz fiber filters have a large specific surface area on which adsorption of gases can occur. A number of other types of filters (e.g., stretched Teflon membrane filters) have much smaller exposed surface areas (Turpin et al., 1994) and appear to be subject to less adsorption (Kirchstetter et al., 2000; Turpin et al., 1994). Tsai and Huang (1995) observed positive sulfate and nitrate artifacts on high-volume PM_{10} quartz filters and attributed the artifacts to interactions between acidic gases SO_2, HONO, and HNO_3 and both the filter media (either glass fiber or quartz) and the coarse particles collected on the filter. Volatilization losses also have been reported to occur during sample transport and storage (Chow, 1995). Evaporative losses of particulate nitrates have been investigated in laboratory and field experiments (e.g., Wang and John, 1988), and in theoretical studies (Zhang and McMurry, 1992). It has been known for some time that volatilization losses of SVOC can be significant (e.g., Eatough et al., 1993).

The theory describing phase equilibria of SVOC continues to be developed. Liang et al. (1997), Jang et al. (1997), and Strommen and Kamens (1997) have modeled the gas/particle partitioning of SVOC on inorganic, organic, and ambient smog aerosols.

Adsorption of organic vapors onto quartz filters is recognized as a source of positive sampling error. This artifact has been examined in experiments in which two quartz fiber filters were deployed in series. The second quartz filter may indicate gaseous VOC adsorbed on both filters (positive artifact) or 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).

The developing state of the art in which diffusion denuder technology is being applied to SVOC sampling (e.g., Eatough et al., 1993; Gundel et al., 1995), as well as for sampling of gas and particulate phase organic acids (Lawrence and Koutrakis, 1996a,b), holds promise for improving the understanding of SVOC sampling artifacts. In a denuder-based system, gas-phase organics are removed by diffusion to an adsorbent surface (e.g., activated carbon, special polymer resins, etc.). Particles then are collected on a filter downstream of the denuder and the remaining organic vapors (i.e., from denuder breakthrough and volatile losses from the collected particles) are collected in an adsorbent downstream of the filter (e.g., charcoal or carbon-impregnated filters, polyurethane foam, or polystyrene-divinylbenzene resin [XAD]).

Finally, Eatough et al. (1999a) have reported on a batch sampler (the Particle Concentrator–Brigham Young University Organic Sampling System [PC-BOSS]) and a continuous sampler (Real-Time Air Monitoring System or RAMS), which attempt to correct simultaneously for volatilization losses of both nitrate and SVOC. These samplers are discussed in more detail in Section 2.2.3.2.

2.2.3.1 Particulate Nitrates

It is well known that volatilization losses of particulate nitrates (e.g., Zhang and McMurry [1992]; see also Hering and Cass [1999] and references therein) occur during sampling on Teflon filters. The impact 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 $PM_{2.5}$ suffers loss of nitrates, similar to the losses 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) examined the errors in $PM_{2.5}$ mass measurements because of volatilization of particulate nitrate by looking at 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 2-12). 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.

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

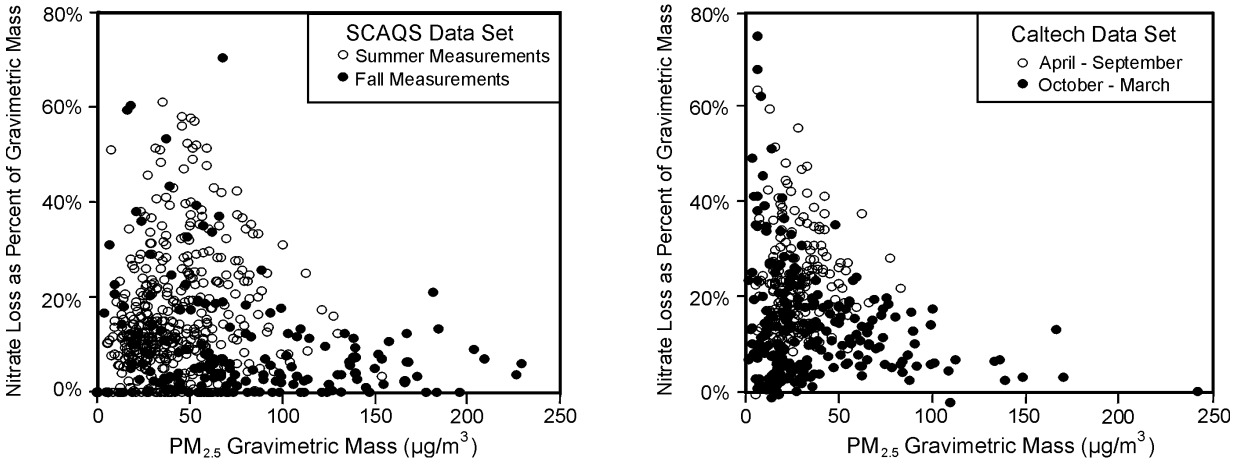

Figure 2-12. Amount of ammonium nitrate volatilized from Teflon filters, expressed as a percentage of the measured $PM_{2.5}$ mass, for the SCAQS and CalTech studies, for spring and fall sampling periods.

Source: Herring and Cass (1999).

(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 during these intercomparison studies, filters or collection surfaces were removed immediately after sampling and placed into vials containing a basic extraction solution. 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) 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 dicot Teflon filter averaged only 13% of the total nitrate. The Teflon filter from the ADS averaged 46% of the total nitrate. The authors conclude that considerable nitrate was lost from the dicot filters during handling, which included weighing and 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.

Several diffusion denuder samplers have been developed to account for the nitrate lost because of volatilization from filters, many of which were discussed in the 1996 PM AQCD (U.S. Environmental Protection Agency, 1996). 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, thus 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., 1988a).

In atmospheres with high sulfate and low ammonia, the PM tends to be acidic (NH_4HSO_4 or H_2SO_4), and nitric acid remains in the vapor phase. In atmospheres with lower sulfate and higher ammonia, there may be sufficient ammonia to fully neutralize the H_2SO_4 and also react with HNO_3 to form NH_4NO_3 particles. In the United States, therefore, loss of nitrate will be a bigger problem in the western United States than in the eastern United States. However, as SO_2 emissions are reduced in the eastern United States, nitrate may become a larger fraction of the suspended PM.

2.2.3.2 Semivolatile Organic Compounds

Semivolatile organic compounds (SVOC) 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. When PM is collected on a quartz filter in a system without a denuder, the quartz filter may adsorb some gas phase organic compounds (positive artifact) as well as SVOC that evaporate from collected particles. A second quartz filter, placed directly after either a quartz or Teflon first filter, could also collect some gas phase organic compounds passing through the first filter as well as SVOC that evaporated from particles collected on the first filter. Some workers (Turpin et al., 2000) suggest subtracting the organic carbon mass on the quartz second filter from that on the quartz first filter to correct for the positive artifact. However, if some SVOC, lost by evaporation from particles collected on the first filter, are adsorbed on the quartz second filter, the negative artifact would be doubled (Eatough et al., 1994; Cui et al., 1998). 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. Because of the absence of the gas phase, SVOC collected on the filter might 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., 2000), the total mass on denuded and undenuded filters were compared and found to be identical within error limits ($R^2 = 0.816$, slope $= 0.961 \pm 0.027$ for total mass compared to $R^2 = 0.940$, slope $= 0.986 \pm 0.020$ for sulfate). This suggests that the major cause of loss of SVOC is the pressure drop across the filter.

In addition to their contribution to suspended PM mass, SVOC are also 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).

Several investigators have observed that collection of particles on a filter can result in underestimation of particulate organic compounds because of losses of semivolatile organic material during sample collection (negative sampling artifact) (Eatough et al., 1993; Tang et al., 1994; Eatough et al., 1995; Gundel et al., 1995; Finn et al., 2000). Positive sampling artifacts also can occur because of the adsorption of gases onto the filter materials (e.g., Gundel et al., 1995). There appears to be a larger positive artifact because of adsorption of organic vapor onto quartz fiber filters than to Teflon filters (Turpin et al., 1994; Chow et al., 1994, 1996; Eatough et al., 1996; Finn et al., 2000). When samples for organic analysis are collected on quartz fiber filters, the amount of adsorbed organic vapor on the quartz filter is sometimes estimated by the amount collected on a second quartz fiber filter behind the first, or by the amount collected on a quartz fiber filter placed behind a Teflon filter in a parallel sampling port (Novakov et al., 1997). Many, but by no means all, investigators subtract this adsorption estimate from the front filter quantity to obtain the mass of collected particulate organic (Turpin et al., 2000).

Kirchstetter et al. (2000) report that adsorptive properties of quartz fiber filters vary with lot number, and therefore front and back-up filters should be taken from the same lot. Recent literature suggests that a Teflon-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-quartz backup, and that the difference between these two adsorption estimates can be substantial for short durations (Kirchstetter et al., 2000; Turpin et al., 2000). The typically lower organic carbon loadings on quartz-quartz back-up filters, relative to Teflon-quartz back-up samples collected concurrently, is believed to occur because adsorption on the quartz front filter acts to reduce the gas-phase concentration downstream until gas phase (i.e., adsorbed phase 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 a quartz filters would depend on the organic composition and would vary by season and location.

2.2.3.3 Use of Denuder Systems To Measure Semivolatile 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, then 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), or 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) (flowrate 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, followed by 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. 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 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).

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 $\approx$5 nmoles/m^3, and gas-phase concentrations as high as 10 nmoles/m^3 were found.

The PC-BOSS system of Eatough et al. (1999a) 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 (i.e., gases and particles smaller than 0.1 μm are removed with the major flow of the virtual impactor and the remaining aerosol enters the denuder). Particulate OC estimates are corrected for particle losses of 46 to 48% in the inlet. The denuder consists of charcoal-impregnated cellulose fiber filter material, and denuder collection efficiencies of greater than 98% are reported for organic gases that adsorb on quartz and charcoal-impregnated filters.

Turpin et al. (1993) developed a sampling system based upon a diffusion separator, which 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., 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 diffuse 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 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 polcyclic aromatic hydrocarbons using annular denuder technology instead of the different method. The method, called the integrated organic vapor/particle sampler (IOVPS), uses a cyclone inlet with a D_{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 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 (lower limits of detection, 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 as determined either 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, and ranged from 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 impacted significantly by increases in relative humidity. The feasibility of outdoor air sampling with the system was demonstrated. Risse et al. (1996) developed a diffusion denuder system for sampling aromatic hydrocarbons in which denuder tubes were coated with charcoal.

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 polyurethane foam (PUF) plug to collect organic material volatilizing off the filter. Denuder samples were analyzed by liquid solvent extraction (CH_2Cl_2) followed by GC-MS 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), which 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 lpm), followed by two denuder tubes, and finally a filter pack with a Teflon filter. The first denuder tube was coated with 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 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 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 more volatile carbon.

Lewtas et al. (2001) concluded that the more volatile carbon 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, the more volatile carbon otherwise would be captured in carbon impregnated filters placed behind quartz filters, so that, in the XAD denuder configuration, the volatile carbon would result in a higher OC concentration and 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). 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., 1988a), significant losses of ammonia and nitric acid were observed for the honeycomb configuration, and 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., 1994). Sioutas et al. (1996b) tested various inlet materials (glass, PFA, and PTFE) in laboratory tests and found that a PTFE Teflon coated inlet minimized loss of sampled gases (1 to 8% losses of HNO_3 observed, and –4 to 2% losses 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

To account for the volatilization losses of semivolatile organic compounds, Turpin et al. (1994) recommended that a quartz filter be placed behind a Teflon filter in a parallel sampler. Addition of a vapor trap (e.g., polyurethane foam plug) downstream of the filter also was suggested as a method to collect semivolatile organic compounds. However, it was noted that addition of some type of trap behind the Teflon filter collected both vapor phase organics as well as “blow-off” from the Teflon filter (i.e., material vaporized from particles collected on Teflon filter [Van Vaeck et al., 1984]). Kim et al. (2000) used a quartz filter behind a Teflon filter recently to account for positive organic artifacts in the South Coast Air Basin. They found that, on an annual average basis, 30% of the $PM_{2.5}$ organic carbon concentration resulted from positive artifacts.

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 use of a particle concentrator to reduce the amount of gas phase organic compounds relative to condensed phase organic compounds (Cui et al., 1998, 1997; Eatough, 1999). Recent 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.

Undenuded quartz-quartz and Teflon-quartz back-up filters have been reported to collect 10 to 50% of the organic mass found on quartz front filters that remove particulate matter with essentially 100% efficiency (Turpin, et al., 2000). Larger percentages were found for samples with shorter collection times and for cleaner locations. Kirchstetter et al. (2000) and Turpin et al. (2000) argue that the quantity of organic material on a quartz back-up filter provides an estimate of the positive artifact (i.e., adsorbed organic vapors), but provides no information about the negative artifact (i.e., volatilized particulate organics). This argument is based on profiles of thermal carbon analyses (i.e., plots of evolved carbon with temperature created during Evolved Gas Analysis [EGA]) and the following argument. Material volatilized from the collected particles will not add significantly to the loading on the quartz backup filter unless the ratio of the mass of semivolatile vapor to the mass of semivolatile condensed phase material is low and the rate of volatilization of the condensed phase semivolatile material is great enough to significantly increase the concentration of the semivolatile vapor passing through the back-up filter (Zhang and McMurry, 1987).

A *net* positive artifact for total particulate organic carbon was reported by Novakov et al. (1997), whose filter-based aircraft measurements had carbon loadings that exceeded the total aerosol mass. Novakov compared estimates of adsorption based on examination of EGA thermograms and estimates of adsorption obtained from quartz-quartz back-up filters and concluded that, if anything, the quartz-quartz back-up filter underestimates the positive sampling artifact. Also, both McDow and Huntzicker (1990) and Turpin et al. (1994) observed that subtraction of the Teflon-quartz backup filter (an estimate of adsorbed organic gases) from the quartz front filter loading removed the face velocity dependence of the particulate organic carbon concentrations obtained at face velocities of 20, 40 and 80 cm/s. Kirchstetter et al. (2000) reported that the organic carbon content of a denuded quartz filter collected in Berkeley, CA was comparable to the carbon content of a concurrently-collected undenuded quartz filter after subtraction of the matching Teflon-quartz backup (i.e., after correction for the positive artifact). As a result, they concluded that volatile losses must not be important for this sample. (Some denuder breakthrough was noted in this study.)

Evidence of a *net* negative artifact is provided by Lewtas et al. (2001), who emphasized that if particulate OC had been measured on a denuded quartz filter without an adsorbent downstream, the negative bias would be large. Their data showed that the sum of a denuded quartz filter and absorbent downstream (average = 9.1 $\mu g/m^3$) was greater than a collocated undenuded quartz filter (average = 7.7 $\mu g/m^3$) in a PC-BOSS sampler after correction for losses (46 to 48%) in the virtual impactor inlet. A net negative artifact for total particulate OC has been reported by Eatough and colleagues in a number of studies (e.g., Cui et al., 1998; Eatough, 1999).

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 sampling 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 up 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 shown to be formed (Pellizzari and Krost, 1984). Similar oxidation of aldehydes and 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., 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 (VOC) 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. The carbon and sulfate contents of their particulate matter are comparable to the chemical composition of ambient fine particles. 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, which could artificially increase the amount of PAHs and other organic compounds attributed to the aerosol. Allen et al. (1999a) 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 (2000) 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 found that the PUF impaction substrate resulted in a much smaller d_{50} at the same flow rate and Reynolds number. Moreover, the lower d_{50} was obtained at a lower pressure drop than with the conventional substrate, which could lead to a reduction of artifact vaporization of semivolatile components.

2.2.3.4 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. In other situations it may be important to know how much of the suspended particle's mass or volume results from particle-bound water. The water content of PM is significant and highly variable. Moreover, there is significant hysteresis in the water adsorption-desorption pathways (Seinfeld and Pandis, 1998), further complicating the mass measurement. Figures 2-8 and 2-9 show the change in diameter of sulfate particles as a function of relative humidity. Figure 2-8 shows 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 with 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 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 (D50 = 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 crystalline 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 2-13. 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.

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 (RH) 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

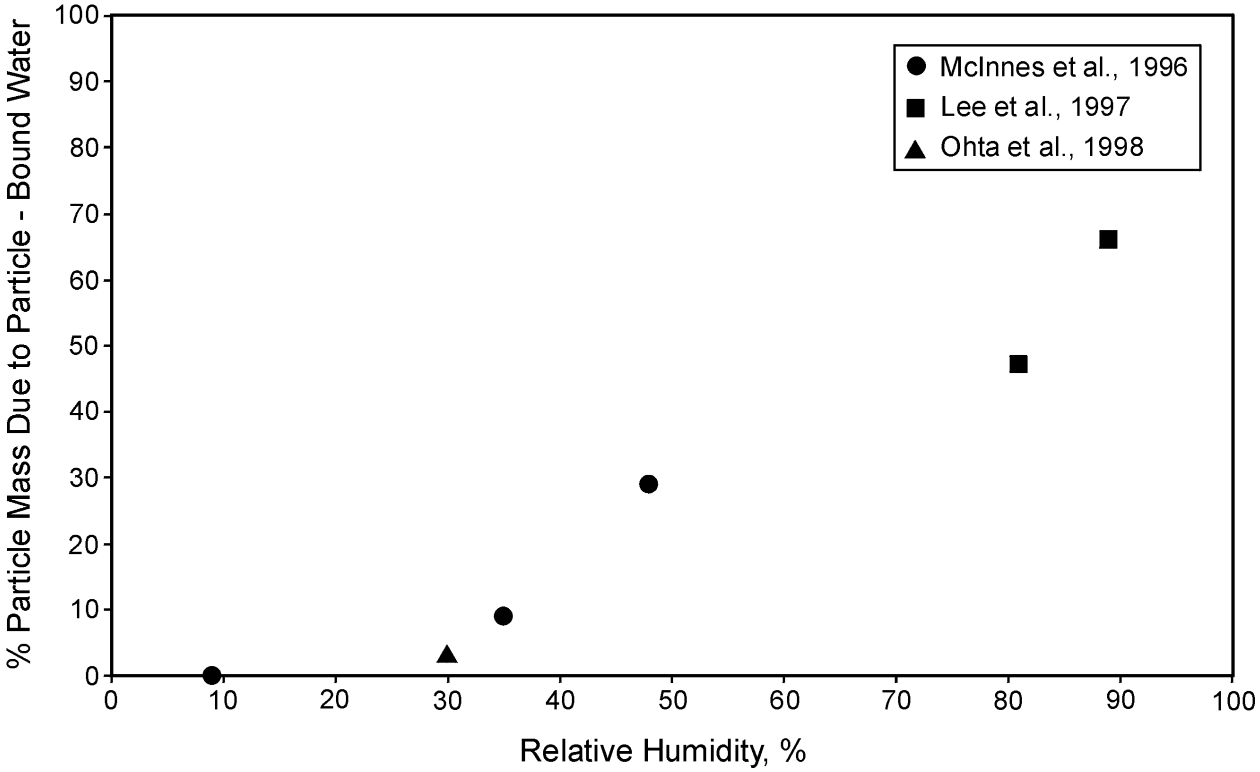

Figure 2-13. Aerosol water content expressed as a mass percentage, as a function of relative humidity.

Source: McInnes et al. (1996); Lee et al. (1997); Ohta et al. (1998).

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 particles size (15% at 0.05 μm to 60% at 0.5 μ m), 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.

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.

2.2.4 U. S. Environmental Protection Agency Monitoring Programs

2.2.4.1 The Federal Reference Methods for Equilibrated Mass

Federal Reference Methods (FRM) have been specified for measuring PM_{10} (Code of Federal Regulations, 1991a,b) and for measuring $PM_{2.5}$ (Code of Federal Regulations, 1999a). The FRM for PM_{10} has been discussed in previous PM AQCD’s and will only be briefly reviewed. 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 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 manufactures 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.

As opposed to the performance-based FRM standard for PM_{10}, the new FRM for $PM_{2.5}$ specifies certain details of the sampler design, as well as of sample handling and analysis, whereas other aspects have performance specifications. 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, and a 47-μm polytetrafluoroethylene (PTFE) filter with a particle collection efficiency greater than 99.7%. The sample duration is 24 h, during which the sample temperature is not to exceed ambient temperatures by more than 5 °C. 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, 1999a).

The FRM also allows for Class I, II, and III equivalent methods for $PM_{2.5}$ (Code of Federal Regulations, 1999b). 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 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).

The strength of the $PM_{2.5}$ FRM is that specification of all details of the sampler design ensures that measurements at all locations, if done properly, should be comparable. For example, the FRM requires maintenance because the oil-soaked impaction substrate could otherwise become loaded with coarse particles. Failure to do so could lead to coarse particle bounce, thus artificially increasing the measured fine particle concentrations. Moreover, the specification of a PM_{10} inlet requires the oil-soaked impaction substrate to collect particles between 2.5 and 10 μm. The implication is that, during sampling periods of high coarse PM concentrations, the impaction substrate could become overloaded, leading to particle bounce. If an inlet with a cutpoint diameter smaller than 10 μm were specified, coarse particle bounce could potentially be reduced, and perhaps the maintenance frequency could be reduced (McMurry, 2000).

Since the implementation of the PM_{10} standard in 1987 (Federal Register, 1987) considerable information has accumulated on the factors that affect the quality of the data gathered from the EPA reference method for PM_{10}. These include inlet losses of coarse fraction particles (e.g., Anand et al., 1992); biases in concentrations due to differences between samplers in large particle cutpoints that are within the EPA’s specified acceptable tolerances (Ranade et al., 1990); and particle bounce tolerances and reentrainment leading to as much as 30% errors (Wang and John, 1988). The sampling issues associated with cutpoint tolerances are predictable, and the particle bounce and reentrainment problems have since been dealt with voluntarily by the manufacturers by recommending operational procedures including oiling of impact surfaces and regular cleaning. The 1996 PM AQCD (U.S. Environmental Protection Agency, 1996) concluded 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}, since the 2.5-μm 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, 1996). These issues have been discussed earlier in this chapter and include gas/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 (SVOC) artifacts (e.g., Eatough et al., 1993), and relative humidity effects (e.g., Keeler et al., 1988).

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 high-volume carbon 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 impact 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). Personal Environmental Monitors (PEMs; MSP, Inc.) also were included but will not be discussed in this section. 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 has 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. (2000) 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 also was 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.

2.2.4.2 Speciation 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, 1999c). A $PM_{2.5}$ chemical speciation network is being deployed that will consist of 54 core National Ambient Monitoring Stations (NAMS) and 250 State and Local Air Monitoring Stations (SLAMS). 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). 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 types of 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 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. The current samplers include three filters: (1) Teflon for equilibrated mass and elemental analysis (EDXRF), (2) a nitric acid denuded Nylon filter for ion analysis (ion chromatography), and (3) a quartz fiber filter for elemental and organic carbon (but without any correction for positive or negative artifacts caused by adsorption of organic gases or the quartz filters or evaporation of semivolatile organic compounds from the collected particles) (thermal optical analysis via NIOSH 5040 method). There are several samplers that are suitable for use in the NAMS/SLAMS network. These samples include an inlet cutpoint comparable to the WINS, FRM; proven denuder technology for ions; and sampler face velocity and sample volume similar to that of the FRM with 46.2-mm diameter filters. 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.

Measurements for Source Category Apportionment

Chemical analyses from the speciation network will be used for source category apportionment via receptor modeling of PM. There are two major approaches to receptor modeling: the chemical mass balance (CMB) receptor modeling approach, and statistically based approaches. The CMB approach requires chemical characterization of all relevant sources. Similar analyses should be used for characterization of receptor samples. One of the advantages of using the CMB approach for receptor modeling is that it can be applied to a single sample, or to a limited number of samples. CMB also uses chemical analyses that are performed routinely on speciation samples, such as EDXRF and ionic species. A considerable amount of receptor modeling work has been conducted with CMB using elemental analyses coupled with OC/EC and some ionic species (e.g., Watson et al., 1994; Hidy and Venkataraman, 1996; McLaren et al., 1996; Vega et al., 1997). Recent developments in receptor modeling include using organic analyses for tracers of specific sources (Benner et al., 1995), very detailed organic analyses for source fingerprinting (Rogge et al., 1991, 1993b,c,d,e, 1994, 1997a,b, 1998), and chemical mass balance receptor modeling (Schauer et al., 1996). Further detail on the organic analyses for these studies is beyond the scope of this chapter.

Statistical models based upon factor analysis or principal component analysis (PCA) do not require detailed source characterization information but have the drawback of requiring a large data set of receptor sample analyses. These statistically based models have an additional benefit in that they also can use other parameters such as meteorology. For a detailed review of factor analysis and PCA, see Henry et al. (1984). In PCA, many intercorrelated variables within a large data set are sorted into a smaller number of independent components, or factors, that account for the variability in the data set. Veltkamp et al. (1996) performed a PCA for a study conducted at Niwot Ridge, CO. Organic constituents of atmospheric aerosols were measured, along with physical and meteorological data. Organic compounds were thermally desorbed from the aerosol particles at 250 ºC in a pure helium atmosphere, separated by gas chromatography, and identified by mass spectrometry. A principle component analysis was conducted using 31 variables that included 18 particulate organic compounds, 11 gas-phase species (e.g., NO, NO_2, HNO_3, HONO, PAN, H_2O_2, etc.), wind direction, and time of day. Several factors were identified that distinguished various sources. These included gas-phase internal combustion products; particulate phase, oxygenated biogenic hydrocarbons; high molecular weight n-alkanes; particulate phase anthropogenic products; and particulate phase biogenic aldehydes.

Pinto et al. (1998) also used a combination of $PM_{2.5}$ chemical speciation and ambient monitoring data in a receptor modeling calculation to determine the relative sources of particulate pollution in an industrial area in the northern Bohemia region of the Czech Republic. During that study, a severe air pollution episode occurred in 1993 during which smoke and SO_2 concentrations were 1800 and 1600 $\mu g/m^3$, respectively.

In addition to chemical speciation for factor analysis and source apportionment, 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 increasing 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. Suarez et al. (1996) used iridium tracer to tag emissions from diesel-burning sanitation trucks in Baltimore and determined the size distribution of soot from the trucks.

Elemental Analyses

X-ray emission, stimulated either by X rays (X-ray fluorescence, XRF) or by proton beams (Proton Induced X-ray Emission, PIXE) are standard techniques for nondestructive analysis of certain elements. Both were discussed in the previous 1996 PM AQCD. Some newer techniques with some advantages have become available in recent years.

Energy Dispersive X-ray Fluorescence (EDXRF). EDXRF by Method IO-4.4 is the method of choice for analysis of trace elements for the NAMS speciation program. 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. The previous 1996 PM AQCD included a detailed discussion of EDXRF, so that will not be repeated here.

Instrumental Neutron Activation Analysis (INAA). INAA was mentioned only briefly in the 1996 PM AQCD and is expanded on here. 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.

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. The previous 1996 PM AQCD compared several methods for measuring elements. 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 such as V, Zn, and Mn.

Atomic Absorption Spectrophotometry (AAS). 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).

Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS). Keeler and Pirrone (1996) also used ICP-MS to determine trace elements Cd, Mn, V, As, Se, and Pb in atmospheric particulate fine ($PM_{2.5}$) and total suspended particulate samples collected in two Detroit sites. The results were then similarly used in a deposition model to estimate the dry deposition flux of trace elements to Lake Erie.

Scanning Electron Microscopy (SEM). Mamane et al. (2000) 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., 2000).

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.

Elemental and Organic Carbon in Particulate Matter. Total carbon in aerosol particles (TC) can be expressed as the sum of organic carbon (OC), elemental carbon (EC), and carbonate carbon (CC), with the contribution of CC to TC usually on the order of 5% or less, for particulate samples collected in urban areas (Appel, 1993). The 1996 PM AQCD (U.S. Environmental Protection Agency, 1996) listed several filter-based, thermal methods for measuring OC and EC, and described the thermal/optical reflectance (TOR) method, which was noted, along with thermal manganese oxidation, to be one of the most commonly applied methods in the United States at the time. In thermal separation methods, thermally evolved OC and EC are oxidized to CO_2 and quantified either by nondispersive infrared detection or electrochemically, or the CO_2 can be reduced to CH_4 and quantified via flame ionization detection (FID). The various methods give similar results for TC, but not for EC or OC.

In a methods comparison study (Countess, 1990), it was shown that it is necessary to minimize or correct for pyrolytically generated EC (“char”), and that CC found in wood smoke and automobile exhaust samples may interfere with some of the thermal methods. Recently, Lavanchy et al. (1999) reported on a study in which the operation of a catalytic oxidation system was modified in an attempt to minimize pyrolysis of OC and at the same time minimize the contribution of $CaCO_3$. The system uses two ovens, one at 340 °C and one at 650 °C. The filter sample is placed in a moveable sample boat. In order to minimize charring, the sample is first flash heated in the 650 °C oven for 1 min. Then it is inserted into the 340 °C stage of the two-stage oven. In both steps OC is oxidized to CO_2 in the presence of O_2. The second step requires 42 min. The filter then is moved into the second-stage oven. During this third step, EC is oxidized to CO_2 at 650 °C for 32 min. This temperature is reported to be sufficient to completely oxidize EC, but with only about 1% of the $CaCO_3$ being vaporized (Lavanchy et al., 1999; Petzold et al., 1997). To test for charring, they challenged their system with atmospheric samples for which duplicates were analyzed via the German reference method for measuring OC and EC in atmospheric samples (Petzold and Niessner, 1995), in which a solvent extraction is used to remove organics before combustion. Lavanchy et al. (1999) reported a high correlation ($R^2 = 0.97$) between their thermal oxidation method and the German method VDI. The slope of the EC:EC VDI line was 0.92, and the intercept was –0.37 μg cm^{-2}. They also reported detection limits of 1.3 μg for EC and 1.8 μg for OC.

Pyrolytic char is corrected for in thermal-optical analysis. In thermal-optical carbon analysis (Birch and Cary, 1996; Chow et al., 1993), punches from a quartz sampling filter are inserted into the carbon analyzer and heated in a helium atmosphere to volatilize organic carbon. Then, the temperature is reduced, and oxygen is added to the carrier gas, so that desorbed compounds are then oxidized to CO_2, reduced to methane, and measured in a flame ionization detector. In order to account for the portion of the OC that is pyrolyzed, a He-Ne laser monitors the sample reflectance (or transmittance). As the pyrolysis occurs, the sample gets darker, and the reflectance decreases. Then, as elemental carbon is removed, the filter lightens, and the reflectance increases until all carbon has been removed from the filter. The split between organic and elemental carbon is considered to be the point at which the reflectance regains its prepyrolysis value, with material removed prior to this point being considered organic, and that after, elemental.

The thermal/optical transmission method (TOT) is similar to the TOR with the primary difference being that light transmission rather than reflectance is monitored on the filter throughout the analysis. The TOT method of Birch and Cary (1996) consists of a two-stage process, with the first stage being conducted in a pure helium atmosphere, and the second stage conducted in a 10% oxygen-helium mix. The temperature is ramped to about 820 °C in the helium phase, during which organic and carbonate carbon are volatilized from the filter. In the second stage, the oven temperature is reduced, and then raised to about 860 °C. During the second stage, pyrolysis correction and EC measurement are made. Figure 2-14, an example of a thermogram, shows temperature, transmittance, and FID response traces. Peaks are evident that correspond to OC, CC, EC, and pyrolitic carbon (PC). As can be seen in this figure, the high temperature in the first stage allows for decomposition of CC. The ability to quantify PC is particularly important in high OC/EC regions (like wood-smoke-impacted airsheds), allowing for

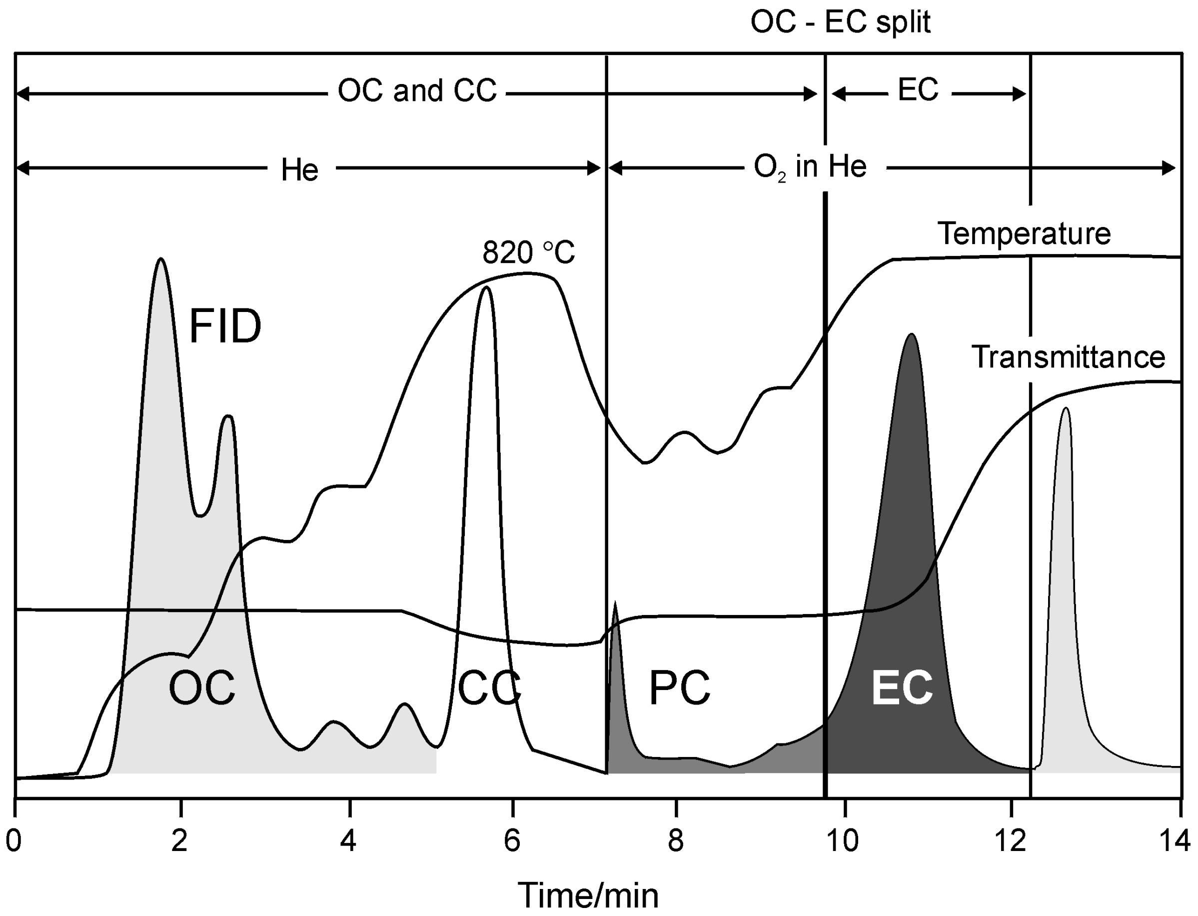

Figure 2-14. This thermogram, for a sample containing rock dust (a carbonate source) and diesel exhaust, shows three traces that correspond to temperature, filter transmittance, and FID detector response. Peaks correspond to organic (OC), carbonate (CC), pyrolytic (PC), and elemental (EC) carbon. The final peak is a methane calibration peak.

Source: Birch and Cary (1996).

the volatilization of any remaining complex organic compounds so they are not apportioned to the EC phase.

The National Institute for Occupational Safety and Health (NIOSH) Method 5040 for monitoring elemental carbon as a marker for particulate diesel exhaust is based upon a TOT method analyzer (Birch and Cary, 1996), while the OC/EC method specified for the IMPROVE network is the TOR method (Chow et al., 2000). Chow et al. (2000) compared the OC, EC, and

TC measurements from NIOSH and IMPROVE methods. The two methods differ in that temperature and atmospheric controls that are used to accomplish carbon speciation, in addition to the use of light transmission in the case of the NIOSH method, as compared to light reflectance in the IMPROVE method, of the filter is measured during the analysis. The IMPROVE thermal protocol specifies organic carbon fractions at 120, 250, 450, and 550 ºC in a nonoxidizing atmosphere (He), and elemental organic fractions at 550, 700, and 800 ºC in an oxidizing atmosphere. The NIOSH method differs in its thermal protocol, which has organic carbon fractions at 250, 500, 650, and 850 ºC in a nonoxidizing atmosphere (also He), and elemental carbon fractions at 650, 750, and 850 ºC in an oxidizing atmosphere. The high temperature before addition of oxygen in the NIOSH method is to quantify particulate carbonate, which evolves between 650 and 830 ºC (Birch and Cary, 1996). The two methods also differ in the specified residence times at each temperature setpoint. The residence times at each setpoint are typically longer for the IMPROVE analysis compared to the NIOSH analysis.

Chow et al. (2000) analyzed 60 quartz filter samples that represented a wide variety of aerosol compositions and concentrations. The TC measurements from each protocol were in good agreement, with no statistically significant differences. A statistically significant difference was observed in the fraction of TC that is attributed to EC, as determined by the IMPROVE and NIOSH thermal evolution protocols, with the IMPROVE EC measurements typically higher than the NIOSH EC measurements. This difference was attributed to the 850 ºC temperature step in the oxidizing atmosphere in the NIOSH protocol. Chow et al. compared the OC for each method and found that the two methods showed good agreement when the 850 ºC nonoxidizing temperature step in the NIOSH method was not included in determination of OC. There was also a difference between the reflectance and transmittance detection methods in the pyrolysis adjustment, although this difference was most noticeable for very black filters for which neither reflectance nor transmittance was able to accurately detect further blackening by pyrolysis. Because OC and EC are operationally defined parameters, Chow et al. pointed out that it is importance 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.

Further refinement of thermal techniques has resulted in the evolved gas analysis (EGA) method, described by Grosjean et al. (1994). This technique involves combustion of particulate matter samples in an oxidizing environment while the temperature is raised from 100 to 600 ^{o}C. The amount of evolved CO_2 contains information about the volatility of the organic aerosol compounds. Grosjean et al. (1994) present thermograms both for specific organic compounds (e.g., adipic acid) and for specific sources (e.g., vehicular traffic). They suggest that EGA may be useful for source apportionment applications. Kirchstetter et al. (2000) and Novakov et al (1997) have used EGA to provide insights regarding organic sampling artifacts.

Black carbon (BC) also is used, in addition to the thermal and thermal/optical methods, for determining EC as a measure of soot (Penner and Novakov, 1996). Both EC and BC define a similar fraction of aerosol, but EC is determined based on thermal properties, whereas BC is based on light-absorption properties. Optical methods for determining BC tend to suffer from calibration problems (Hitzenberger et al., 1996). Lavanchy et al. (1999) compared their EC concentrations as determined from their catalytic thermal oxidation method to BC concentrations determined using an aethalometer operated at the same site, and found that the instrumental calibration factor provided by the manufacturer was on the order of two times the calibration factor they determined (9.3 ± 0.4 m^2g^{-1}). It is possible to calculate a theoretical specific absorption coefficient (B_a) from Mie theory given a known size distribution and refractive index, and typically BC aerosols have values of B_a between 3 and 17 m^2g^{-1} (Hitzenberger et al. [1996] and references therein). The B_a is defined as absorption per mass concentration and can be calculated given the sample filter area, the total deposited mass, and absorption signals for both the loaded and unloaded filters. Often, when no direct measurements are available, values of B_a on the order of 10 m^2g^{-1} have been used (Hitzenberger et al. (1996), and references therein). European countries are trying to set air pollution standards that target diesel vehicles, one of the principal sources of BC in urban areas (Hitzenberger et al. (1996), and references therein) and so it is essential that accurate values for B_a are available. 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. Based on samples collected during a 10-day period in May 1994, they determined that the usually assumed value of 10 m^2g^{-1} was also applicable to aerosol BC occurring in Vienna.

Hitzenberger et al. (1999) recently reported on a study in which 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 so well correlated.

In 1986, the Carbonaceous Species Methods Comparison Study (CSMCS) was conducted in Los Angeles, during which a number of methods for the measurement of this species were intercompared. The CSMCS was mentioned in the 1996 PM AQCD (U.S. Environmental Protection Agency, 1996). Hansen and McMurry (1990) specifically compared two very dissimilar methods for aerosol elemental carbon—collection of impactor samples backed by a quartz fiber afterfilter, followed by EC analysis by oxidation in helium over a MnO_2 catalyst, and real-time measurements using an aethalometer (an optical absorption technique)—and 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]). The implications for data analysis are twofold: (1) the analysis method used must be reported with particulate carbon data, and (2) comparative analyses should not be conducted with data analyzed by more than one carbon analysis method unless the mutual compatibility of the methods has been demonstrated. Carbon analysis methods currently are being compared as a part of the Atlanta Supersite.

Turpin et al. (1990) reported on an in situ, time-resolved analyzer for particulate organic and elemental carbon that could operate on a time cycle as short as 90 min. The analyzer consists of a filter-based sampling section and a thermal-optical carbon detector. Adsorbed organic material 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 in a 98% He-2% O_2 atmosphere, at 350 °C. Correction is made for pyrolytic conversion of some of the organic particulate matter. The instrument was operated with a 2-h time resolution during the Southern California Air Quality Study (SCAQS) in 1987 (Turpin and Huntzicker, 1991), as well as during the Carbonaceous Species Methods Comparison Study (CSMCS) in 1986.

EC/OC Summary. The state of the art for soot measurements continues to develop, and, although advances are being made, the definitions of EC and BC continue to be operational and determined by the method employed. Similarly, the distinction between OC and EC also is defined operationally. Therefore, reports of EC/OC measurements should 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.

Ions. Aerosol ions refers to the water-soluble portion of suspended PM. Ion chromatography (IC) is widely used for analyzing ionic species. 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 might volatilize from the PM during collection. The 1996 PM AQCD (U. S. Environmental Protection Agency, 1996) 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.

2.2.5 Continuous Monitoring

The EPA expects that more than 200 local agency monitoring sites throughout the States 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 mass or chemical components will be discussed in this section.

2.2.5.1 Tapered Element Oscillating Microbalance

The advantages of continuous PM monitoring, and the designation of the Tapered Element Oscillating Microbalance (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 philosophically 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. Moreover, the TEOM samples at a constant temperature, 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 heated to 30 °C rather than the 50 °C specified, during the cooler times of the year, and by using Nafion dryers on the inlet.

This philosophical difference in operation and implications for fine particle measurements were examined by researchers at 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, thus 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 mo (Mignacca and Stubbs, 1999). A third TEOM operating at 40 °C was operated for 2 mo during this period. They found that, on average, the 1-h 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. In most parts of Canada, and including the Greater Vancouver Regional District, TEOMs for both PM_{10} and $PM_{2.5}$ are operated with this revised protocol.

A new sample equilibration system (SES) was developed to allow conditioning of the sample stream to lower humidity and temperature, to reduce losses of semivolatile species from the TEOM (Meyer et al., 2000). The SES utilizes a Nafion dryer designed for low particle loss, and humidity sensors. The dryer fits between the flow splitter that follows the size-selective inlet and the sensor unit. A dry purge gas flow over the exterior of the Nafion tubing 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.

Patashnick et al. (2000) 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 would allow for correcting the effective mass as measured from 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.

2.2.5.2 Real-Time Total Ambient Mass Sampler

A Real-Time Total Ambient Mass Sampler, RAMS, based on diffusion denuder and TEOM monitor technology has been developed, validated, and field tested (Eatough et al., 1999a; Obeidi and Eatough, 1999; Pang et al., 2001) for the real-time determination of total fine particulate mass, including semivolatile species. The RAMS measures 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 2-15. 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.

2.2.5.3 Continuous Ambient Mass Monitor

Koutrakis and colleagues (Koutrakis et al., 1996; Wang, 1997) have developed the Continuous Ambient Mass Monitor (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, 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 like the method of Koutrakis et al. (1996) that use the pressure drop method may be subject to additional uncertainties if used in an environment where the ambient relative humidity cannot be controlled

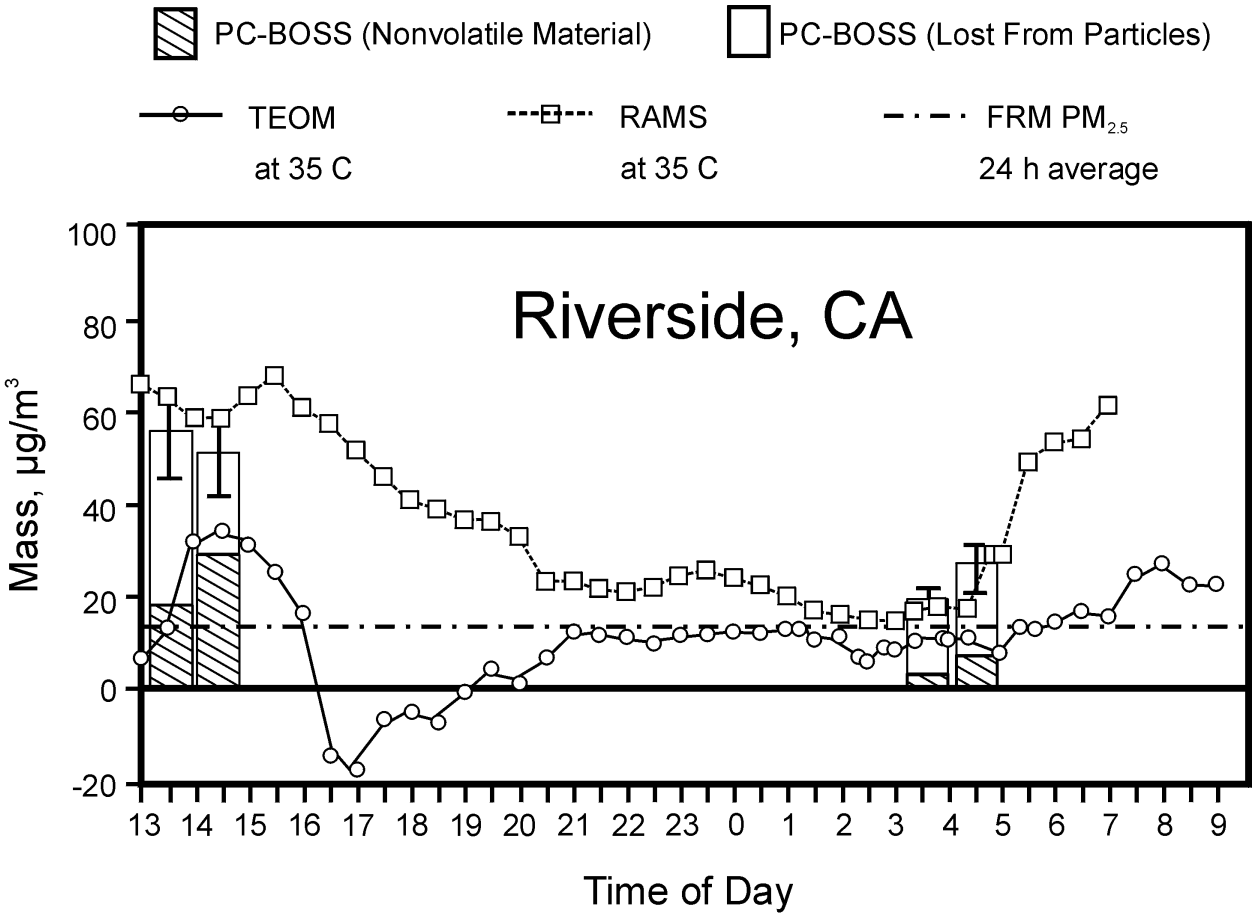

Figure 2-15. Comparison of mass measurements with collocated RAMS (real-time data), PC-BOSS (1-h data), FRM $PM_{2.5}$ sampler (24-h data), and a conventional TEOM monitor (real-time data). The semivolatile fine particulate matter is sampled with the RAMS and PC-BOSS, but not with the TEOM monitor or 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).

accurately. The current version of the CAMM (Wang, 1997) uses a particle concentrator, a Nafion dryer, and frequent changes of the position on the filter tape where the pressure drop measurement is made to avoid artifacts due to semivolatile components.

The CAMMS 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).

2.2.5.4 Light Scattering

The evaporation of ammonium nitrate aerosol in a heated nephelometer was examined by Bergin et al. (1997). This is of interest, because nephelometers are frequently operated with the sampled airstream heated to a low reference relative humidity of 40%, in order to measure the light scattering because of the dry aerosol rather than that caused by particle-bound water. Bergin et al. conducted laboratory experiments at low relative humidity ($\approx$10%) and as a function of temperature (300 to 320 K), 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 accurately describe 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 from 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 generally is expected to be less than 20%.

Morawska et al. (1996) examined the correlations between PM_{10}, visibility, and submicron concentration data in Brisbane, and concluded that the different principles of operation for each instrument and the different aerosol characteristics measured by each technique make it difficult to observe any relationships. Morawska et al. (1998b) reported on a long-term monitoring program that included the criteria pollutants as well as light scattering, number/size distributions, number concentrations, and elemental analysis via inductively coupled plasma mass spectrometry. Particle size classification was conducted using a TSI scanning mobility particle sizer (SMPS) for the size range of 0.016 to 0.7 μm, and a TSI aerodynamic particle sizer (APS) for the size range of 0.7 to 30 μm. They reported correlation coefficients between the light-scattering coefficient and PM_{10}, SMPS concentration, and APS concentration of 0.58, 0.38, and 0.37, respectively. They also reported a correlation coefficient between PM_{10} and the SMPS concentration of 0.25. A lower correlation between PM_{10} mass and the SMPS concentration is consistent with the notion that PM_{10} mass measurements would provide less information about smaller particles in the 0.016 to 0.7 μm range.

2.2.5.5 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., 1981; 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 was 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, however, which was operated at ambient temperature, was sensitive to relative humidity, yielding significantly higher mass concentrations relative to the Sierra Anderson 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%.

2.2.5.6 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 to then use 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. By measuring both positive and negative ions from the same particle, information can be obtained about the chemical composition, not just the elemental composition, of individual particles of known aerodynamic diameter. This information is especially useful in determining sources of particles. An example of the type of information that can be determined is shown in Figure 2-16.

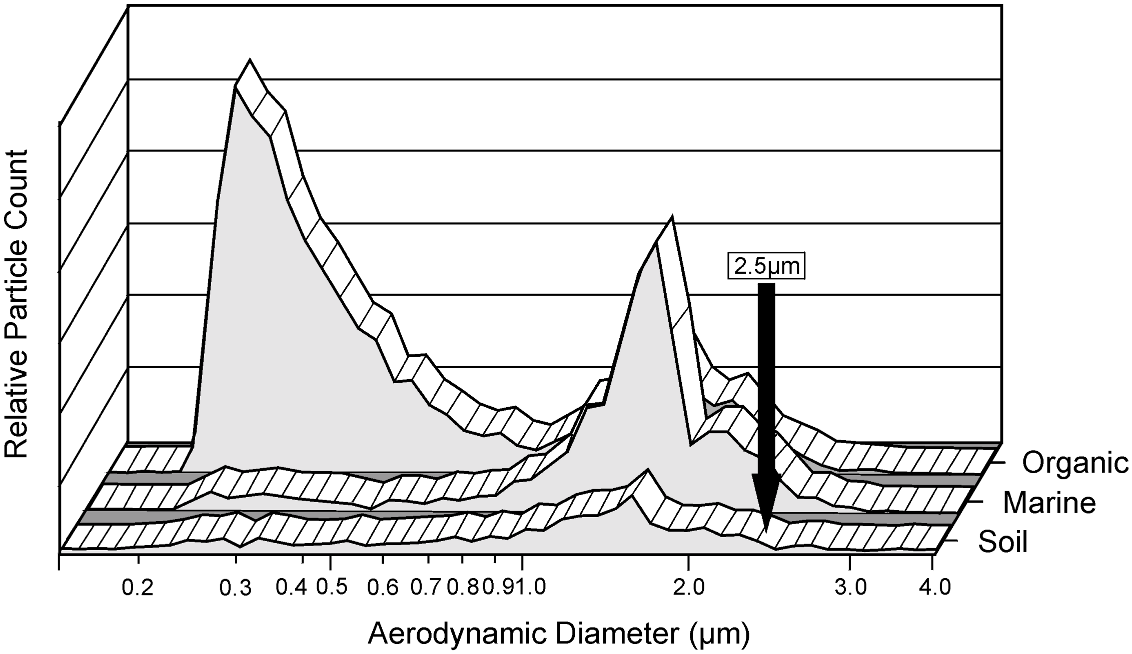

Figure 2-16. Size distribution of particles divided by chemical classification into organic, marine, and crustal.

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 MS 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; Neubauer et al., 1998; Noble and Prather, 1998; Reilly et al., 1998; Silva and Prather, 1997).

Until recently, single particle 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 a single particle, TOFMS instrument that is able to size, count, and provide chemical composition on individual particles ranging in size from 10 nm to 2 μm.

Noble and Prather (1996) used ATOFMS to provide compositionally resolved particle-size distributions. Their instrument is capable of analyzing, at typical ambient concentrations, size and chemical composition of 50 to 100 particles/min, and up to 600/min at high particle concentrations. Data storage requirements are met using a Pentium 90 mHz personal computer.

2.2.5.7 Automated Fine Particulate 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 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 Harvard EPA annular denuder sampler (HEADS), as well as 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.

2.2.5.8 Semi-continuous Carbon Analysis

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 we describe instruments that have been used to collect and analyze atmospheric organic PM with better than 2-h time resolution. These instruments were all present at the Atlanta Supersite experiment during the summer of 1999, and an intercomparison of results is underway.

An "in situ carbon analyzer" measured total particulate organic and elemental carbon (i.e., μg of carbon/m^3) with 1 to 2 h resolution in Glendora and Claremont, CA, during 1986 and 1987 (Turpin and Huntzicker, 1991; Turpin and Huntzicker, 1995), and in Atlanta, GA, during 1999 (Supersite experiment, unpublished). 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. This in situ carbon analyzer collects particulate matter on a quartz fiber filter mounted in a thermal-optical transmittance carbon analyzer (Turpin et al., 1990). The material on a quartz fiber filter behind a Teflon filter in the second sampling port provides an estimate of the positive sampling artifact (i.e., gas adsorption on the quartz sampling filter).

An automated carbon analyzer with 15-min to 1-h time 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 a sizable fraction of EC is in particles < 0.2 μm. 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, 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).

An aethalometer is an 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). It is also commercially available. 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., 1999b; Liousse et al., 1993). For instance, Allen et al. (1999b) 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 $\mu g/m^3$).

The most recent semi-continuous carbon method is currently being tested by Dr. Susanne Hering (unpublished). This is a flash volatilization method in which particles are impacted on a surface and flash volatilized. Higher collection efficiencies are obtained for smaller particles by growing the particles by humidification prior to impaction. This device was first demonstrated at the Atlanta Supersite.

2.2.5.9 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. (2000) 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 for measuring particle charge concentration (EAD, TSI, Inc., Model 3070). The three sensor signals were inverted to obtain the aerosol size distribution using a lognormal 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 lognormal function was then integrated to calculate the total surface area concentration. Woo et al. demonstrated that this method can give near real-time measurements of aerosol surface area.

2.2.6 Data Quality

Although much of the recent work in instrument development for airborne particulate matter measurement has focused on addressing sampling artifacts associated with loss or gain of semivolatile species, or development of real-time measurements of aerosol concentrations, other recent efforts have examined issues associated with improving the quality of data being collected.

2.2.6.1 Errors in Gravimetric Analyses

Issues of precision and accuracy associated with gravimetric analyses have been examined in several studies. It is well known that weighing of particle sampler filters is subject to fluctuations of environmental conditions in the weighing. Gravimetric analysis issues reviewed by Allen et al. (1999c) 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. Lawless and Rodes (1999) 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. They noted that the role of humidity control in the laboratory did not seem to be as critical of a factor as the humidity under which the sample was collected. Koistinen et al. (1999) give an excellant discussion of the procedures developed to overcome problems associated with gravimetric measurements of $PM_{2.5}$ mass in the EXPOLIS Study. They discuss factors such as corrections for buoyancy, elimination of static charge, and increases in the mass of blank filters with time.

Mass concentration measurements of coarse particulate matter are inherently less precise than the corresponding $PM_{2.5}$ or PM_{10} measurements (Allen et al., 1999c). Coarse particulate mass concentrations are determined either by difference between collocated PM_{10} and $PM_{2.5}$ samplers or more directly by use of a dichotomous sampler. The difference method suffers from errors because of the use of two independent measurements. The dichotomous sampler also has potential errors caused by postexposure loss of particles from unoiled filters and uncertainties in the coarse mass channel enrichment factor. Allen et al. (1999c) summarized several sampling issues to consider in measuring coarse particulate mass, including the use of identical instrumentation (except cutpoints) such as 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); avoiding excessive filter loading; and full characterization of the cutpoint characteristics of the FRM without the $PM_{2.5}$ WINS inlet.

2.2.6.2 Quality Assurance

EPA has undertaken extensive studies to evaluate the quality of the 1999 $PM_{2.5}$ FRM data including precision and bias statistics, data reporting statistics, etc. Following a peer review, EPA will issue a report that documents the quality assurance (QA) activities that were undertaken for the $PM_{2.5}$ environmental data operations for the calendar year January 1, 1999, to December 31, 1999, which was the first year of implementation the $PM_{2.5}$ monitoring program. The QA report will evaluate the adherence to the quality assurance requirements described in 40 CFR Part 58 Appendix A (Code of Federal Regulations, 1999c) and evaluate the data quality indicators of precision, accuracy/bias, completeness, comparability, and detectability. The report also will provide conclusions and recommendations for future improvements.

2.3 SUMMARY

Atmospheric particles originate from a variety of sources and possess a range of morphological, chemical, physical, and thermodynamic properties. The composition and behavior of airborne particles 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. Particulate is an adjective and should only be used as a modifier, 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. 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 its behavior, such as its 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 (i.e., the diameter of a unit density sphere that would have the same terminal settling velocity as the real particle) is the most widely used equivalent diameter. Therefore, in this document, particle diameters, unless otherwise indicated, refer to the aerodynamic diameter.

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 aerosols is their multimodal nature. Volume distributions, measured in ambient air in the United States, almost always are found to be bimodal, with a minimum between 1.0 and 3.0 μm. The distribution of particles that are mostly larger than the minimum is termed the coarse mode. The distribution of particles that are mostly smaller than the minimum is termed the fine mode. Fine-mode particles include both the accumulation mode and the nuclei mode. Accumulation-mode particles are that portion of the fine particle fraction with diameters above about 0.1 μm. The nuclei mode, that portion of the fine particle fraction with diameters below about 0.1 μm, 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. Toxicologists and epidemiologists use ultrafine to refer to particles in the nuclei-mode size range. Aerosol physicists and material scientists tend to use nanoparticles to refer to particles generated in the laboratory in this size range.

The aerosol community uses four 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 (i.e., the particle size at which 50% of the particles enter and 50% of the particles are rejected); (3) dosimetry or occupational sizes, based on the entrance into various compartments of the respiratory system; and (4) legally specified, regulatory sizes for air quality standards. Over the years, the terms fine and coarse, as applied to particle sizes, have lost the original precise meaning of fine mode and coarse mode. 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-mode particles are not equivalent. In this document, the term “mode” is used with fine and coarse when it is desired to specify the distribution of fine-mode particles or coarse-mode particles as shown in Figures 2-4 and 2-5.

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 accumulation mode particles do not grow into the coarse mode.

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 to thousands 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. 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 (i.e., they 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; 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 fine particles are kept suspended by normal air motions and have very low deposition rates to surfaces. 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. Coarse mode particles of less than ≈10-μm diameter as well as accumulation-mode and nuclei-mode (or ultrafine) particles all have the ability to penetrate deep into the lungs and be removed by deposition in the lungs. 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.

The role of particles in reducing visibility and affecting radiative balance through scattering and absorption of light is evident as are the effects of particles in soiling and damaging materials. EPA addresses visibility effects through regional haze regulations. The direct effects of particles in scattering and absorbing light and the indirect effects of particles on clouds are being addressed in climate change programs in several government agencies.

The role of PM in acid deposition has not always been recognized. Acid deposition and PM are intimately related, however, first, because particles contribute significantly to the acidification of rain and, second, 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 acid deposition and PM concentrations. Sulfuric acid, ammonium nitrate, 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 also can contribute to the ecological damages caused by acid deposition.

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 also 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 needed to develop information to guide implementation of standard (i.e., by identifying sources of particles; to determine whether or not a standard has been attained; and to determinate 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 $PM_{2.5}$ FRM sampler consists of a PM_{10}

inlet/impactor, a $PM_{2.5}$ impactor with an oil-covered impaction substrate to remove particles larger than 2.5 μm, and a 47-mm polytetrafluoroethylene (PTFE) filter with a particle collection efficiency greater than 99.7%. Both techniques provide relatively precise (±10 %) methods for determining the mass of material remaining on a Teflon filter after equilibration. The goal of a PM indicator might be to accurately measure the material that exists as a particle in the atmosphere. However, numerous uncertainties 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. It is currently not possible to accurately characterize the material that exists as a particle in the atmosphere. There is no reference standard for particles suspended in the atmosphere; there is no accepted way to remove particle-bound water without losing some of the semivolatile components of PM, such as ammonium nitrate and semivolatile organic compounds and particle-bound water. It also is difficult to cleanly separate fine-mode and coarse-mode 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.

Fine-mode and coarse-mode particles differ not only in size and morphology (e.g., smooth droplets versus rough solid particles), but also in formation mechanisms; sources; and chemical, physical, and biological properties. It is desirable to separate fine-mode PM and coarse-mode PM as cleanly as possible in order to properly allocate health effects to either fine-mode PM or coarse-mode PM and to correctly determine sources by factor analysis or chemical mass balance. In areas with high concentrations of wind-blown soil, the current practice of separating fine- and coarse-mode particles at 2.5-μm AD may not provide the best separation of exposure, epidemiologic, and source apportionment studies. A cut near 1 μm would provide a good indicator of fine-mode PM if the air stream could be dehumidified to remove particle-bound water without evaporating semivolatile components.

Current filtration-based mass measurements lead to 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. Loss of these components may significantly impact 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.

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 nitrate) preceded by a denuder to remove 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. Semivolatile organic compounds (SVOCs) similarly can be lost from Teflon filters because of volatilization during or after collection. Such losses can cause the $PM_{2.5}$ mass to be significantly underestimated. Positive sampling artifacts also can occur as the result of the adsorption of organic gases onto the filter materials. There is a larger positive artifact caused by adsorption of organic vapor onto quartz fiber filters than onto Teflon filters. Denuder-based sampling systems also have been developed for measuring particulate phase organic compounds. This technique is an improvement over the filter/adsorbent collection method. In most denuder systems, a denuder that removes gas-phase absorbable organic gases is followed by a filter pack. The first filter collects particles. It is followed by a charcoal-impregnated glass-fiber filter that absorbs semivolatile material that evaporates from particles on the front filter. The FRM for $PM_{2.5}$ will suffer loss of particulate nitrates and SVOC, 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 composition, but that liquid water can represent a significant mass fraction of the aerosol concentration at relative humidities above 60%. Relative humidity may affect particle size, growth, and other properties. Accumulation-mode particles are usually hygroscopic. 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 to shrink with increasing relative humidity because of a structural change. The effects of relative humidity on the sorption of SVOC 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.

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 include three filters: (1) Teflon for equilibrated mass and elemental analysis, (2) a Nylon filter with a nitric acid denuder to collect nitrate, and (3) a quartz fiber filter for elemental and organic carbon (but without any correction for positive or negative artifacts because of adsorption of volatile organic compounds on the quartz filters or evaporation of semivolatile organic compounds from the collected particles). The IMPROVE network of samplers provides four 24-h integrated filter samples: (1) a PM_{10} filter and (2) a $PM_{2.5}$ Teflon filter for gravimetric determination of mass and for analysis of heavy elements by X-ray fluorescence; (3) 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 (4) a quartz filter for measurement of elemental carbon (EC) and organic carbon (OC) by thermal optical analysis. The EC/OC measurement method utilized in the IMPROVE network is based on optical correction of pyrolytic char using optical reflectance, whereas the EC/OC method specified in the NIOSH method 5040 (for diesel soot) is based on optical transmission for correction for pyrolytic char. These methods also differ in their temperature profiles. The two methods agree on total carbon but differ in the split of total carbon into EC and OC.

The EPA expects that more than 200 local agency monitoring sites throughout the states will operate continuous PM monitors. However, EPA has not yet provided any guidance regarding appropriate continuous monitoring techniques. All currently available techniques for continuous measurements of suspended particle mass, such as the integrating nephelometer, the beta-absorption monitor, and the Tapered Element Oscillating Microbalance (TEOM) share the problem of dealing with semivolatile PM components (i.e., 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 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. However, the FRM is required to operate at no more than 5 °C above the ambient temperature. This philosophical difference in operation leads to differences between the TEOM and integrated mass concentrations for both PM_{10} and $PM_{2.5}$.

Several candidates 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. In addition to continuous mass measurement, a number of techniques for continuous measurement of sulfate, nitrate, or elements are being tested.

Aerosol time-of-flight mass spectroscopy (ATOFMS) provides a new technique for real-time measurement of correlated size and composition profiles of individual atmospheric aerosol particles. Measurements are made in situ by combining a dual-laser aerodynamic particle sizing system to size and track individual particles through the instrument and laser desorption/ionization time-of-flight mass spectrometry to obtain correlated single particle composition data. ATOFMS technology is able to size, count, and provide chemical composition on individual particles ranging in size from 10 nm to 2 μm. However, there is still controversy over the calibration of such techniques.

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

3.1 INTRODUCTION

This chapter incorporates material from Chapters 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 year of operation of the recently deployed nationwide network of Federal Reference Method $PM_{2.5}$ monitors are presented. Results of field studies that have characterized the composition of organic compounds in the ambient aerosol are summarized in Appendix 3A as a complement to the data for the inorganic composition of ambient particles that was presented in Appendix 6A in the 1996 PM AQCD. Data for characterizing the daily and seasonal variability of $PM_{2.5}$ concentrations are discussed in Section 3.2.1, the intraday variability of $PM_{2.5}$ concentrations in Section 3.2.2, the relations among different size fractions in Section 3.2.3, the interrelations and correlations among PM components in Section 3.2.4, and the spatial variability of various PM components 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. Estimates of contributions of various sources to ambient PM levels given by source apportionment studies also are presented in Section 3.3. More detailed information about the composition of emissions from various sources is given in Appendix 3B. 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 3.4.1 and uncertainties in emissions estimates in Section 3.4.2.

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 increasing uncertainties in these areas.

3.2 TRENDS AND PATTERNS IN AMBIENT $PM_{2.5}$ CONCENTRATIONS

A significant amount of data for characterizing PM_{10} mass concentrations and trends exists and that available up to about 1994 was presented in the 1996 PM AQCD. However, data sets for characterizing $PM_{2.5}$ and $PM_{(10-2.5)}$ mass or trends were not as extensive. Sources of data on $PM_{2.5}$ (fine) and $PM_{(10-2.5)}$ (coarse), which were discussed in the 1996 PM AQCD, include EPA's Aerometric Information Retrieval System (AIRS) (U. S. Environmental Protection Agency, 2000a), 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 calendar year 1999 data from this network, and provides an approximate characterization of nationwide $PM_{(10-2.5)}$ by comparing PM_{10} to $PM_{2.5}$ measurements at sites where both types of compliance monitors are located. In addition, a small number of recent studies in which daily mass and composition measurements are available for extended periods will be discussed in this section.

Summary tables giving the results of 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 A to Chapter 6 of the 1996 PM AQCD. The summary tables included data for mass, organic carbon, elemental carbon, nitrate, sulfate, and trace elements. The results of 66 studies were separated and 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. Summary tables showing data for organic carbon, elemental carbon and organic compounds in ambient particles are given in Appendix 3A. Data for the gross chemical composition of $PM_{2.5}$ particles sampled in rural air by the IMPROVE network and for the aerosol composition studies cited in the 1996 PM AQCD (which were carried out mainly in urban areas) are summarized in Table 3-1. Data are shown separately for the eastern and western United States. The IMPROVE data are annual average concentrations for 1998. Quality assured aerosol composition data for urban areas from the $PM_{2.5}$ speciation network are not yet available for comparison to the IMPROVE data set. Many features are reflected broadly in both data sets (i.e., increasing organic carbon, nitrate, and minerals and decreasing sulfate in going from east to west). The annual average $PM_{2.5}$ concentration of 11.0 μg/m^3 reported by eastern IMPROVE sites is almost three times higher than 3.9 μg/m^3 reported by IMPROVE sites in the western United States. The data shown in Table 3-1 refer only to components that have been identified and quantified. There may be other unidentified components that can represent a significant contribution to the total measured mass, as indicated in the 1996 PM AQCD.

TABLE 3-1. GROSS CHEMICAL COMPOSITION OF $PM_{2.5}$ PARTICLES OBTAINED IN RURAL AREAS OF THE EASTERN AND WESTERN UNITED STATES BY THE IMPROVE NETWORK AND IN MIXED RURAL, SUBURBAN, AND URBAN AREAS OBTAINED BY STUDIES SUMMARIZED IN THE 1996 PARTICULATE MATTER AIR QUALITY CRITERIA DOCUMENT

	IMPROVE[1]		1996 PM AQCD[2]	
	Eastern U.S.	Western U.S.	Eastern U.S.	Western U.S.
	% Contribution		% Contribution[a]	
$SO_4^=$	56	33	44	11
EC	5	6	5	14
OC	27	36	27	38
NO_3	5	8	1	15
Crustal	7	17	6	14
	Reconstructed $PM_{2.5}$ Concentration (μg/m^3)		$PM_{2.5}$ Concentration (μg/m^3)	
$PM_{2.5}$	11.0	3.9	31.0	37.3

[a] Note that contributions do not add to 100% because a portion of the measured total mass was not characterized chemically.

Sources: (1) IMPROVE network (1998); (2) U.S. Environmental Protection Agency (1996).

PM_{10} Concentrations and Trends

Nationwide PM_{10} annual mean concentrations from AIRS for calendar year 1999 are shown in Figure 3-1. Concentrations in most areas of the country were below the level of the annual PM_{10} standard (50 μg/m^3) in 1999. Exceptions include central South Carolina, Puerto Rico, and several places in the southwestern United States and central California.

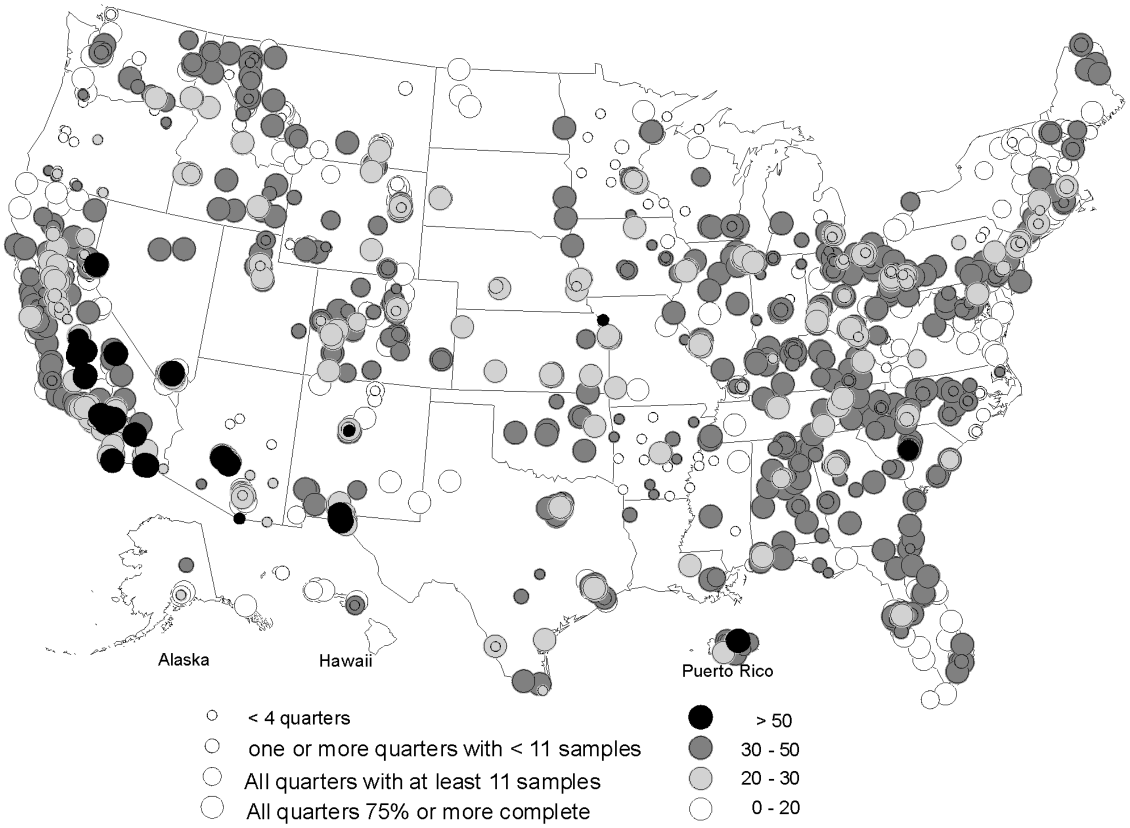


Figure 3-1. 1999 annual mean PM_{10} concentrations (μg/m^3).

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

Nationwide trends in annual mean PM_{10} concentrations from 1989 through 1998 based on data obtained at 138 rural sites, 355 suburban sites, and 413 urban sites reporting to AIRS are shown in Figure 3-2 (U.S. Environmental Protection Agency, 2000b). Though average concentration levels differ among sites, with higher levels at urban and suburban sites, the overall nationwide trend shows a decline. Figure 3-3 shows the annual mean PM_{10} trend summarized by EPA region. Decreases were greater in the western United States than in the eastern United States, ranging from about 20% in the East to about 38% in the Northwest.

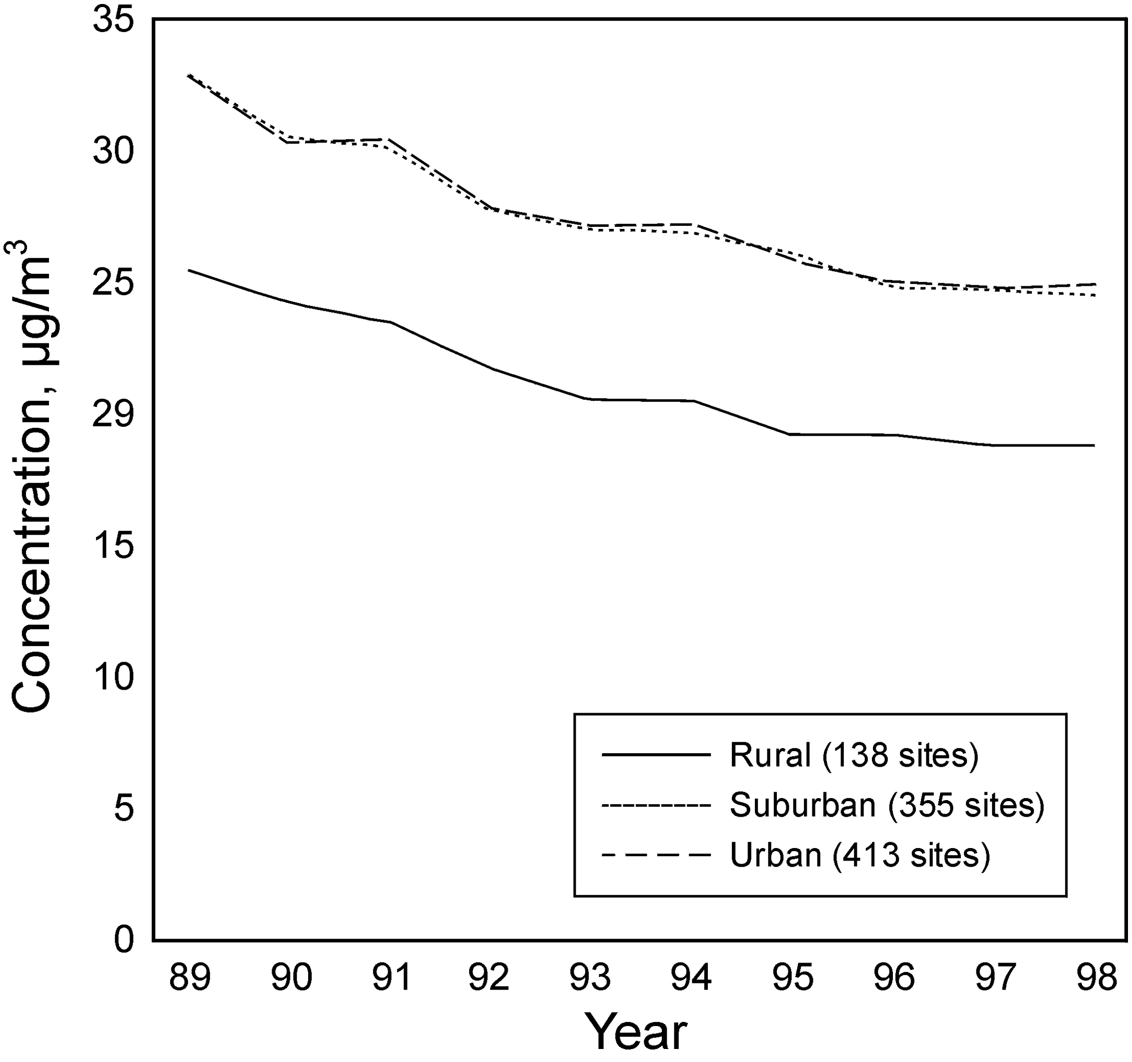
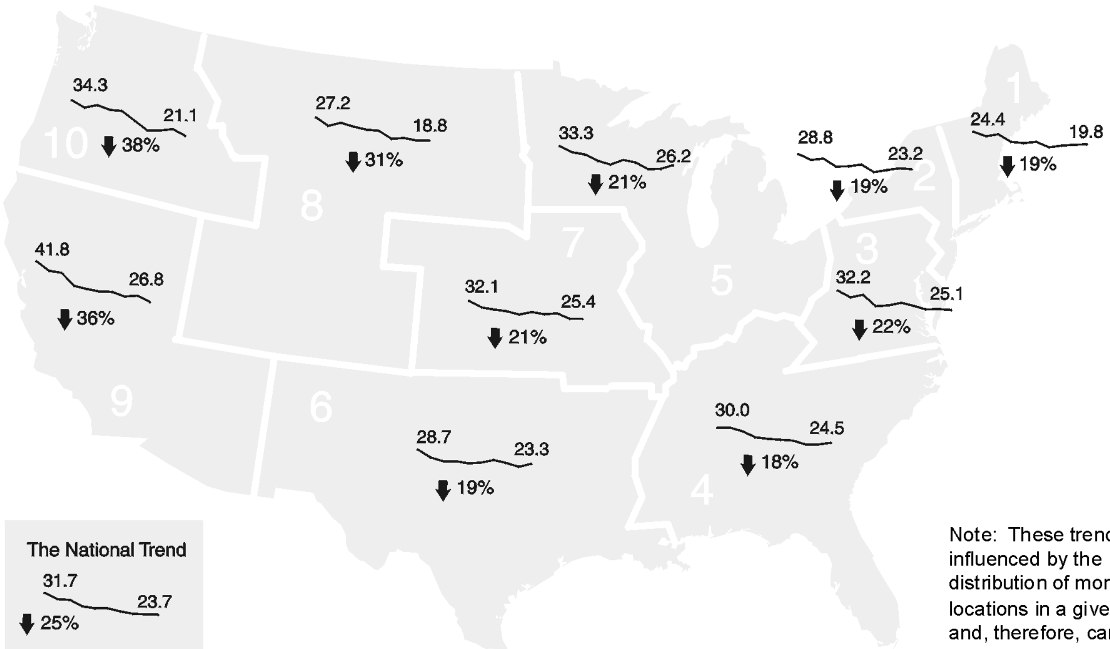


Figure 3-2. Nationwide trend in ambient PM_{10} concentration from 1989 through 1998.

Source: U.S. Environmental Protection Agency (2000b).



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.

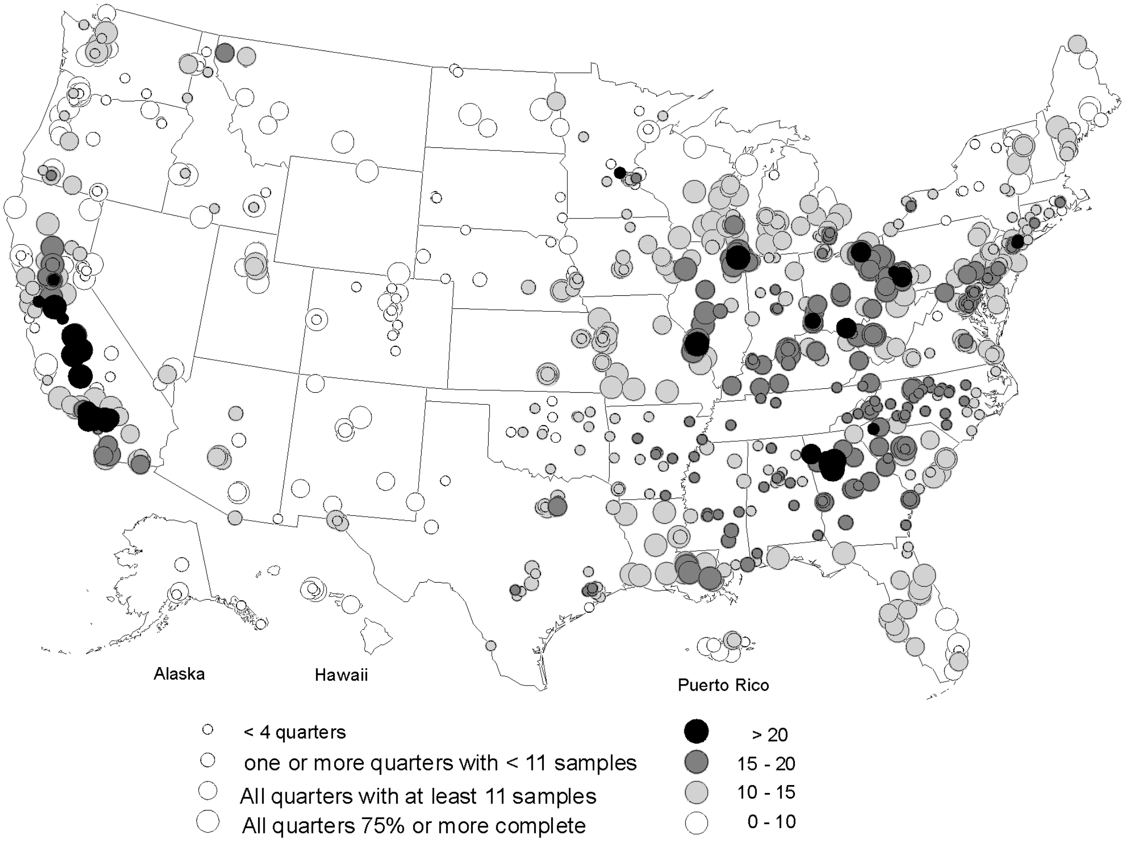
Alaska is in EPA Region 10; Hawaii, EPA Region 9; and Puerto Rico, EPA Region 2. Concentrations are µg/m3.

Figure 3-3. Trend in PM_{10} annual mean concentrations by EPA region, 1989 through 1998 ($\mu g/m^3$).

Source: U. S. Environmental Protection Agency (2000a).

$PM_{2.5}$ Concentrations and Trends

Nationwide $PM_{2.5}$ concentrations from the 1999 compliance network are shown in Figures 3-4a and 3-4b. By the end of 1999 the network consisted of over 1025 monitors. Annual mean $PM_{2.5}$ concentrations were above 15 $\mu g/m^3$ in many areas of the country, especially throughout the eastern United States, and above 20 $\mu g/m^3$ in several major urban locations. The 98th percentile 24-h average concentrations were generally below 65 $\mu g/m^3$. Most of the sites with levels above 65 $\mu g/m^3$ are located in California. As shown by the size of the dots on the maps, the picture for 1999 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. Further, at the time these maps were created some states such as Massachusetts and New Hampshire had not reported valid data to AIRS from all monitoring sites. It is premature to



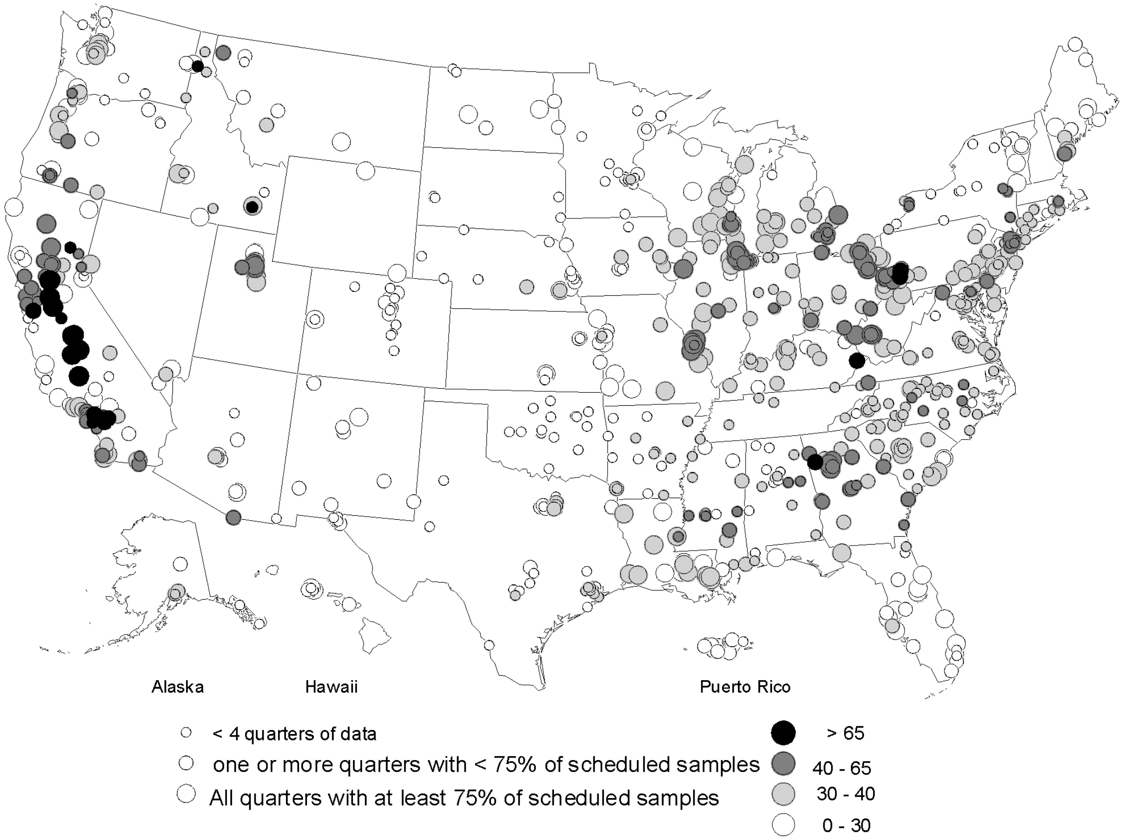
Source: US EPA AIRS Data Base as of 7/12/00 without data flagged as 1, 2, 3, 4, T, W, Y, or X.

Figure 3-4a. 1999 annual mean $PM_{2.5}$ concentrations ($\mu g/m^3$).

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

make judgments on whether an area likely will attain the 1997 $PM_{2.5}$ standards based on this single year of data, not only because the 1999 data is not complete, but also because the 1997 standard is defined in terms of 3-year average concentrations.

Annual average $PM_{2.5}$ obtained as part of 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), PTEAMS (Riverside, CA), MAACS (Philadelphia, PA; Washington, DC; and Nashville, TN), South Boston Air Quality and Source Apportionment Study (Boston, MA); NPMRMN



Source: US EPA AIRS Data Base as of 7/12/00 without data flagged as 1, 2, 3, 4, T, W, Y, or X.

Figure 3-4b. 1999 98th percentile 24-h average PM$_{2.5}$ concentrations (μg/m^3).

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

(Phoenix, AZ). Remaining sites were part of the 24-cities study. 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 conclusions can be reached. Darlington et al. (1997) proposed that because the consistent reductions in PM$_{10}$ levels were found in a wide variety of environments ranging from urban to rural over large areas, that common factors or controls might be responsible for these reductions, and that these factors affected fine particles more strongly than coarse particles because fine particles can be transported over longer distances. The longest time series of PM$_{2.5}$ concentration and composition data have been obtained by the California Air Resources Board. Their data show that annual average PM$_{2.5}$ concentrations decreased about 50% in the South Coast Air

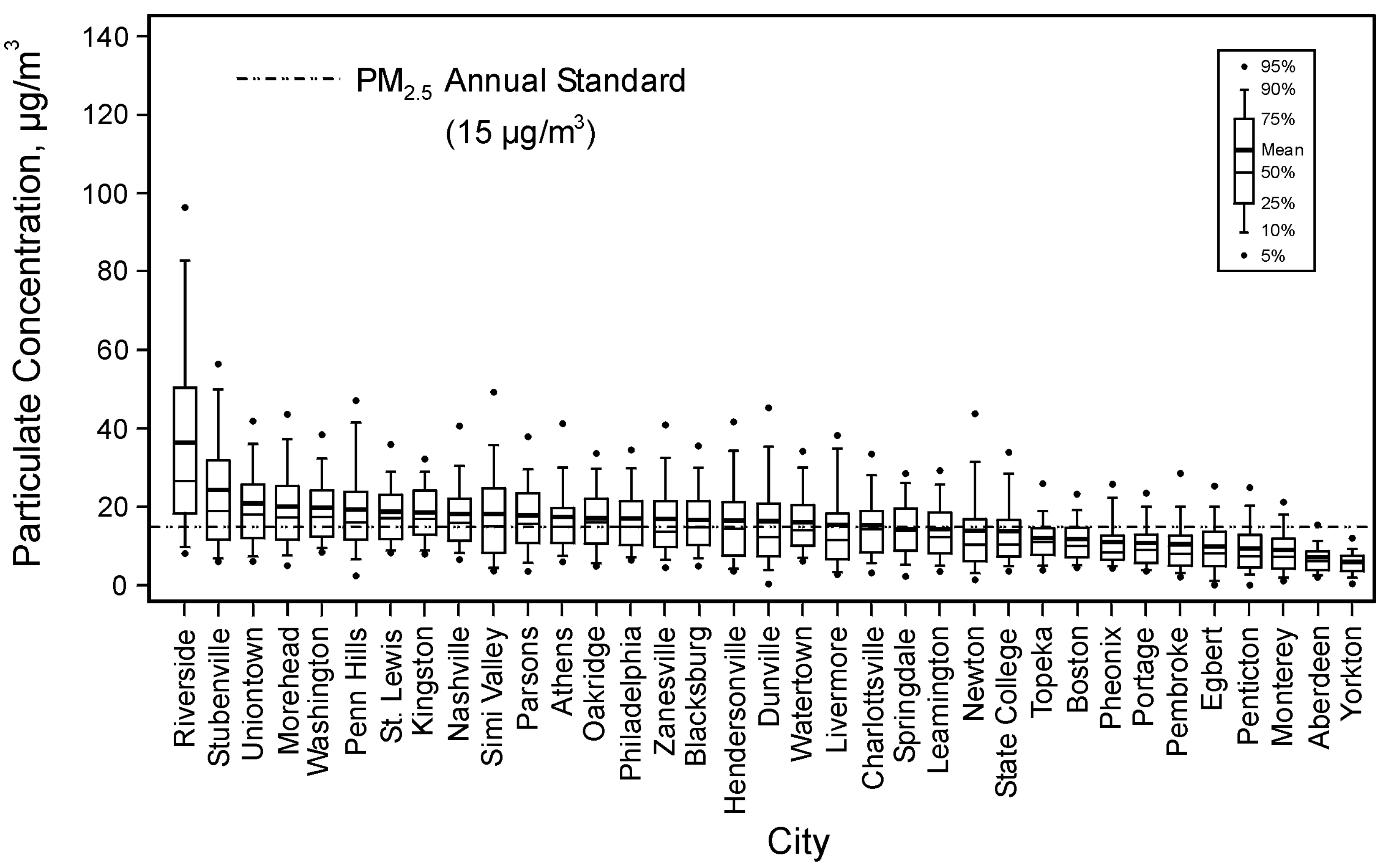


Figure 3-5. Annual distribution of 24-h average $PM_{2.5}$ concentrations observed in U.S. and Canadian health studies.

Source: Bahadori et al. (2000a).

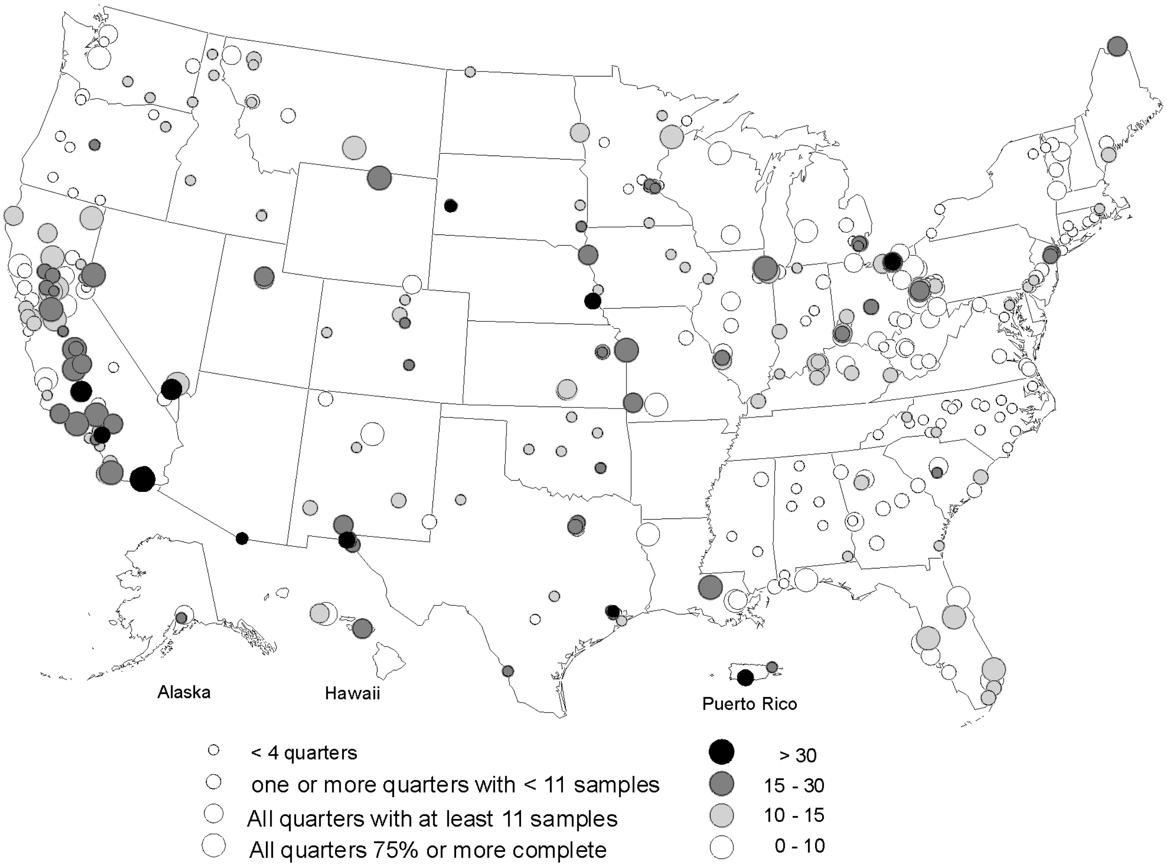
Basin, 35% in the San Joaquin Valley, 30% in the San Francisco Bay Area, and 35% in the Sacramento Valley from 1990 to 1995 (Dolislager and Motallebi, 1999). $PM_{2.5}$ data have been collected continuously since 1994 as part of the children's health study in 12 communities in southern California (Taylor et al., 1998). Data obtained at all sites show decreases ranging from 2% at Santa Maria to 37% at San Dimas/Glendora in $PM_{2.5}$ from 1994 through 1998. These decreases were accompanied by decreases in major components such as nitrate, sulfate, ammonium, and acids. However, undefined components showed a mixed pattern of increases and decreases at the same sites.

In common usage, the term "background concentrations" refers to concentrations observed in remote areas relatively unaffected by local pollution sources. However, as noted in Chapter 6 of the 1996 PM AQCD, several definitions of background concentrations are possible.

The two definitions chosen in that document as being most relevant for regulatory purposes are based on estimates of contributions from uncontrollable sources that can affect concentrations in the United States. The first definition refers to the concentration resulting from anthropogenic and natural emissions outside North America and natural sources within North America. The second definition refers to the concentration resulting from natural sources only within and outside of North America. Because of long-range transport from anthropogenic source regions in North America, it is impossible to obtain background concentrations defined above solely on the basis of direct measurement in remote areas in North America. Annual average natural background levels of PM_{10} (according to definition 1) 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 (U.S. Environmental Protection Agency, 1996). Although the values shown in Table 3-1 are broadly consistent with those given above, the data shown in Table 3-1 represent only upper limits to background concentrations, because of contributions from long-range transport from anthropogenic sources within North America. Peak 24-h average natural background concentrations may be substantially higher than the annual or seasonal average natural background concentrations. Estimates of levels for background 2 are not yet available. However, recent information about contributions to background concentrations that fall under definitions 1 and 2 because of long-range transport from sources outside the United States is given in Section 3.3.2.

PM$_{(10-2.5)}$ Concentrations

Using AIRS data from the 1999 PM$_{10}$ and PM$_{2.5}$ compliance networks it is possible to construct a preliminary picture of coarse PM across the country. This is accomplished by pairing data from nearly 400 compliance monitoring sites where PM$_{10}$ and PM$_{2.5}$ monitors are col-located, and subtracting the mass concentrations of PM$_{2.5}$ from PM$_{10}$. The results of this simple difference method are shown in Figure 3-6. Because of potential problems with this approach, the results should be viewed with caution. Using this approximate method, annual mean PM$_{(10-2.5)}$ concentrations are as high as 54 μg/m^3, with a nationwide median concentration of 10 μg/m^3. The higher values occur mainly in the western United States, particularly in California.



Source: US EPA AIRS Data Base as of 7/12/00 without data flagged as 1, 2, 3, 4, T, W, Y, or X.

Figure 3-6. 1999 annual mean PM$_{(10-2.5)}$ concentrations (μg/m^3).

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

3.2.1 Daily and Seasonal Variability

Data for $PM_{2.5}$ concentrations obtained as part of the nationwide NAMS/ SLAMS network during 1999 are summarized in Figures 3-7a through c for individual sites in selected urban areas across the United States. As far as possible, the cities were chosen because air pollution-health outcome studies had been performed there, and others were added for the sake of geographic coverage. At least two sites within each of the seven aerosol characteristic regions of the United States identified in Chapter 6 of the 1996 PM AQCD and later adopted by the Health Effects Institute for grouping the results of air pollution-epidemiology studies were chosen. The figures show the range of 24-h average values within each calendar quarter as box and whisker plots and the annual average concentrations for 1999 are shown above each figure. Because FRM measurements of $PM_{2.5}$ began only in January, data tend to be limited in many areas, especially for the first quarter. As can be seen from the figures, the pattern of seasonal variability for 1999 varied across the United States. At all of the sites shown for the eastern United States, except for the site in Miami, FL, highest quarterly mean values and maximum values occurred during the third quarter (summer) of 1999. This pattern was found, in general, at other sites within the same MSAs, although there were exceptions. At sites west of the Mississippi River, highest mean values occurred during the first or fourth quarter (winter or autumn) of 1999, except for the site in Kansas City, where the highest quarterly mean and maximum values occurred in the third quarter. Generally, similar patterns of seasonal variability were found at all other sites within MSAs sampled, although there were exceptions, which may have been related to contributions from local sources as opposed to contributions from regional background sources. At the sites in Miami and Puerto Rico, maximum concentrations occurred during the second quarter, and may have been related to the transport of dust from the Sahara Desert. Because of the limited nature of these data, definitive conclusions regarding long-term patterns of seasonal variability cannot be drawn from these data alone.

Longer time series for making more definitive statements about seasonal variations in $PM_{2.5}$ concentrations are available from a few studies which have had as their goal the characterization of $PM_{2.5}$ and PM_{10} concentrations in major urban areas. The Metropolitan Acid Aerosol 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).

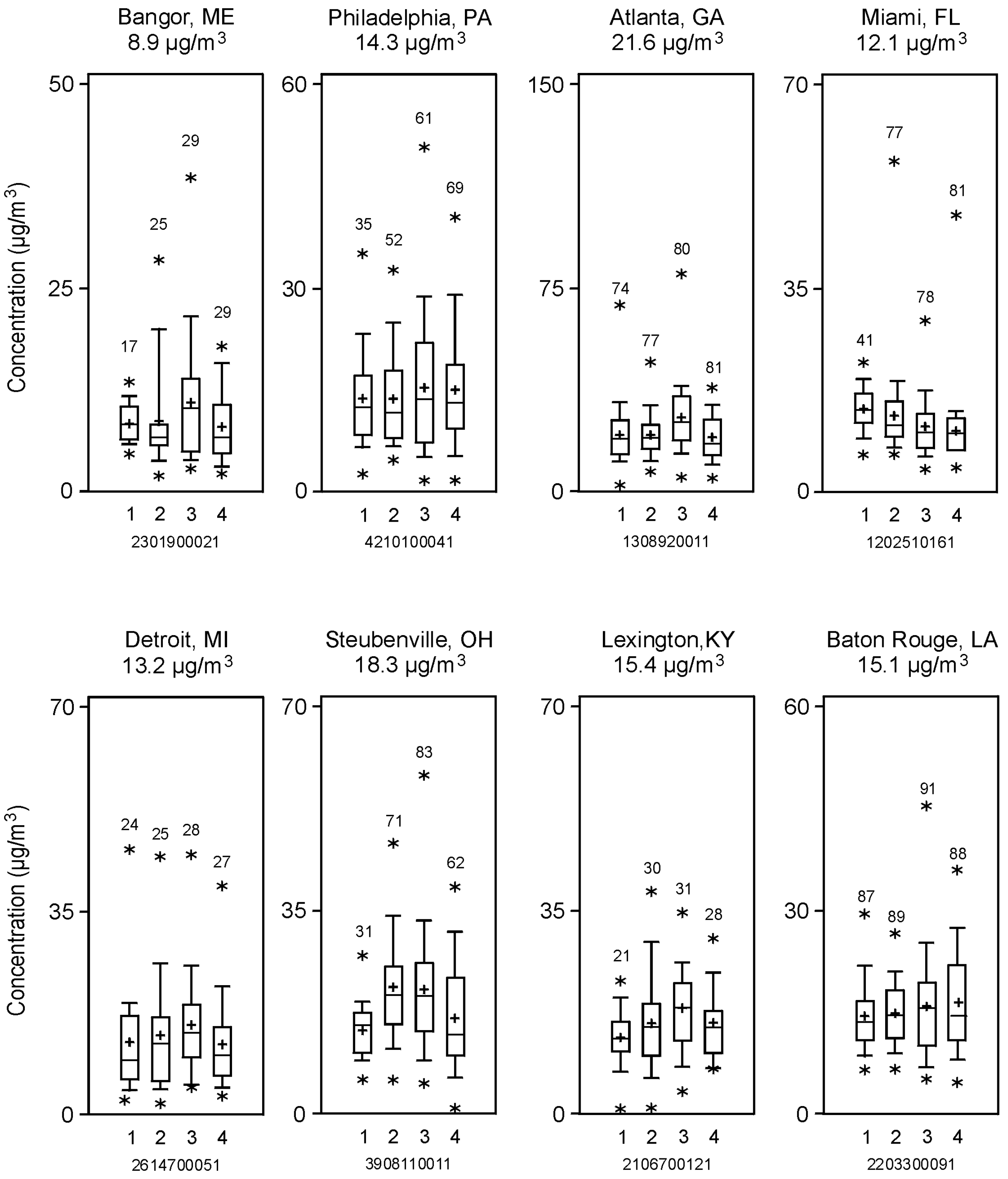


Figure 3-7a. Quarterly distributions of 24-h average $PM_{2.5}$ concentrations obtained in eight eastern U.S. cities by the nationwide SLAMS/ NAMS network of $PM_{2.5}$ FRM monitors during 1999. The data show the lowest, lowest tenth percentile, lower quartile, median, highest quartile, highest tenth percentile, and highest $PM_{2.5}$ values. Values given above the highest extreme value in the graphs refer to the number of observations. Annual average concentrations are shown immediately above each graph.

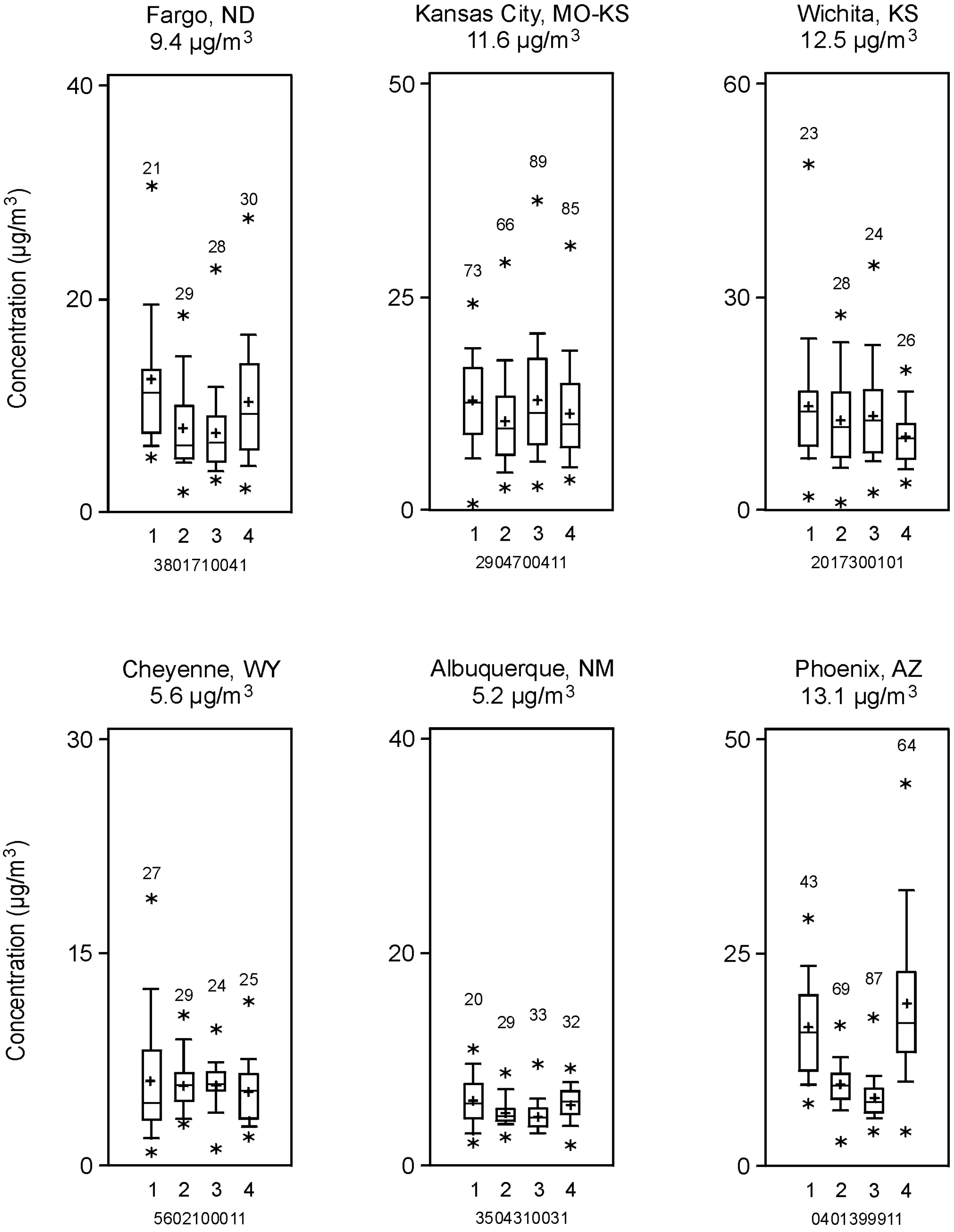


Figure 3-7b. **Quarterly distributions of 24-h average $PM_{2.5}$ concentrations obtained in six central and mountain U.S. cities by the nationwide SLAMS/ NAMS network of $PM_{2.5}$ FRM monitors during 1999. The data show the lowest, lowest tenth percentile, lower quartile, median, highest quartile, highest tenth percentile, and highest $PM_{2.5}$ values. Values given above the highest extreme value in the graphs refer to the number of observations. Annual average concentrations are shown immediately above each graph.**

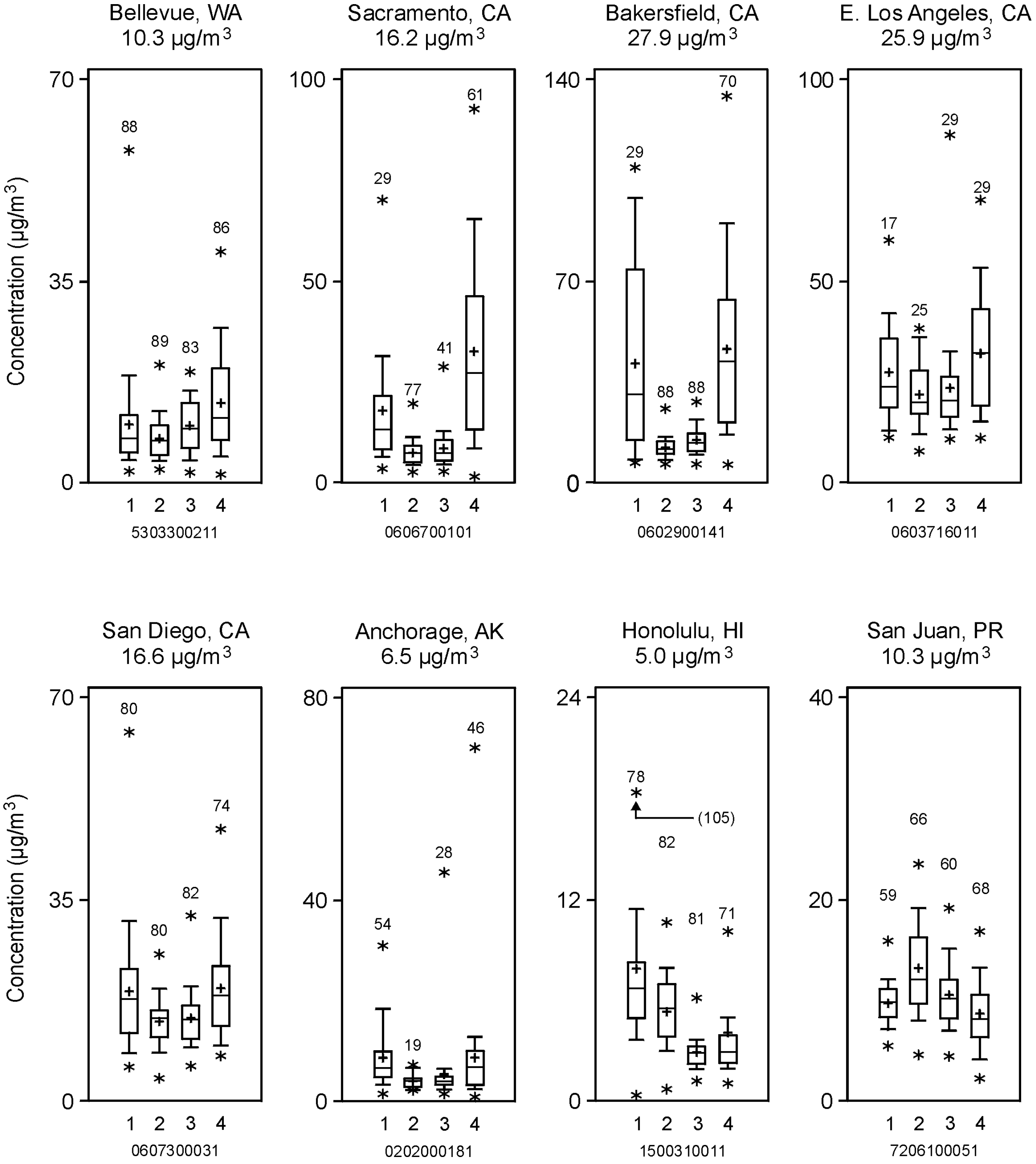


Figure 3-7c. **Quarterly distributions of 24-h average $PM_{2.5}$ concentrations obtained in seven western U.S. cities and San Juan, PR, by the nationwide SLAMS/ NAMS network of $PM_{2.5}$ FRM monitors during 1999. The data show the lowest, lowest tenth percentile, lower quartile, median, highest quartile, highest tenth percentile, and highest $PM_{2.5}$ values. Values given above the highest extreme value in the graphs refer to the number of observations. For Honolulu, HI the highest value observed is shown in parentheses. Annual average concentrations are shown immediately above each graph.**

Seasonal variations in $PM_{2.5}$ and PM_{10} concentrations obtained during the course of this study are shown in Figure 3-8.

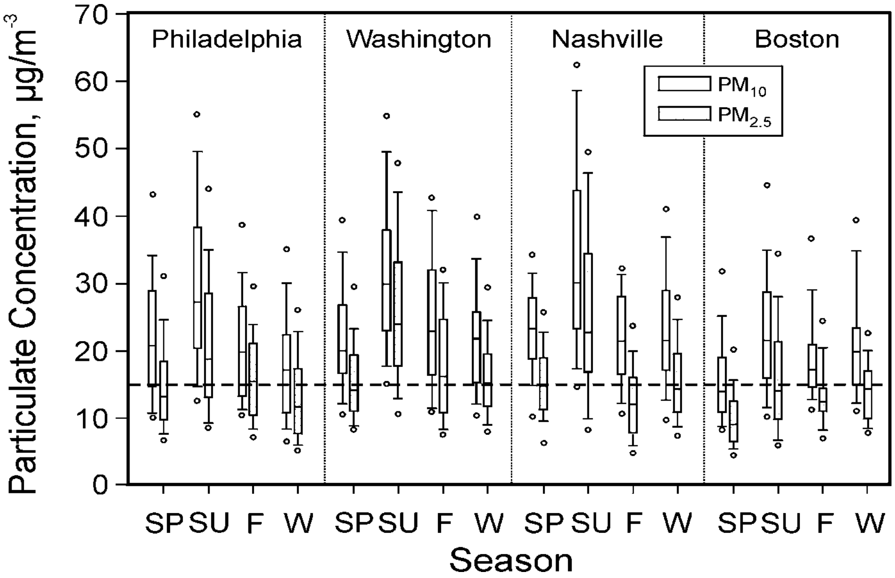


Figure 3-8. Concentrations of $PM_{2.5}$ and PM_{10} measured in the four MAACS cities. The data show the lowest, lowest tenth percentile, lowest quartile, median highest quartile, highest tenth percentile, and highest $PM_{2.5}$ 24-h average values. The dashed line shows the level of the annual $PM_{2.5}$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

Source: Bahadori et al. (2000b).

The data for the four cities included in MAACS are presented as box plots showing the lowest, lowest tenth percentile, lowest quartile, median, highest quartile, highest tenth percentile, and highest $PM_{2.5}$ and PM_{10} values in Figure 3-8. Highest $PM_{2.5}$ and PM_{10} values are found during the summer in all four cities, and mean values are highest during the summer in all cities, although the seasonal pattern in Boston appears to be more nearly bi-modal with an additional winter peak. This seasonal pattern, based on 2- to 3-year sampling periods for each city during 1992 through 1996, is in accord with that obtained from the FRM monitors in the NAMS and SLAMS network.

Frequency distributions for $PM_{2.5}$ concentrations obtained in Philadelphia are shown in Figure 3-9 (Bahadori et al., 2000b). Concentrations predicted from the log-normal distribution, using geometric mean values and standard deviations derived from the data, also are shown. 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. Day-to-day concentration differences in the data set are 6.8 ± 6.5 $\mu g/m^3$ for $PM_{2.5}$ and 8.6 ± 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}.

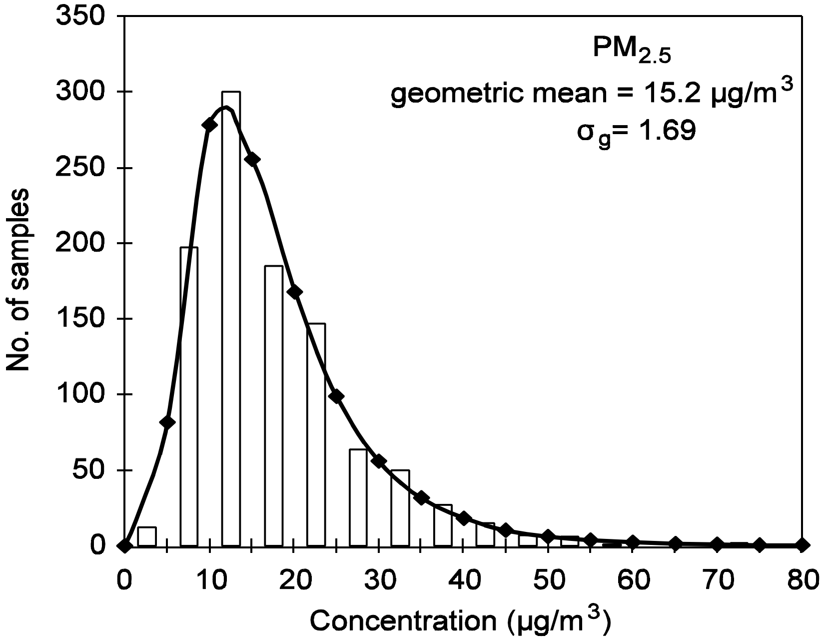


Figure 3-9. Frequency distribution of 24-h average $PM_{2.5}$ concentrations measured at the PBY site in southwestern Philadelphia. Log-normal distribution fit to the data shown as solid line.

Different conclusions could be drawn about data collected elsewhere in the United States. $PM_{2.5}$ concentrations obtained in Phoenix, AZ, from 1995 through 1997 are summarized in Figure 3-10 and frequency distributions of $PM_{2.5}$ concentrations obtained in Phoenix are shown in Figure 3-11. Day-to-day concentration differences in this data set are 2.9 ± 3.0 $\mu g/m^3$ with a

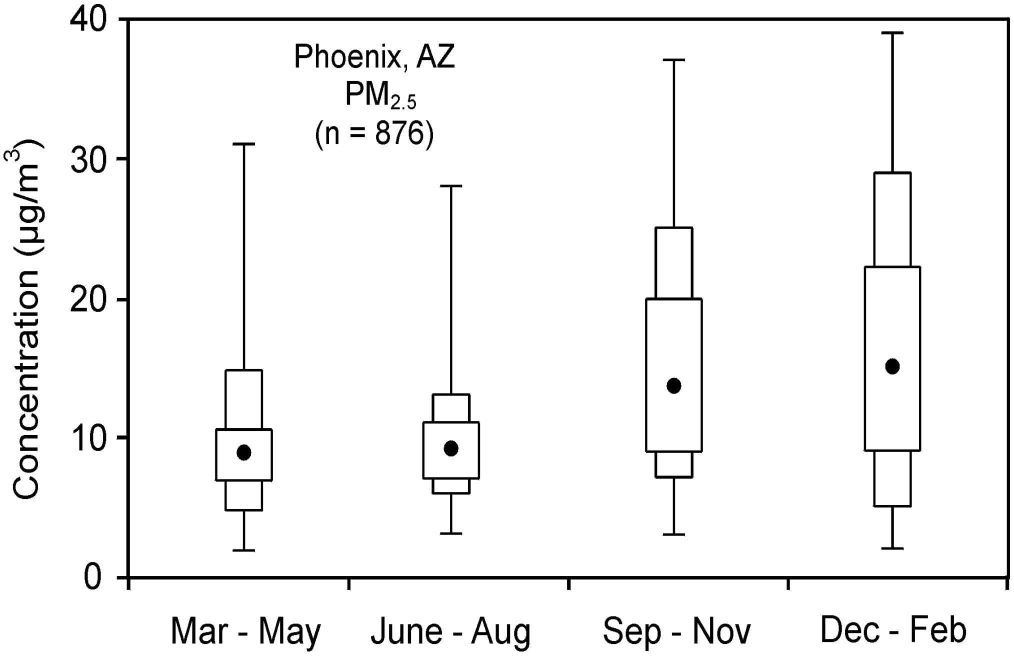


Figure 3-10. Concentrations of 24-h average $PM_{2.5}$ measured at the EPA site in Phoenix, AZ. The data show the lowest, lowest tenth percentile, lowest quartile, median (black circles), highest quartile, highest tenth percentile, and highest $PM_{2.5}$ values.

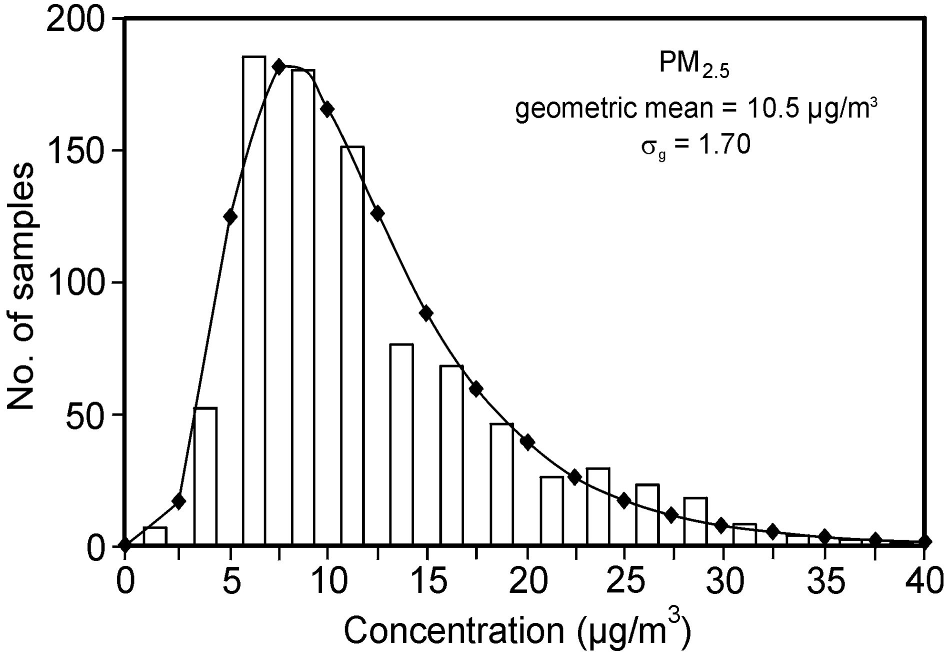


Figure 3-11. Frequency distribution of 24-h average $PM_{2.5}$ concentrations measured at the EPA site in Phoenix, AZ.

maximum day-to-day concentration difference of 23 μg/m^3. $PM_{2.5}$ and $PM_{(10-2.5)}$ data were obtained at a number of sites in California on a sampling schedule of every 6 days with dichotomous samplers from 1989 through 1998. Histograms showing the frequency distribution of the entire set of $PM_{2.5}$ and $PM_{(10-2.5)}$ concentrations obtained by the CARB network of dichotomous samplers from 1989 to 1998 are shown in Figures 3-12 and 3-13. Also shown are log-normal distributions generated 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 3-14. The frequency distribution of $PM_{2.5}$ concentrations obtained at Riverside-Rubidoux from 1989 to 1994 is shown in Figure 3-15. It can be seen that the data are not as well fit by a log-normal distribution as can the data shown in Figure 3-9, for example, mainly as the result of a significant number of days with $PM_{2.5}$ >100 μg/m^3.

An examination of the data from the four MAACS cities, Phoenix, AZ, and Riverside, CA, indicates that substantial differences exist in aerosol properties between widely separated geographic regions. Fine-mode particles make up most of the PM_{10} mass observed in the MAACS cities and appear to drive the daily and seasonal variability in PM_{10} concentrations there. Coarse-mode particles represent a larger fraction of PM_{10} mass in Phoenix and Riverside and drive the seasonal variability in PM_{10} seen there. The ratio of $PM_{2.5}$ to PM_{10} concentrations is much larger in the MAACS cities of Philadelphia (0.72); Washington, DC (0.74); and Nashville (0.63) than in either Phoenix (0.34) or Riverside (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 dust suspension at Riverside. In addition, the seasonal variability of $PM_{2.5}$ concentrations observed in Phoenix, AZ, and Riverside, CA, 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

The variability of PM concentrations on time scales shorter than a day can, in principle, be characterized by measurements made by TEOMs and β-gauge monitors that are currently used

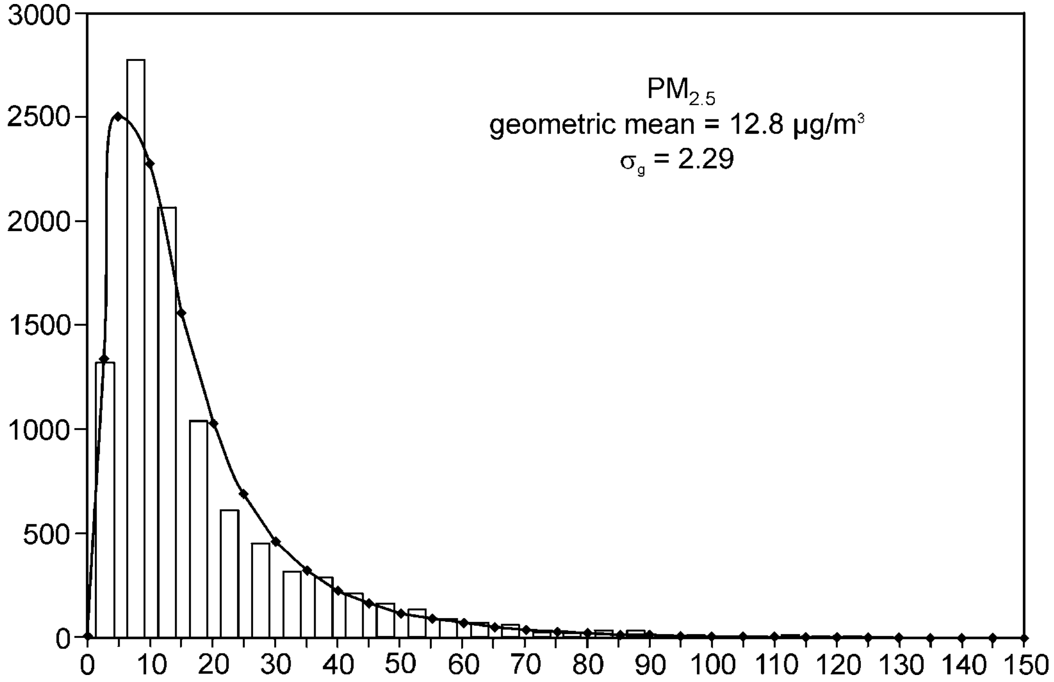


Figure 3-12. Frequency distribution of 24-h average $PM_{2.5}$ measurements obtained from all California Air Resources Board dichotomous sampler sites from 1989 to 1998.

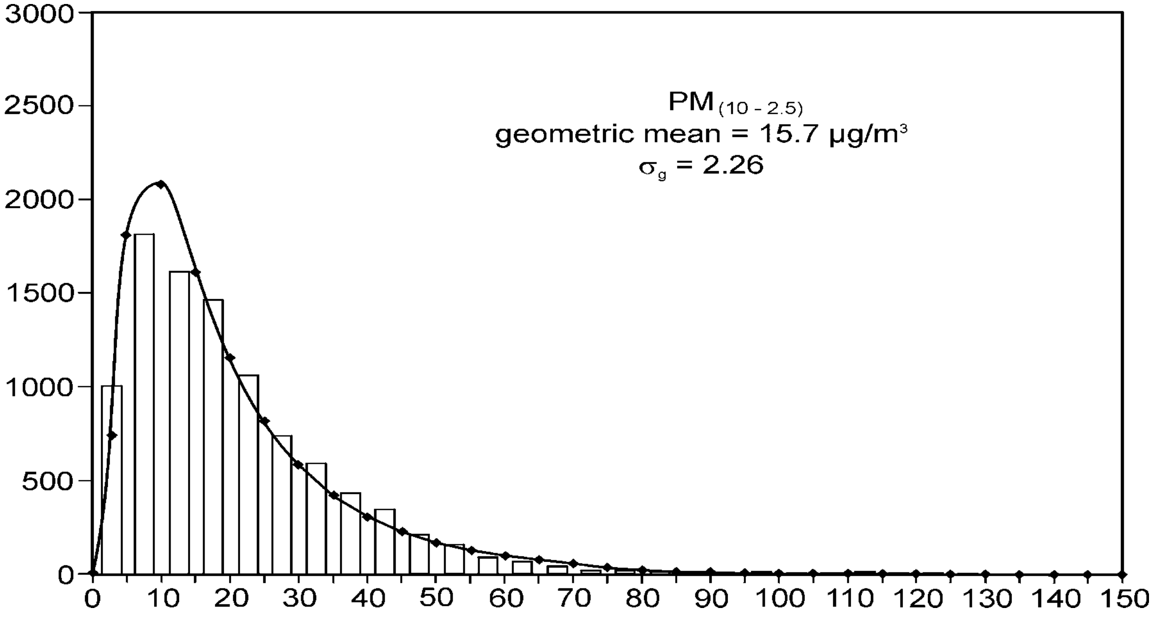


Figure 3-13. Frequency distribution of 24-h average $PM_{(10\text{-}2.5)}$ concentrations obtained from all California Air Resource Board Dichotomous sampler sites from 1989 to 1998.

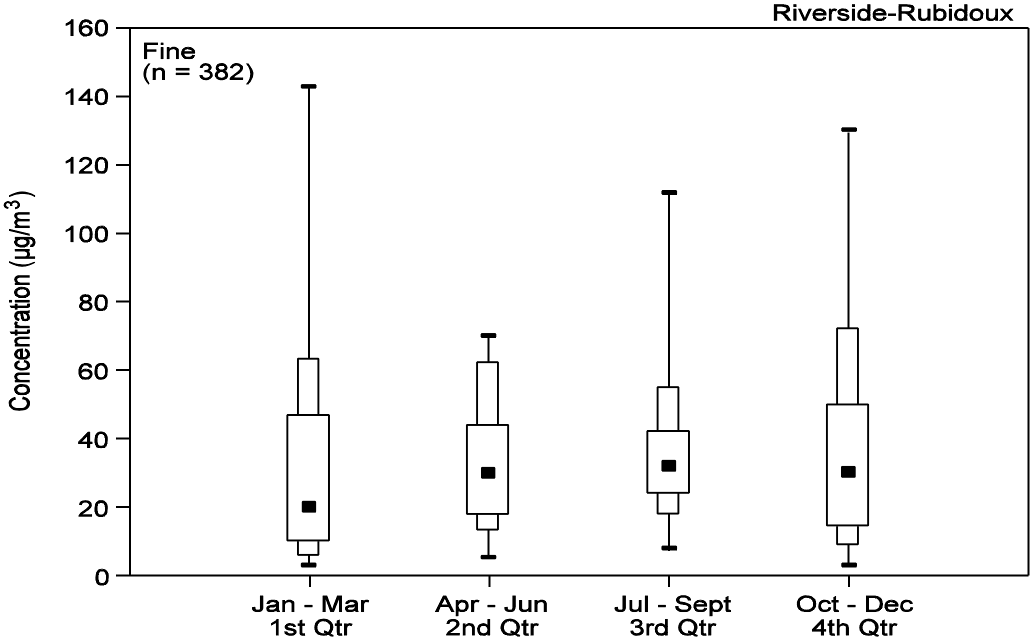


Figure 3-14. Concentrations of 24-h average $PM_{2.5}$ measured at the Riverside-Rubidoux site. The data show the lowest, lowest tenth percentile, lowest quartile, median (black squares), highest quartile, highest tenth percentile, and highest $PM_{2.5}$ values.

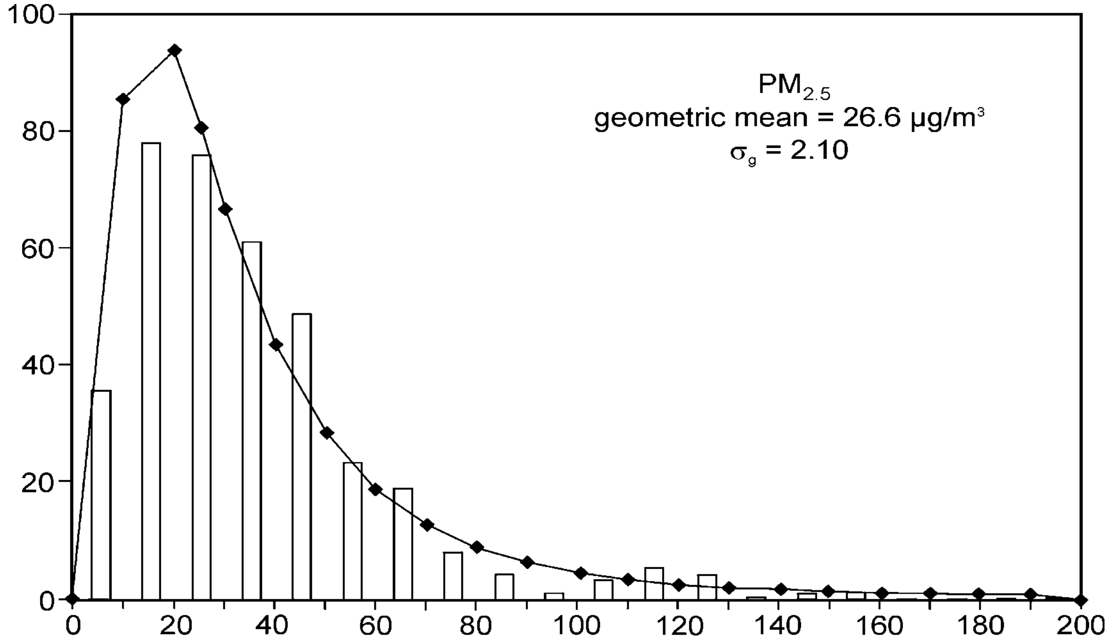


Figure 3-15. Frequency distribution of 24-h average $PM_{2.5}$ concentrations measured at the Riverside-Rubidoux site.

to provide Air Quality Index (API) information to the public. A description of these methods was given in Section 2.2.5. However, as shown in Chapter 2, continuous methods are subject to artifacts because, in large part, of heating of their inlets, which results in the loss of components such as water, ammonium nitrate, and semi-volatile organic compounds (cf. Sections 2.2.1.1 and 2.2.3 for further details concerning the chemistry of volatilizable components), so caution should be used in interpreting results obtained by these techniques.

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 3-16. 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-gauge monitors with unheated inlets there. It should be noted in examining the diurnal variations shown in Figure 3-16, that there is substantial day-to-day variability in the diurnal profile of $PM_{2.5}$ measured at the same location which is then 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 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, 2000c). 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 are greatest. Secondary aerosol components that are produced by photochemical reactions such as secondary organic compounds may have a daily maximum in the afternoon, by analogy with ozone. PM produced by residential heating (e.g., from wood burning), on the other hand, reach maximum levels during the night.

Although the interquartile ranges for hour-to-hour changes in $PM_{2.5}$ concentrations shown in Figure 3-16 encompass several $\mu g/m^3$, extreme values for the hour-to-hour variations can be

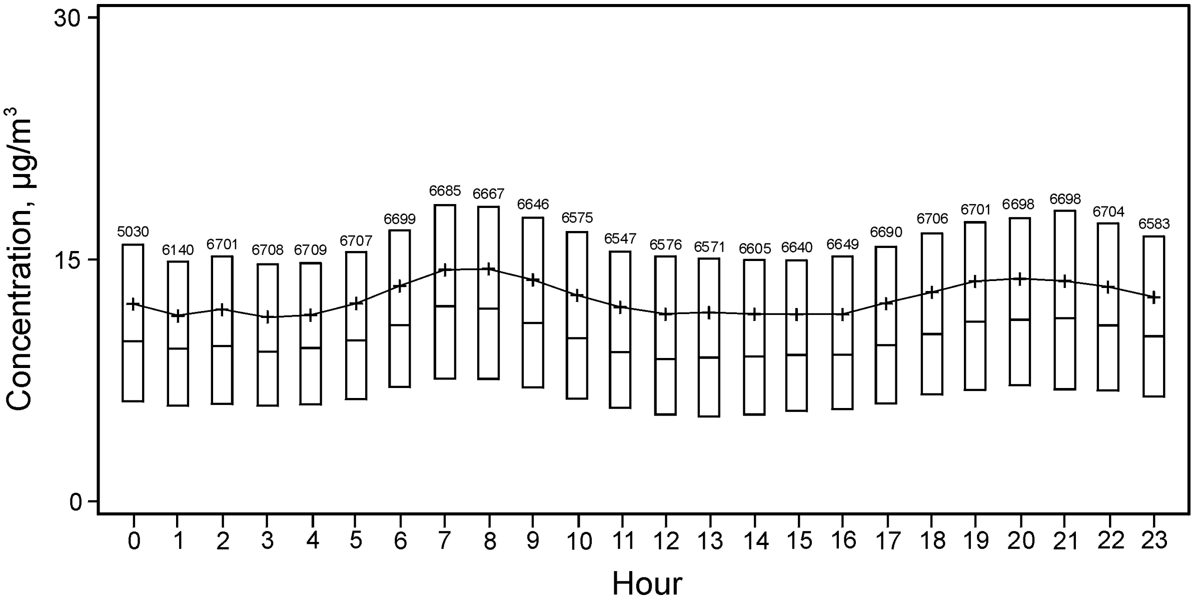


Figure 3-16. Intraday variability of hourly average $PM_{2.5}$ concentrations across the United States. Interquartile ranges, median and mean (+) values are shown. Values above the box plots refer to the number of observations during 1999. Median, mean (+) and interquartile ranges are shown.

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

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 considerations add uncertainty to the interpretation of the hour-to-hour changes that are observed, as discussed earlier 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 3-2 for each of the seven aerosol characteristic regions identified in Chapter 6 of CD 96. 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 A to Chapter 6 of CD 96. In that compilation, 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 3-2, 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 3-2 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, many of which arise because the ratios are based on two independent measurements. Measurement imprecisions play a role when the ratios are large and especially when concentrations are small. Differences in the behavior of semi-volatile components in the two samplers also could occur. The results also may be the result of errors in sampler placement, field, laboratory, or data processing procedures.

Ultrafine Particle Concentrations

Data for characterizing the levels of ultrafine particles (<0.15-μm AD) and the relations between ultrafine particles and larger particles are sparse. Perhaps the most extensive data set for ultrafine particle properties is that described by Woo et al. (2000) for a site located 10 km to the northwest of downtown Atlanta, GA. Size distributions from 3 to 2000 nm were being measured every 12 min for 24 mo 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

TABLE 3-2. 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]
		384	16,343										

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

Source: U.S. EPA Aerometric Information Retrieval System.

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 a.m.) and then to decrease through the day and to increase again after 6 p.m., consistent with a traffic 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 $PM_{2.5}$ particles based on X-ray fluorescence (XRF) analyses have been obtained at a few locations across the United States. Time series of components of the organic carbon fraction of the aerosol have not yet been obtained. The filter samples that were collected at the PBY site in southwestern Philadelphia and were used in the construction of Figures 3-8 and 3-9 also were analyzed by XRF. Concentrations of the trace elements and correlations between trace elements and the total mass of particles in the $PM_{2.5}$ size range are shown in Table 3-3. Also shown in Table 3-3 are similar results obtained for filter samples collected in Phoenix, AZ. Filters from both monitoring studies were analyzed by the same X-ray spectrometer at the EPA facility in Research Triangle Park, NC. As can be seen from inspection of Table 3-3, the analytical uncertainty (given in parentheses next to concentrations) as a fraction of the absolute concentration is highly variable, and 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.

There are a number of distinct differences between the two data sets. For instance, sulfate and associated cations and water 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 Phoenix data set. The highest $PM_{2.5}$ values were observed in Philadelphia during episodes driven by high sulfate abundances and are caused, at least partly, by higher sulfate concentrations. Correlation coefficients between $SO_4^=$ and $PM_{2.5}$ were 0.97 during the summer of 1993. Similar

TABLE 3-3. CONCENTRATIONS OF $PM_{2.5}$ (μg/m^3) AND SELECTED ELEMENTS (ng/m^3) IN THE $PM_{2.5}$ SIZE RANGE AND CORRELATIONS BETWEEN ELEMENTS AND $PM_{2.5}$ MASS

(Values in parentheses refer to analytical uncertainty in X-ray fluorescence determinations.)

	Philadelphia, PA[a]		Phoenix, AZ[b]	
	Concentration	r	Concentration	r
$PM_{2.5}$	17.0 ± 0.8 μg/m^3	1	9.4 ± 0.5 μg/m^3	1
Al	4.0 (31.1) ng/m^3	0.10	68.9 (27.2) ng/m^3	0.23
Si	116 (21.1)	0.51	209 (48.4)	0.35
P	8.6 (10.3)	0.31	7.6 (4.5)	0.52
S	2100 (143)	0.92	408 (30.9)	0.16
Cl	5.1 (3.4)	-0.01	11.4 (2.4)	0.13
K	60.4 (4.7)	0.50	78.6 (8.2)	0.67
Ca	46.6 (4.2)	0.39	76.5 (9.7)	0.51
Ti	4.9 (4.1)	0.44	7.2 (3.3)	0.44
V	8.8 (1.8)	0.37	0.7 (1.0)	-0.28
Cr	0.7 (0.7)	0.15	0.4 (0.4)	0.41
Mn	3.1 (0.8)	0.39	4.3 (0.6)	0.64
Fe	109 (10.5)	0.50	112 (15.1)	0.80
Co	0.1 (1.4)	0.04	-0.2 (0.8)	-0.01
Ni	7.3 (1.4)	0.22	0.4 (0.4)	0.38
Cu	4.8 (1.1)	0.25	3.3 (0.7)	0.69
Zn	36.9 (3.7)	0.21	12.7 (1.7)	0.64
As	0.6 (1.2)	0.18	1.3 (0.6)	0.50
Se	1.5 (0.6)	0.63	0.3 (0.3)	0.40
Br	5.0 (0.9)	0.11	3.1 (0.6)	0.57
Pb	17.6 (2.5)	0.19	4.5 (1.0)	0.69

[a] n = 1105.
[b] n = 643.

correlations between $SO_4^=$ and $PM_{2.5}$ were found at a site in northeastern Philadelphia (24 km distant from the site under discussion) during the summer of 1993.

Concentrations of “crustal elements” (e.g., Al, Si, K, Ca, Ti, Mn, and Fe) constitute a larger fraction of $PM_{2.5}$ mass in the Phoenix data set than they do in the Philadelphia data set. Sulfur is very highly correlated with $PM_{2.5}$ r = 0.92) in the Philadelphia data set, whereas it is only weakly correlated r = 0.16) with $PM_{2.5}$ in the Phoenix data set. 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 (e.g., for trace metals such as Co).

3.2.5 Spatial Variability

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 for $PM_{2.5}$ monitors located in the Atlanta, GA; Detroit, MI; Phoenix, AZ; and Seattle, WA, MSAs are shown in Tables 3-4a through d. Only sites with at least 100 measurement days were chosen, and, furthermore, only days with concurrent measurements were selected from this subset of monitoring sites. As can be seen from Table 3-4a through d, $PM_{2.5}$ concentrations tend to be highly correlated among sites within all of the MSAs shown, although there can be exceptions, as shown in the results for Atlanta, GA. There are a number of factors that could lower intersite correlations. These include field measurement and laboratory analysis errors, placement of monitors close to active sources, and transient local events.

In the Philadelphia area, $PM_{2.5}$ was found to be strongly correlated ($r > 0.9$) between seven urban sites and one background site (Valley Forge, PA) during the summer of 1993 (Suh et al., 1995). Similar relationships also were found during the summer of 1994 at four monitoring sites as part of a separate study (Pinto et al., 1995). The data collected in these studies also indicate that $PM_{2.5}$ and $SO_4^=$ concentrations are spatially uniform throughout the Philadelphia metropolitan area, and that variability in PM_{10} levels is caused largely by variability in $PM_{2.5}$ (Wilson and Suh, 1997).

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

TABLE 3-4. PEARSON CORRELATION COEFFICIENTS FOR THE SPATIAL VARIATION OF $PM_{2.5}$ CONCENTRATIONS IN SELECTED METROPOLITAN STATISTICAL AREAS

(AIRS site ID numbers without the state code are used to identify sites.)

(a) Atlanta, GA (n = 46)

	08920011	12100321	12110011	06300911	12100391	08900021
08920011	1	0.87	0.89	0.86	0.90	0.48
12100321		1	0.88	0.78	0.91	0.33
12110011			1	0.93	0.90	0.42
06300911				1	0.86	0.39
12100391					1	0.36
08900021						1

(b) Detroit, MI (n = 52)

	09900091	14700051	16300011	16300161
09900091	1	0.98	0.96	0.97
14700051		1	0.94	0.93
16300011			1	0.95
16300161				1

(c) Phoenix-Mesa, AZ (n = 45)

	01399901	01399971	01399911	01399921
01399901	1	0.92	0.89	0.84
01399971		1	0.97	0.90
01399911			1	0.89
01399921				1

(d) Seattle-Bellevue-Everett, WA (n = 78)

	03300211	03300571	03300801	03320041	06110071
03300211	1	0.96	0.95	0.95	0.81
03300571		1	0.93	0.92	0.80
03300801			1	0.94	0.83
03320041				1	0.90
06110071					1

Source: Fitz-Simons et al. (2000); data from EPA Aerometric Information Retrieval System (AIRS).

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[1]. Examples comparing downtown Los Angeles with Burbank and with Riverside-Rubidoux are shown in Figures 3-17 and 3-18, respectively. As the composition of two sampling sites become more similar, the COD approaches zero; as their compositions diverge, the COD approaches one. Cluster analyses based on the COD between individual data sets can be used to determine the degree of similarity among a number of data sets. 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. The first two methods could be applied either to aerosol data sets collected at multiple sites within a given geographic region or to aerosol data sets collected at widely different locations or times while the third method is best used to characterize sites within a particular geographic region.

Correlation coefficients showing the spatial relations 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 3-5. 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). Pb, Br, and Mn were used as markers for motor vehicle exhaust (mv). NO_3^-, NH_4^+, and $SO_4^=$ represent secondary PM components (sec). The average of the correlation coefficients of marker elements within each source category are shown in Table 3-3. 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

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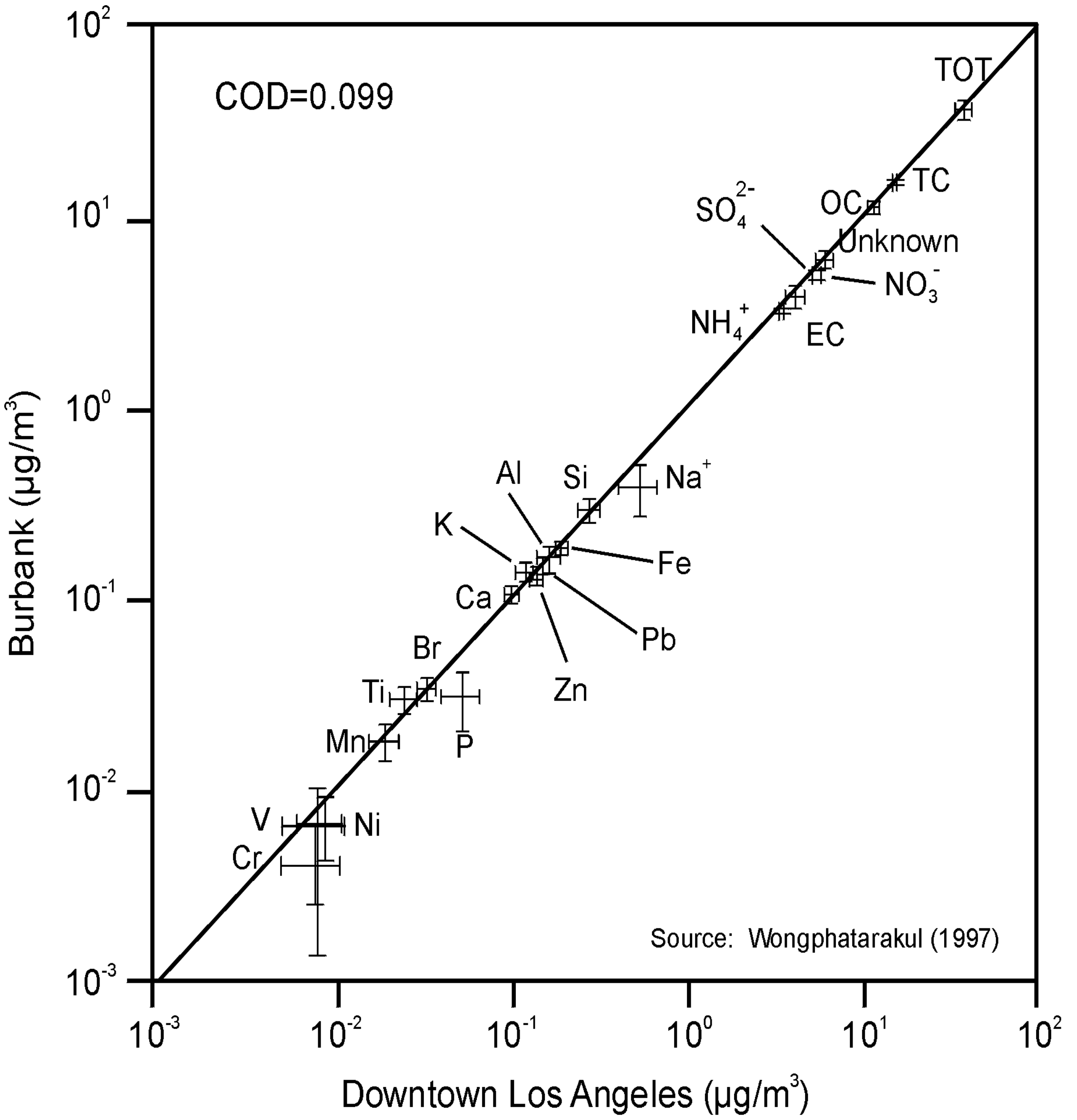
[1] The COD for two sampling sites is defined as follows:

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

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.

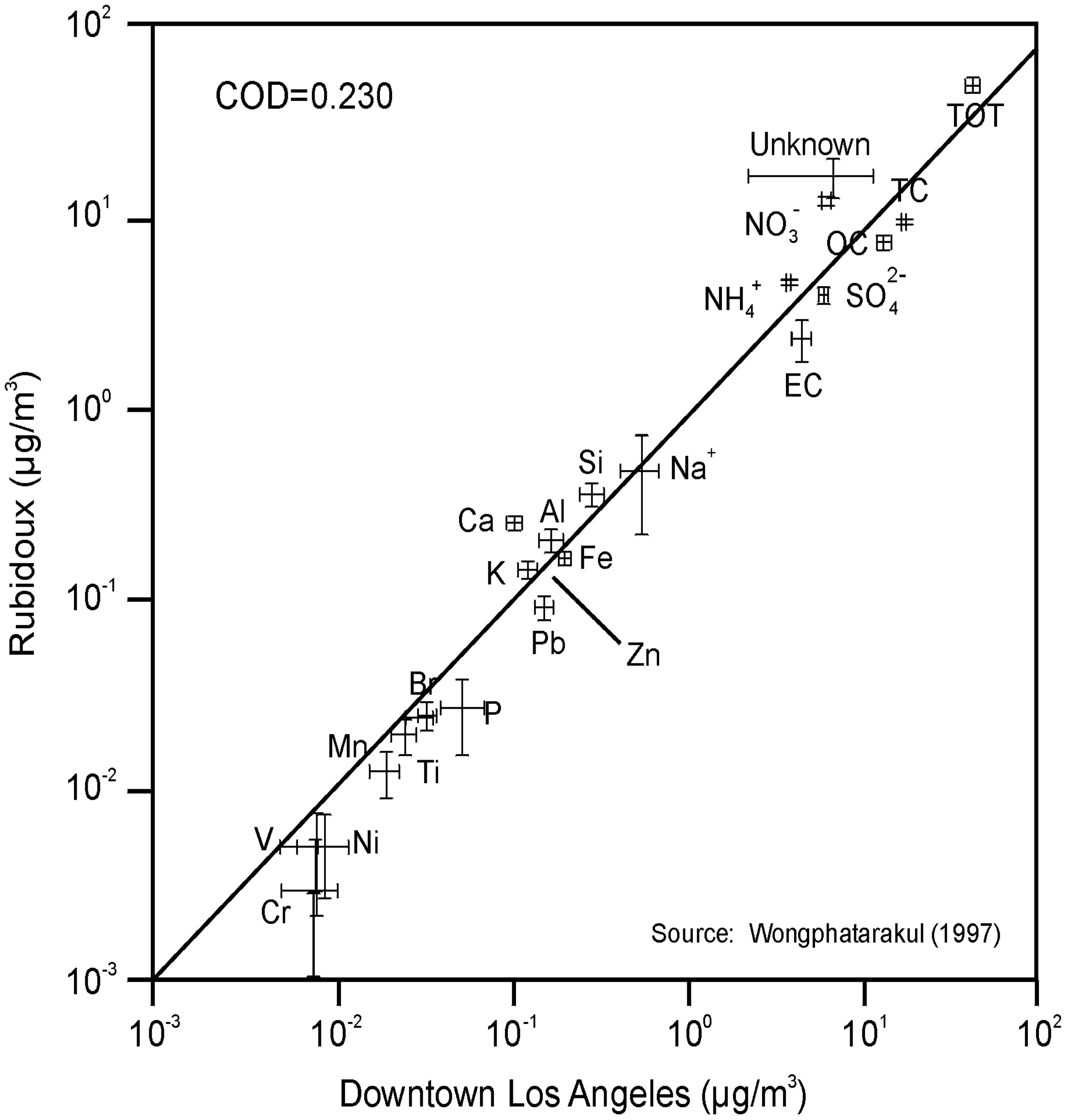


*Jan. 2 - Dec. 28, 1986 (63 data points), 24 hours sampling, sampling every 6 days, d_p < 2.5 µm

**Jan. 2 - Dec. 28, 1986 (61 data points), 24 hours sampling, sampling every 6 days, d_p < 2.5 µm

Figure 3-17. $PM_{2.5}$ chemical components in downtown Los Angeles and Burbank (1986) have similar characteristics.

Source: Wongphatarakul, et al. (1998).



*Jan. 2 - Dec. 28, 1986 (63 data points), 24 hours sampling, sampling every 6 days, $d_p < 2.5$ µm

**Jan. 2 - Dec. 28, 1986 (60 data points), 24 hours sampling, sampling every 6 days, $d_p < 2.5$ µm

Figure 3-18. 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 3-13).

Source: Wongphatarakul (1998).

TABLE 3-5. 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).

contributions from secondary PM formation and automobiles than from crustal material and localized stationary sources.

Correlation coefficients in Philadelphia air 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 3-6. 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. 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

TABLE 3-6. 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).

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 relatively spatially uniform and are highly correlated between sites with uniform traffic density and emissions patterns. Very few studies have compared aerosol composition in urban areas to that in nearby rural areas. Tanner and Parkhurst (2000), for example, found 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, they found the situation was largely reversed, with organic carbon constituting a larger fraction of aerosol mass than sulfate.

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 3-7 summarize anthropogenic and natural sources for the major primary and secondary aerosol constituents of fine and coarse particles. Major sources of each constituent are shown in boldface type. Anthropogenic sources can be further divided into stationary and mobile sources. Stationary sources include 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

TABLE 3-7. CONSTITUENTS OF ATMOSPHERIC PARTICLES AND THEIR MAJOR SOURCES[1,2]

	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
$SO_4^=$ 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 reentrainment	Fugitive dust paved and unpaved roads, agriculture, and forestry	Erosion and reentrainment	**Fugitive dust, paved and unpaved road dust, agriculture, and forestry**	—	—
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)	Wild fires	**Prescribed burning, wood burning, motor vehicle exhaust,** and cooking	—	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)	Wild fires	**Motor vehicle exhaust, wood burning,** and cooking	—	—	—	—
Metals	Volcanic activity	**Fossil fuel combustion, smelting,** and brake wear	Erosion, reentrainment, 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.
[2] Major source of each component shown in boldface type.

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 nonroad sources. In addition to fossil fuel combustion, biomass in the form of wood can be burned for fuel. Vegetation can be burned to clear new land for agriculture and for building construction, to dispose of agricultural and domestic waste, to control the growth of animal or plant pets, and to mange forest resources (prescribed burning). Also shown are sources for precursor gases whose oxidation forms secondary particulate matter. A description of the atmospheric chemical processes producing secondary PM is given in Section 3.4.

In general, the nature of sources of fine particulate matter is very different from that for coarse particulate matter. A large fraction of the mass in the fine size fraction is derived from material that has been formed during combustion (primary), has been volatilized in combustion chambers and then recondensed to form primary PM, or has been formed in the atmosphere from precursor gases as secondary PM. Because precursor gases and fine particulate matter are capable of traveling great distances, it is difficult to identify individual sources of constituents. The coarse PM constituents have shorter lifetimes in the atmosphere, so their impacts tend to be more localized. Only major sources for each constituent within each broad category shown at the top of Table 3-7 are listed. Chemical characterizations of primary particulate emissions from a wide variety of natural and anthropogenic sources as shown in Table 3-7 were given in Chapter 5 of 1996 PM AQCD. Summary tables of the composition of source emissions presented in 1996 PM AQCD and updates are given in Appendix B. These profiles were based in large measure on the results of various studies collecting source 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, that regulate 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 considerable debate about characterizing emissions from wild fires (i.e., unwanted fires) as either natural or anthropogenic. Approximately 70 to 90% of wildfires may be ignited directly as the result of human activities, either deliberately through prescribed burning and arson, or inadvertently through the improper disposal of flammable material or fugitive sparks (Andreae, 1991), with the remainder ignited by lightning strikes. On the other hand, human intervention also suppresses wildland fires that are ignited by natural causes (e.g., lightning strikes). Fire suppression allows the buildup of fire fuels and increase the susceptibility of forests to more severe and infrequent fires from whatever cause. Prescribed burning may limit the growth of these fuels and the chances for more catastrophic fires.

Receptor models are perhaps the primary means used to estimate source category contributions to particulate matter 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. They 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. 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 principal components analysis (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 nonnegative factors. Both the CMB and the PMF approaches find a solution based on least squares fitting and minimize an object function and both methods provide error estimates. 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.

A number of specialty conference proceedings, review articles, and books have been published to provide greater detail about source category apportionment receptor models as described in CD 96. 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 1996 PM AQCD. The collection of the source category characterization profiles shown in Appendix 3B has been motivated in many cases by the need to use them in receptor modeling applications.

3.3.1 Source Contributions to Ambient Particulate Matter

The results of several source apportionment studies will be discussed in this section to provide an indication 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 will be discussed and presented in Table 3-8. 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 3-9. The sampling sites represent a variety of different source characteristics within different regions of Arizona, California, Colorado, Idaho, Illinois, Nevada, and Ohio. Several of these are background sites, specifically Estrella Park, Gunnery Range, Pinnacle Peak, and Corona de Tucson, AZ, and San Nicolas Island, CA. Definitions of source categories also vary from study to study. The results of the PM_{10} source apportionment studies were given in 1996 PM AQCD and are presented here to allow easy comparison with results of $PM_{2.5}$ source apportionment studies.

There are several differences between the source categories shown at the tops of Tables 3-8 and 3-9. These differences reflect the nature of sources that are important for producing fine and coarse particulate matter shown in Table 3-7. 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). It has been only recently that motor vehicle emissions can be

TABLE 3-8. RECEPTOR MODEL SOURCE CONTRIBUTIONS TO $PM_{2.5}$

		% Contribution[3]										
Sampling Site	Time Period	Diesel	Gasoline Vehicles	Road Dust, Soil	Vegetation Burning	Secondary Sulfate	Secondary Nitrate	Misc. Source 1	Misc. Source 2	Misc. Source 3	Misc. Source 4	Measured $PM_{2.5}$ Concentration
Pasadena, CA (Schauer et al., 1996)	1982	18.8	5.7	12.4	9.6	20.9	7.4	5.3[a]	9.2[b]	8.5[c]	1.1[d]	28.2
Downtown LA, CA (Schauer et al., 1996)	1982	35.7	6.5	11.1	5.8	20.3	9.2	3.7[a]	9.2[b]	5.2[c]	0.6[d]	32.5
West LA, CA (Schauer et al., 1996)	1982	18.0	5.7	12.2	11.0	24.1	7.8	4.1[a]	9.4[b]	8.2[c]	1.6[d]	24.5
Rubidoux, CA (Schauer et al., 1996)	1982	12.8	0.7	13.1	1.2	13.8	24.7	4.5[a]	12.1[b]	4.5[c]	0.5[d]	42.1
Sacramento, CA (Motallebi, 1999)	Winter 1991-1996	24.5[e]	—	1.2	18.1	4.5	36.6	—	—	—	—	39.5
Bakersfield, CA (Magliano et al., 1998)	Winter 1996	16[e]	—	<3	20	7	34	—	—	—	—	52
Fresno, CA (Magliano et al., 1998)	Winter 1996	13[e]	—	<3	19	5	32	—	—	—	—	63
Philadelphia, PA (Dzubay et al., 1988)	Summer 1982	8.5[e]	—	4.4	—	81.9[f]	—	2.2[g]	1.9[h]	0.4[i]	—	27.0
Camden, NJ (Dzubay et al., 1988)	Summer 1982	9.2[e]	—	3.2	—	81.3[f]	0.4	2.5[g]	2.5[h]	0.7[i]	—	28.3
Clarksboro, NJ (Dzubay et al., 1988)	Summer 1982	5.8[e]	—	2.7	—	84.6[f]	—	0.8[g]	1.5[h]	0.4[i]	—	26.0
Grover City IL ENE[j]; (Glover et al., 1991)	1986 to 1987	—	—	2.3	—	83.2[f]	—	9.7[k]	3.0[l]	1.2[g]	—	
Grover City, IL SSW[j]; (Glover et al., 1991)	1986 to 1987	—	—	—	—	59.0[f]	—	11.6[k]	11.9[l]	4.1[g]	4.6[m]	
Grover City, IL WNW[j]; (Glover et al., 1991)	1986 to 1987	2.4[e]	—	5.1	—	88.5[f]	—	2.8[k]	—	—	—	
Grover City, IL NNW[j]; (Glover et al., 1991)	1986 to 1987	—	—	3.1	—	86.6[f]	—	3.4[l]	3.0[n]	—	—	
Welby, CO (Lawson and Smith, 1998)	Winter 1997	10	28	16	5	10[o]	25[p]	4[c]	2[n]	—	—	
Brighton, CO (Lawson and Smith, 1998)	Winter 1997	10	26	11	2	15[o]	32[p]	2[c]	2[n]	—	—	
Reno, NV (Gillies et al., 2000)	Summer 1998	68[e]	—	14.5	4	11	2	0.6[q]	—	—	—	7.8
Phoenix, AZ (Ramadan et al., 2000)	Summer 1995-1998	10.9	36.2	1.8	15.0	—	—	20.8[n]	4.9[r]	6.7[s]	3.6[q]	8.3
Phoenix, AZ (Ramadan et al., 2000)	Winter 1995-1998	14.5	38.9	1.1	8.9	—	—	9.5[n]	4.5[r]	18.7[s]	4.1[q]	13.8

[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 3-9. RECEPTOR MODEL SOURCE CONTRIBUTIONS TO PM_{10}

		% Contribution										
Sampling Site	Time Period	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	Measured PM_{10} Concentration
Central Phoenix, AZ (Chow et al., 1991)	Winter 1989-1990	51.6	0.0	39.0	3.6	0.3	4.4	0.0	0.0	0.0	0.0	64.0
Craycroft, AZ (Chow et al., 1992a)	Winter 1989-1990	55.6	0.0	35.5	0.0	3.0	2.6	5.1[a]	0.0	0.0	0.0	23.4
Hayden 1, AZ (Garfield) (Ryan et al., 1988)	1986	4.8	1.9[b]	0.0	0.0	3.8	0.0	70.5[c]	4.8[d]	1.0[e]	0.0	105.0
Hayden 2, AZ (Jail) (Ryan et al., 1988)	1986	35.6	6.8[b]	0.0	0.0	6.8	0.0	47.5[c]	0.0	1.7[e]	0.0	59.0
Phoenix, AZ (Estrella Park) (Chow et al., 1991)	Winter 1989-1990	67.3	0.0	18.2	1.6	2.9	0.0	0.0	0.0	0.0	0.0	55.0
Phoenix, AZ (Gunnery Rg.) (Chow et al., 1991)	Winter 1989-1990	74.1	0.0	20.4	0.0	3.7	0.0	0.0	0.0	0.0	0.0	27.0
Phoenix, AX (Pinnacle Pk.) (Chow et al., 1991)	Winter 1989-1990	58.3	0.0	24.2	8.3	7.5	0.0	0.0	0.0	0.0	0.0	12.0
Rillito, AZ (Thanukos et al., 1992)	1988	53.7	17.4[b]	1.5[f]	0.0	0.0	0.0	14.6[g]	0.0	0.0	0.0	79.5
Scottsdale, AZ (Chow et al., 1991)	Winter 1989-1990	45.5	0.0	34.5	13.5	1.1	6.5	0.0	0.0	0.0	0.0	55.0
West Phoenix, AZ (Chow et al., 1991)	Winter 1989-1990	43.5	0.0	36.2	14.5	0.6	4.5	0.0	0.0	0.0	0.0	69.0
Bakersfield, CA (Magliano, 1988)	1986	40.5	4.4	8.1	14.2[l]	8.3	0.0	0.7[j]	0.0	0.0	0.0	67.6
Bakerfield, CA (Chow et al., 1992b)	1988-1989	53.9	2.0	9.7	8.2	6.9	16.0	1.3[m]	1.9[n]	0.8[k]	0.0	79.6
Crows Landing, CA (Chow et al., 1992b)	1988-1989	61.3	0.0	4.2	6.5	5.3	12.4	1.0[m]	1.9[n]	2.3[k]	0.0	52.5
Fellows, CA (Chow et al., 1992b)	1988-1989	53.1	2.6	3.8	6.2	9.3	13.7	12.8[m]	2.6[n]	2.6[k]	0.0	54.6
Fresno, CA (Magliano, 1988)	1986	35.6	1.5	8.3	19.1[l]	3.7	0.0	0.2[j]	0.0	0.0	0.0	48.1
Fresno, CA (Chow et al., 1992b)	1988-1989	44.5	0.0	9.5	7.1	5.0	14.5	0.4[m]	1.9[n]	0.1[k]	0.0	71.5
Indio, CA (Kim et al., 1992)		56.9	5.2	7.6	12.2	6.2	7.1	0.3[j]	1.7[h]	0.0	0.0	58.0
Kern Wildlife Refuge, CA (Chow et al., 1992b)	1988-1989	31.6	4.2	4.6	8.4	6.9	3.1	1.0[m]	3.1[n]	1.5[k]	0.0	47.8
Long Beach, CA (Gray et al., 1988)	1986	39.9	0.0	9.8[i]	0.0	15.4	17.7	0.2[j]	3.9[h]	12.3[k]	0.0	51.9
Long Beach, CA (Summer) (Watson et al., 1994)	Summer 1987	24.1	0.0	13.7	0.0	23.6	1.7	0.2[j]	4.8[h]	0.0	0.0	46.1
Long Beach, CA (Fall) (Watson et al., 1994)	Fall 1987	11.8	0.0	44.5	0.0	4.0	24.1	0.0[j]	2.8[h]	0.0	0.0	96.1
Riverside, CA (Chow et al., 1992c)	1988	50.9	0.0	10.9	0.0	7.5	33.4	0.5[j]	2.0[h]	1.7[o]	0.0	64.0
Rubidoux, CA (Gray et al., 1988)	1986	49.3	4.6	6.4[i]	0.0	7.3	24.4	0.3[j]	1.1[h]	6.8[k]	0.0	87.4
Rubidoux, CA (Summer) (Watson et al., 1994)	Summer 1987	30.4	3.9	15.1	0.0	8.3	23.9	0.0[j]	4.4[h]	0.0	0.0	114.8
Rubidoux, CA (Fall) (Watson et al., 1994)	Fall 1987	17.1	14.4	27.1	0.0	1.9	28.2	0.0[j]	1.0[h]	0.0	0.0	112.0
Rubidoux, CA (Chow et al., 1992c)	1988	55.2	0.0	11.7	0.0	6.1	24.9	0.6[j]	1.7[h]	6.6[o]	0.0	87.0
San Nicolas Island, CA (Summer) (Watson et al., 1994)	Summer 1987	9.2	0.0	5.2	0.0	21.3	2.9	0.0[j]	24.7[h]	0.0	0.0	17.4

TABLE 3-9 (cont'd). RECEPTOR MODEL SOURCE CONTRIBUTIONS TO PM_{10}

		% Contribution										
Sampling Site	Time Period	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	Measured PM_{10} Concentration
Stockton, CA (Chow et al., 1992b)	1989	55.1	0.8	8.3	7.7	5.0	11.2	1.1[m]	2.9[n]	0.0[k]	0.0	62.4
Pocatello, ID (Houck et al., 1992)	1990	8.3	7.5[q]	0.1	0.0	0.0	0.0	0.0	0.0	84.1[r]	0.0	100.0
S. Chicago, IL (Hopke et al., 1988)	1986	34.0	3.0	3.5	0.0	19.2[s]	—	18.9[t]	2.7[u]	0.0	0.0	80.1
S.E. Chicago, IL (Vermette et al., 1992)	1988	35.9[v]	0.0	2.2[f]	0.0	18.8	—	2.0[t]	0.7[h]	2.7[w]	18.8[g]	41.0
Reno, NV (Chow et al., 1988)	1986-1987	497	0.0	33.3	6.3	4.3	2.0	0.0	0.0	0.0	0.0	30.0
Sparks, NV (Chow et al., 1988)	1986-1987	36.8	0.0	28.3	32.7	6.6	2.2	0.0	0.0	0.5[k]	0.0	41.0
Follansbee, WV (Skidmore et al., 1992)	1991	15.2	0.0	53.0	0.0	24.2	—	14.1[t]	0.0	0.0	0.0	66.0
Mingo, OH (Skidmore et al., 1992)	1991	20.0	0.0	23.3	6.8	25.0	—	5.7[t]	18.3[x]	0.0	0.0	60.0
Steubenville, OH (Skidmore et al., 1992)	1991	18.0	0.0	30.4	1.7	30.4	—	8.3[t]	10.9[x]	0.0	0.0	46.0

[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.

broken down into contributions from diesel and gasoline vehicles through the use of organic tracers. 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, wild fires, prescribed burning and burning of agricultural 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 compounds are used to differentiate among source categories, it can be seen from Tables 3-8 and 3-9 that only a relatively small number of sources are needed to account for the mass of $PM_{2.5}$ and PM_{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, associated cations and water also represent the major components of $PM_{2.5}$ found in monitoring studies in the eastern United States (Table 3-1). Motor vehicle emissions, arising mainly from diesels, are other major sources of $PM_{2.5}$. Contributions from road dust and soils are relatively minor, typically constituting less than 10% of $PM_{2.5}$ in the studies shown in Table 3-8. Studies in the western United States shown in Table 3-8 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 3-8 and PM_{10} shown in Table 3-9 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 3-9. The fraction is higher in locations located away from specific sources such as sea spray or smelters. Emissions of fugitive dust are concentrated mainly in the $PM_{(10-2.5)}$ size range. The average fugitive dust source contribution is highly variable among sampling sites within the same urban areas, as seen by differences between the Central Phoenix (33 $\mu g/m^3$) and Scottsdale (25 $\mu g/m^3$) sites in Arizona, and it is also seasonally variable, as evidenced by the summer and fall contributions at Rubidoux, CA. The variability in fugitive dust loadings reflects the sporadic nature of its emissions and its short lifetime in the atmosphere.

In Table 3-9, primary motor vehicle exhaust contributions account for up to 40% of average PM_{10} at many 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 virtually has been eliminated from vehicle fuels. However, organic species have replaced Pb as a source marker for motor vehicle emissions (e.g., Rogge et al., 1993).

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 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. These are especially noticeable at sites in California’s San Joaquin Valley (Bakersfield, Crows Landing, Fellows, Fresno, Kern Wildlife, and Stockton) and in the Los Angeles area.

Samples selected for chemical analysis are often biased toward the highest PM_{10} mass concentrations in the studies shown in Table 3-9, so average source contribution estimates are probably not representative of annual averages. 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 Table 3-6 range from 10 to 50%. Uncertainties of source contribution estimates are not usually reported with the average values summarized in Table 3-9. Estimates of standard errors are calculated in source apportionment studies, and typically range from 15 to 30% of the source contribution estimate. They are much higher when the chemical source profiles for different sources are highly uncertain or 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 3-8, Dzubay et al. (1988) found a uniform distribution of sulfate among the NE Airport in Philadelphia, PA; downtown Camden, NJ; and Clarksboro, NJ, during the summer of 1982. The longest 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 μg/m^3, vegetation burning contributed from 5.1 to 11.1 μg/m^3, ammonium sulfate contributed 2.4 to 3.4 μg/m^3, and ammonium nitrate contributed 19.3 to 24.6 μg/m^3 to PM$_{10}$ at the sites in Bakersfield. Mobile sources contributed 13.9 to 22.5 μg/m^3, vegetation burning contributed 8.2 to 15.7 μg/m^3, ammonium sulfate contributed 1.8 to 2.3 μg/m^3, and ammonium nitrate contributed 14.5 to 18.9 μg/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.

3.3.2 Long-Range Transport of Particulate Matter from Sources Outside the United States

Apart from sources within the continental United States, particulate matter can be brought in by long-range transport from sources outside the United States. For example, 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. Windblown dust from individual 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 into the middle and upper troposphere (4 to 5 km altitude), where it is transported by strong westerly winds out over the Pacific Ocean (Duce, 1995). Satellite images have been 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 μg 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 (Interagency Monitoring of Protected Visual Environments) network. Their analysis 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 have persisted for about 10 days, principally during the summer. As can be expected, the frequency of dust events is highest in the southeastern United States; about half are observed only within the state of Florida, with these being associated with dense hazes in Miami (Figure 3-19) during the summer (Prospero et al., 1987), such that African dust is the dominant aerosol constituent in southern Florida during the summer (Prospero, 1999). The mass median diameter of mineral dust over the oceans is typically between 2 and 3 μm (Duce, 1995). North African dust has been tracked as far as Illinois (Gatz and Prospero, 1996) and to Maine (Perry et al., 1997). Larger scale events typically covered from 15 to 30% of the area of the continental United States and resulted in increases of $PM_{2.5}$ levels of 8.7 ± 2.3 μg m^{-3} throughout the affected areas, with mean maximum dust contributions of 19.7 ± 8.4 μg m^{-3} during these events and a peak contribution of 32 μg m^{-3} to 24-h average $PM_{2.5}$ levels.

Husar et al. (2000) documented 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 $\mu g/m^3$ during the rest of April and May. Data from the IMPROVE network indicated that PM_{10} concentrations were over 100 $\mu g/m^3$ in central British Columbia, Washington State, and Oregon. The highest PM concentrations observed were 120 $\mu g/m^3$ for PM_{10} and 50 $\mu g/m^3$ for $PM_{2.5}$ at Chilliwack Airport in northwestern Washington State (Figure 3-20). Aircraft measurements made over the northwestern United States were consistent with a mass median diameter of the dust being between 2 and 3 μm. Three-dimensional model simulations of the transport of inert tracers from Asia indicate that substantial additions to PM concentrations also occurred throughout the north and mid-western United States and southwestern Canada (Hanna et al., 1999).

Biomass burning for agricultural purposes occurs normally during the spring of each year in Central America and southern Mexico. During the spring of 1988, fires burned uncontrollably because of abnormally hot and dry conditions associated with the intense El Niño of 1997 to

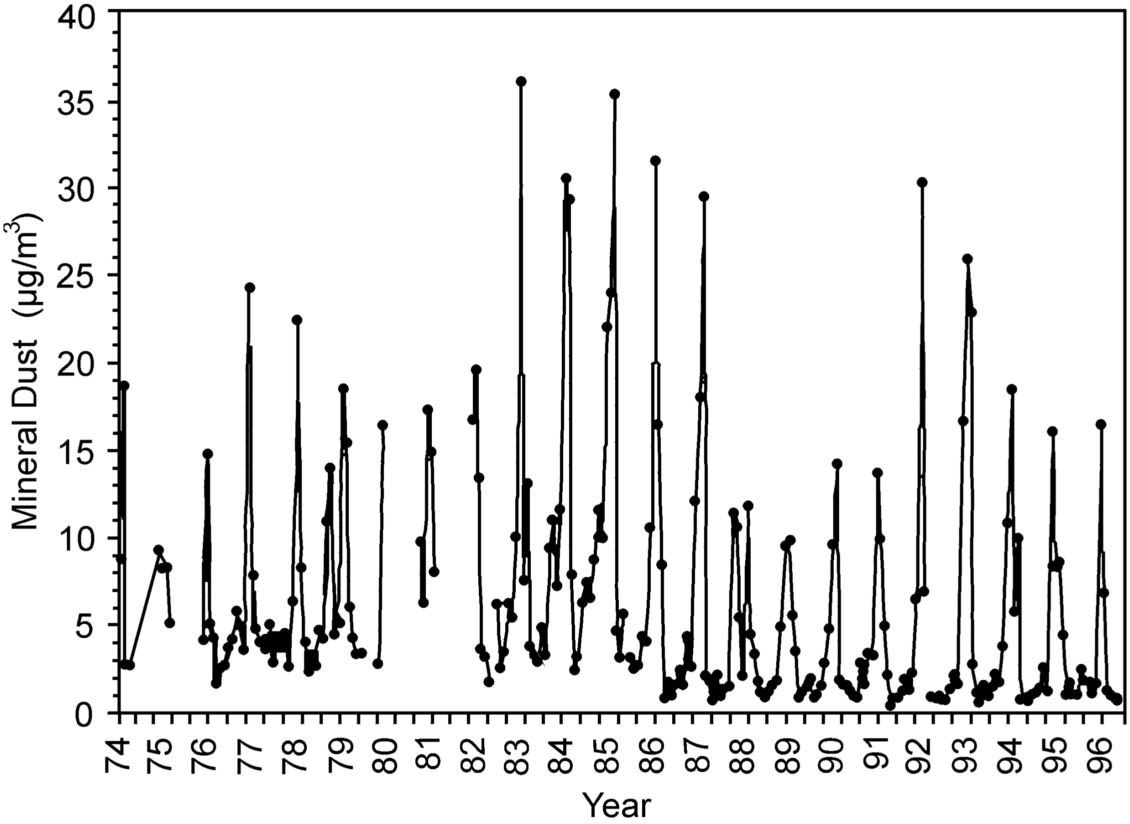


Figure 3-19. Monthly average Saharan dust components of the aerosol sampled in Miami, FL, during 1974 to 1996.

Source: Prospero (1999).

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 3-21. Elevated $PM_{2.5}$ and PM_{10} concentrations also were found as far north as St. Louis, MO (Figure 3-22). As can be seen from Figure 3-21 and Figure 3-22, the elevations in PM concentrations were limited in duration. However, 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. For example, approximately 26,000 km^2 were consumed during 2000 in the western United States.

Wildfires also occur in the boreal forests of northwestern Canada. Wotowa and Trainer (2000) suggested that the plume from fires occurring in the Northwest Territories of Canada in

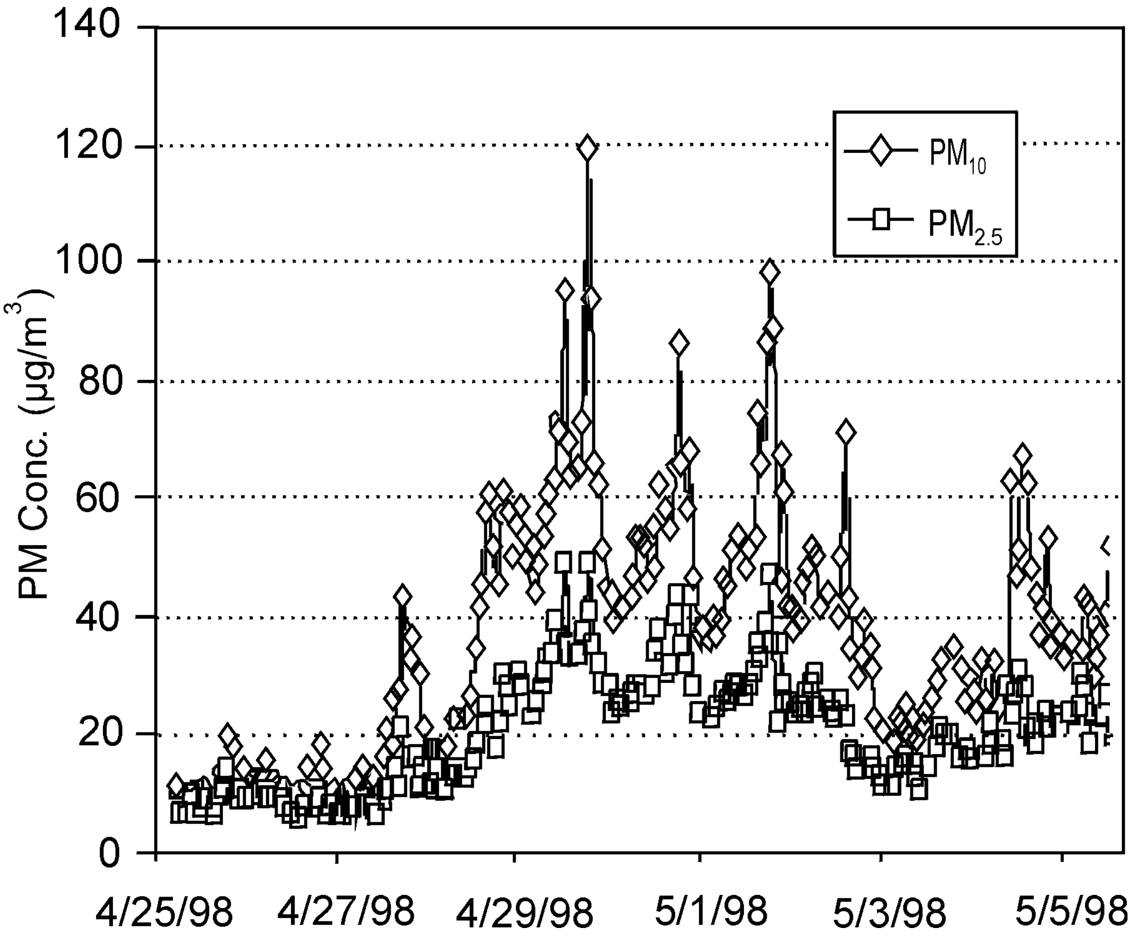


Figure 3-20. $PM_{2.5}$ and PM_{10} concentrations measured at Chilliwack Airport, located in northwestern Washington State, just before and during the Asian desert dust episode of April and May 1998.

Source: U.S. EPA Aerometric Information Retrieval System (AIRS).

early July 1995 may have extended throughout most of the eastern United States, resulting in elevated levels of carbon monoxide (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 increasing to close to 100 μg/m^3 in the northern Plains States.

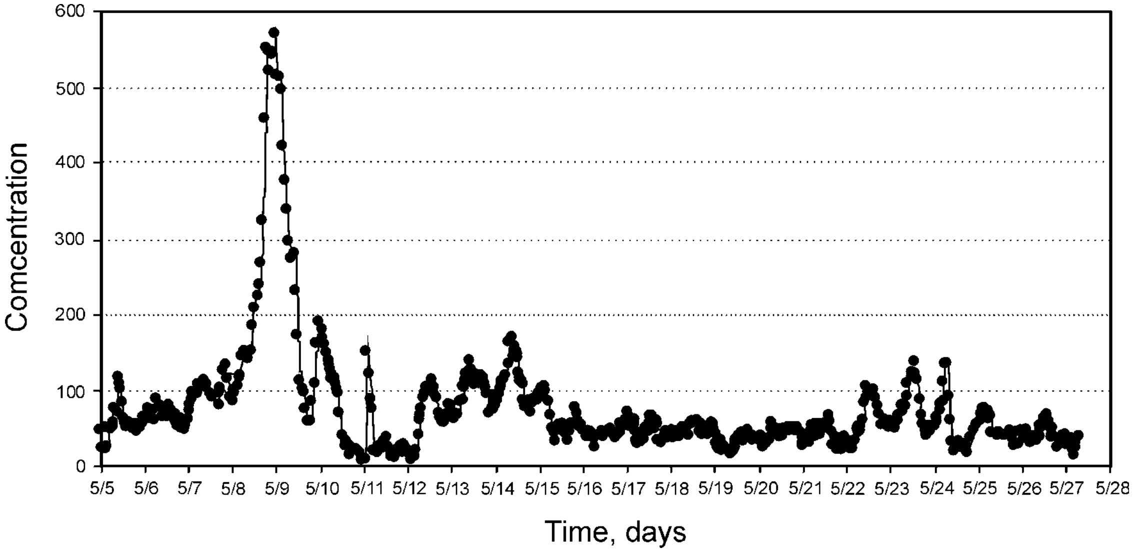


Figure 3-21. Time series of 24-h average PM_{10} concentrations observed in the Rio Grande Valley during May 1998.

Source: U.S. EPA Aerometric Information Retrieval System (AIRS).

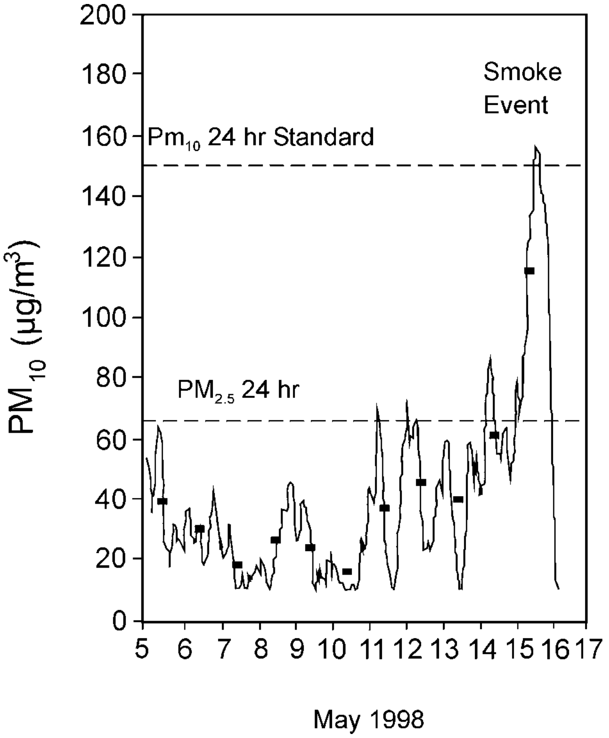


Figure 3-22. PM_{10} concentrations observed in St. Louis, MO, during May 1998.

Source: U.S. EPA Aerometric Information Retrieval System (AIRS).

3.4 EMISSIONS ESTIMATES AND THEIR UNCERTAINTIES

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. Air pollution model predictions represent averages over the area of a grid cell, which in the case of the Urban Airshed Model typically has been 25 km^2 (5 km × 5 km). 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 impact 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.

Estimates of nationwide emissions of primary $PM_{2.5}$ and gaseous precursors to secondary PM formation are given in Section 3.4.1. Uncertainties in emissions estimates are discussed in Section 3.4.2.

3.4.1 Emissions Estimates for Primary Particulate Matter and Sulfur Dioxide, Nitrogen Oxides, and Volatile Organic Compounds in the United States

Estimated emissions of primary $PM_{2.5}$ from different sources in the United States are summarized in Figure 3-23. The estimates are based on information presented in the EPA National Air Pollutant Emission Trends Report, 1900-1998 (U.S. Environmental Protection Agency, 2000b), to which the reader is referred for detailed tables showing trends in $PM_{2.5}$ emissions from a number of source categories from1990 to 1998, descriptions of the methodology used in the construction of these tables, and descriptions of the uncertainties

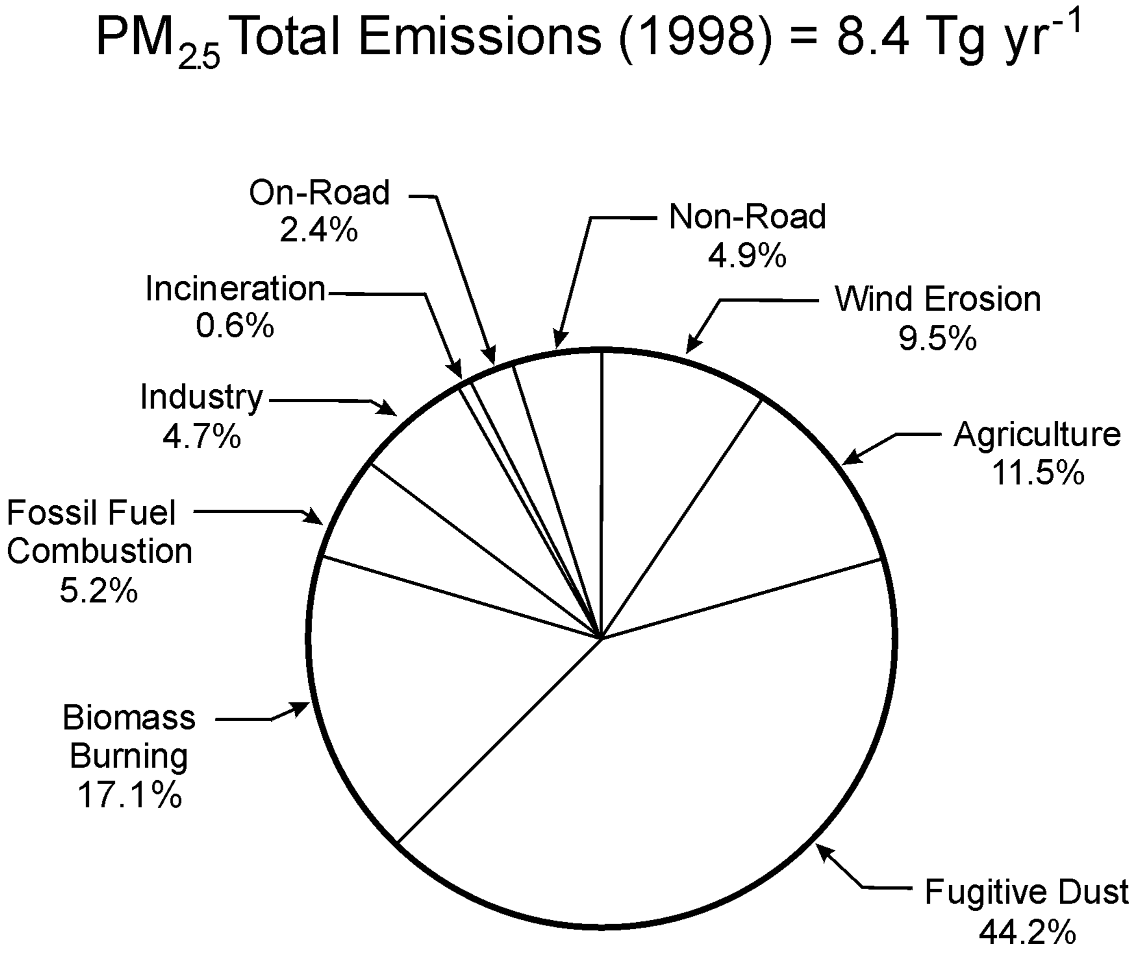


Figure 3-23. 1998 directly emitted national particulate matter ($PM_{2.5}$) emissions by principal source categories for nonfugitive dust sources (see Section 3.4.2 for discussion of uncertainties associated with emissions estimates).

Source: U.S. Environmental Protection Agency (2000b).

involved in the estimation process. This document also provides information about emissions of PM_{10}, sulfur dioxide (SO_2), nitrogen oxides (NO_x), volatile organic compounds (VOC), and ammonia (NH_3). Although uncertainties associated with these estimates are not given, a discussion of uncertainties in emissions estimates is given in Section 3.4.2.

Estimated total nationwide emissions of primary $PM_{2.5}$ were 8.4 Tg year^{-1} in 1998. The category of fossil fuel combustion referred to in Figure 3-23 includes fossil fuel burning by electric utilities, industry, and residences. The industry category includes contributions from metals processing, petroleum refining, agricultural products processing, mining, and the storage and transport of industrial goods. Incineration refers to the burning of nonbiomass waste by residences and municipalities. The on-road vehicles category includes contributions from gasoline- and diesel-powered vehicles. The nonroad engines and vehicles category includes contributions from transportation (marine vessels, aircraft, trains, etc.); construction; and other commercial, industrial, and recreational activities. Wind erosion refers to the raising of crustal material by the wind. The biomass burning category includes contributions from residential wood burning, open burning of vegetation, and forest fires. The agriculture category includes contributions from emissions of crustal material related to the production of agricultural crops and livestock. Fugitive dust refers mainly to crustal material raised by on-road and nonroad vehicles during their operation. As can be seen from inspection of Figure 3-23, the raising of crustal material by wind erosion, agriculture, and as fugitive dust emissions constitutes the largest source (65.2%) of primary $PM_{2.5}$ on a nationwide basis. Note that wind erosion emissions are difficult to interpret, owing to the relatively short duration of wind gusts. Biomass burning constitutes the second largest source (17.1%) of primary $PM_{2.5}$. The gross composition of emissions from most of these categories is summarized in Table 3-5 in the EPA report, National Air Pollution Emission Trends, 1900-1998 (U. S. Environmental Protection Agency, 2000b). Total emissions of primary $PM_{2.5}$, as well as contributions from individual source categories, were relatively constant over the period from 1990 to 1998 (U.S. Environmental Protection Agency, 2000b).

Estimated contributions from individual sources to emissions of gaseous precursors to secondary PM formation are summarized in Figure 3-24 for SO_2 , NO_x , VOC, and NH_3. Information about the yield of PM formed during the oxidation of VOC is given in Section 3.4.

Although total emissions of gaseous precursors (SO_2, NO_x, VOC, and NH_3) are shown in Figure 3-24, it should be remembered that these values cannot be translated directly into production rates of PM. Dry deposition and precipitation scavenging of some of these gases can 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. Although the chemical oxidation of SO_2 will lead quantitatively to the formation of $SO_4^=$, the yield of particulate matter from the

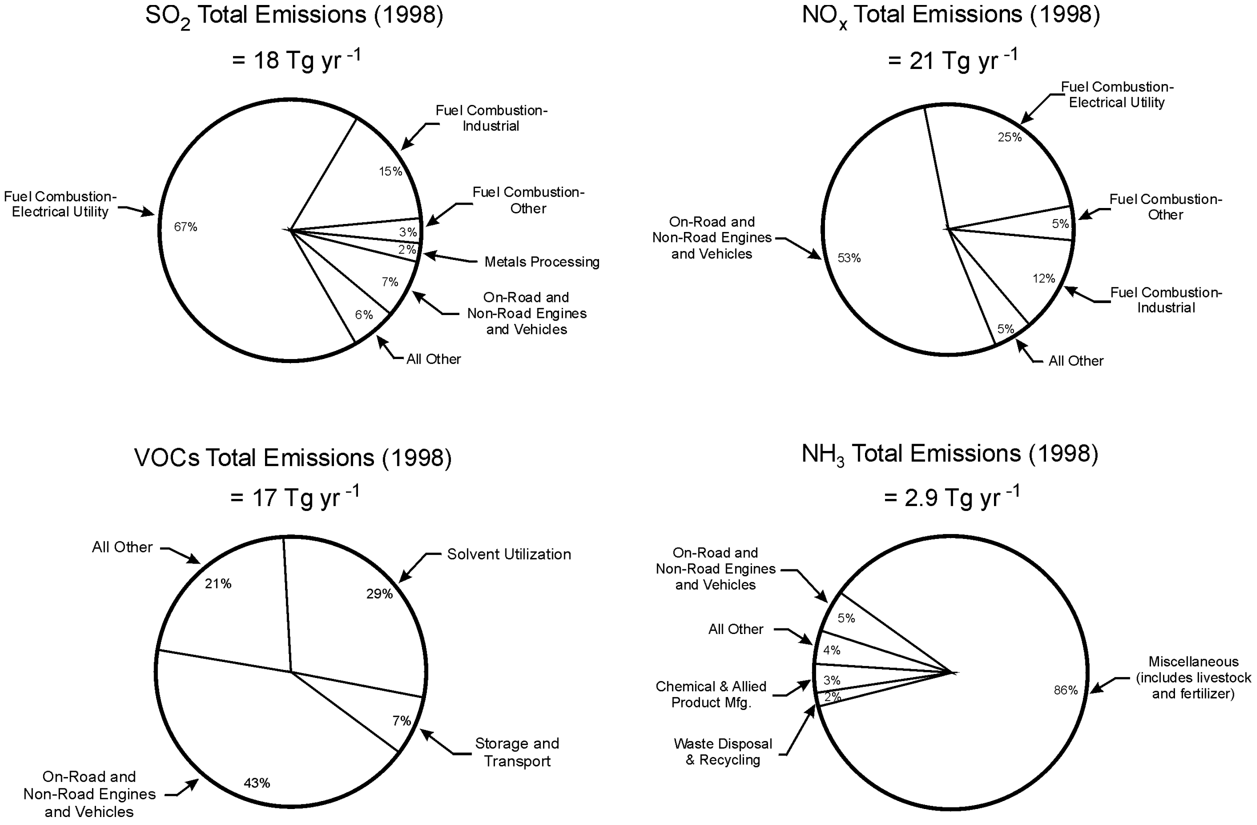


Figure 3-24. Nationwide emissions of SO_2, NO_x, VOC, and NH_3 from various source categories (see Section 3.4.2 for discussion of uncertainties associated with emissions estimates).

Source: U.S. Environmental Protection Agency (2000b).

oxidation of VOC will be much less because only a small fraction of VOC react to form particles, and those that do have efficiencies less than 10% (see Section 3.4).

The values shown in this section are based on annual totals. However, annual averages do not reflect the seasonality of a number of emissions categories. 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). Planting, fertilizing, and harvesting are also seasonal activities. 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.

Trends in nationwide, annual average concentrations of PM_{10}, and precursor gases (SO_2, NO_2, and VOC) over the 10 years from 1989 to 1998 are shown in Table 3-10. As can be seen from Table 3-10, 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 VOC; there also have been substantial decreases in the emissions of all the species shown in Table 3-10, except for NO_2, although its average concentration has decreased by 14%. These entries suggest that decreases in the average ambient concentration of PM_{10} could have been produced 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 eastern and central United States, 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 impact on $PM_{2.5}$ concentrations in the western United States than in the eastern United States because nitrate is a larger component of the aerosol in the western United States. 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. Measurements of aerosol nitrate and sulfate concentrations have been obtained at North Long Beach and Riverside, CA, since 1978 (Dolislager and Motallebi, 1999). Downward trends in aerosol nitrate have tracked downward trends in NO_x concentrations, and 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 air shed 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, 2000b). Other reasons are related to uncertainties in ambient measurements and in emissions inventories.

TABLE 3-10. NATIONWIDE CHANGES IN AMBIENT CONCENTRATIONS AND EMISSIONS OF PM_{10} AND GASEOUS PRECURSORS TO SECONDARY PARTICULATE MATTER FROM 1989 TO 1998

	% Change 1989-1999	
	Ambient Concentration(1)	Emissions(1)
PM_{10}	−25%	−35%
$PM_{2.5}$	Urban east −5%(2) Rural east +3%(2) Rural west −11%(2)	+5% (1990 to 1998)
$SO_4^{=}/SO_2$	−39% (sulfate)	−16% (SO_2)
NO_3^-/NO_x	−14% (nitrate)	+2% (NO_x)
VOC	—	−20%

Source: (1) U. S. Environmental Protection Agency (2000a); (2) U. S. Environmental Protection Agency (2000d).

3.4.2 Uncertainties of Emissions Inventories

As described in the 1996 PM AQCD, it is difficult to assign uncertainties quantitatively 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, 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 accurate production records need to be kept. On the other hand, activity rates for a number of really dispersed 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, their age, their 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 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 Figures 3-23 to 3-24) 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 over 60% of the total $PM_{2.5}$ inventory, they constitute less than about 15% of the source strengths inferred from the PM composition data shown in Table 3-1 and the receptor modeling studies shown in Table 3-6. However, it should be remembered that secondary components (sulfate, nitrate, and some fractions of organic carbon) often represent a significant fraction of ambient samples. Therefore, this discrepancy is smaller than the factor of four that is obtained by comparing primary dust emissions to the sum of primary and secondary components in the ambient aerosol. The reasons for this apparent discrepancy are not clear. In addition to errors in inventories or source apportionments, weather-related factors (wind speed and ground wetness) and the dominance of local sources on spatial scales too small to be captured in inventories may be involved. It should be remembered that dust emissions are dispersed widely and are highly sporadic. Dust particles also have short atmospheric residence times and as a result their dominance in emissions inventories may not be reflected in samples collected near specific sources.

Although mineral dust sources account for most of the emissions, their contributions are distributed much more widely than are those from combustion sources. Watson and Chow (1999) examined a number of possible causes for this discrepancy. In large part, it is related to the method used to obtain emissions factors for 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, not stable winds, characterize atmospheric flow patterns immediately adjacent to the surface (Garratt, 1994). The depth of this turbulent layer is determined by surface roughness elements, and, if particle monitors are sampling within this layer, there is a high probability of particles being entrained in turbulent eddies and redepositing on the ground. 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. Gravitational settling can be an important loss mechanism for particles larger than a few microns in aerodynamic diameter and precipitation or scavenging by cloud droplets also removes smaller particles during transport from the source area.

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. Given (a) uncertainties in the deposition of SO_2 and its oxidation rate; (b) the variability seen in OC and EC emissions from motor vehicles, along with the findings from past verification studies for NMHC and CO to NO_x ratios; (c) ranges of values found among independent estimates for emissions of individual species (NH_3, OC); and (d) the predominance of fugitive emissions, PM emissions rates should be regarded as order-of-magnitude estimates.

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. Results have been ambiguous because of contributions from fugitive sources, nonsteady wind flows, and general logistic difficulties.

3.5 SUMMARY AND 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 over 20 $\mu g/m^3$. In the eastern United States, the 1999 data indicate that highest quarterly mean concentrations and maximum concentrations were reached during the summer. In the western United States, highest quarterly mean values and maximum values occurred during the winter at a number of sites, although there were exceptions to these general patterns. 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. The 1999 FRM $PM_{2.5}$ data indicate that, in general, $PM_{2.5}$ concentrations are highly correlated among sites in several MSAs (Atlanta, GA; Detroit, MI; Phoenix-Mesa, AZ; and Seattle-Bellevue-Everett, WA), although there are exceptions to this rule. These findings are consistent with those of earlier studies in Philadelphia, PA, and Los Angeles, CA, examining the spatial variability of $PM_{2.5}$ and its components. $PM_{2.5}$ to PM_{10} ratios were generally higher in the East than in the West, and values are consistent with those found in numerous earlier studies presented in the 1996 PM AQCD.

Ambient particulate matter contains both primary and secondary components. The results of ambient monitoring studies and receptor modeling studies in the eastern United States indicate that $PM_{2.5}$ is dominated by secondary components. Depending on the origin of OC in ambient samples, $PM_{2.5}$, on average, also may be dominated by secondary components throughout the rest of the United States. Primary constituents represent smaller but still important components of $PM_{2.5}$, on average. Crustal materials constitute the largest fraction of $PM_{(10-2.5)}$ throughout the United States. 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 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 3-7. 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. Also, most forest fires in the United States could be classified as human in origin, either through prescribed burning; by accident; or through forest management practices that allow the buildup of combustible material, thereby increasing the likelihood of fire from whatever cause.

Emissions inventories are generally not the most appropriate way to apportion material in ambient samples. Receptor modeling has proven to be an especially valuable tool in this regard. Receptor modeling can help bound emission inventories and establish uncertainty estimates. Compositional profiles developed for receptor modeling applications are perhaps the most accessible and reliable means of characterizing the composition of emissions. Techniques are under development to use emission inventories and receptor modeling to reduce the uncertainty in the overall source apportionment (U. S. Environmental Protection Agency, 2000e).

The results of receptor modeling studies throughout the United States indicate that the combustion of fossil and biomass fuels is a major source of $PM_{2.5}$. Fugitive dust, found mainly in the $PM_{(10-2.5)}$ range size, represents the largest source of PM_{10} in many locations in the western United States. Quoted uncertainties in source apportionments 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 most of the observed mass of PM in these studies.

Improvements in the ability of receptor models to allocate sources of ambient PM continue to be made. Recently developed techniques such as positive matrix factorization allow quantitative determinations of contributions from different categories of PM sources to be made on the basis of ambient data alone. Improvements in the accuracy of PM emissions inventories also continue to be made. Recent studies have identified causes of the overrepresentation of crustal material in emissions inventories. The causes are related to the neglect of near-source PM deposition in the development of emissions factors.

As seen in Table 3-7, 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). Nevertheless, concentrations of crustal material can be appreciable, especially during dust events. It also should be remembered that much 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.

Uncertainties in emissions inventories are difficult to quantify. They may be as low as 10% for well-defined sources (e.g., for SO_2) and may range up to a factor of 10 or so for windblown dust. As a rule, total PM emissions rates should be regarded as order-of-magnitude estimates. Because of the large uncertainty associated with emissions of suspended dust, trends of total $PM_{2.5}$ PM_{10} emissions should be viewed with caution, and emissions of specific components are best discussed on an individual basis. Receptor modeling, especially when coupled to accurate measurements of the composition of emissions, can be useful in providing bounds for emission inventories.

Although most emphasis in this chapter has been on sources within the United States, it also should be remembered that sources outside the United States contribute to ambient PM levels that can, at times, exceed the ambient NAAQS level for PM. Perry et al. (1997) have found that the highest concentrations of mineral dust in the $PM_{2.5}$ fraction are found in the eastern United States during the summer and not in arid areas of the western United States. This dust has been emitted in the Sahara Desert and then transported across the Atlantic Ocean. Large-scale dust storms in the deserts of central Asia recently have been found to contribute to

PM levels in the Northwest on an episodic basis. Uncontrolled biomass burning in central America and Mexico may have contributed to elevated PM levels that exceeded the daily NAAQS level for PM in Texas. Wildfires throughout the United States, Canada, Mexico, and Central America all contribute to background concentrations of PM in the United States.

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APPENDIX 3A

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 “semi-volatile” 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 3A 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 3A-1 lists a number of recent urban and some rural measurements of particulate organic and elemental carbon in μg of carbon/m^3. Emphasis was placed on measurements published after 1995. The analysis method and artifact correction procedure, if any, are indicated. Table 3A-2 presents information on recent (post 1990) studies concerning concentrations of particulate organic compounds found at selected U.S. sites.

TABLE 3A-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	PM1.0; 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 3A-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]

TABLE 3A-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$_{2.5}$							
Chow et al. (1996)	Point Reyes, CA	July-Aug 1990	1.5 (2.7)	0.4 (0.6)		5-7 h	PM$_{2.5}$; 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)			
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		

TABLE 3A-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
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 3A-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				
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				

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n-Alkanoic Acids (cont'd)								
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-octadecanedienoic 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 3A-2 (cont'd). PARTICULATE ORGANIC COMPOUND CONCENTRATIONS (in ng C/m^3) BASED ON STUDIES PUBLISHED AFTER 1990 AT SELECTED SITES

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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 3A-2 (cont'd). PARTICULATE ORGANIC COMPOUND CONCENTRATIONS (in ng C/m^3) BASED ON STUDIES PUBLISHED AFTER 1990 AT SELECTED SITES

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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				

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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)

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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	

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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**				

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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**				

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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 3B

Composition of Particulate Matter Source Emissions

This appendix includes discussions of the elemental composition of emissions from various source categories discussed in Table 3-7. 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. The primary emphasis in the discussions is on the composition of $PM_{2.5}$ particle sources.

Soil and Fugitive Dust

The compositions of soils and average crustal material are shown in Table 3B-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 conditions. 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, and agricultural tilling in addition to wind erosion. Figure 3B-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 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

TABLE 3B-1. AVERAGE ABUNDANCES OF MAJOR ELEMENTS IN SOIL AND CRUSTAL ROCK

Elemental Abundances (ppmw)			
		Crustal Rock	
Element	Soil (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).

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 3B-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 3B-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

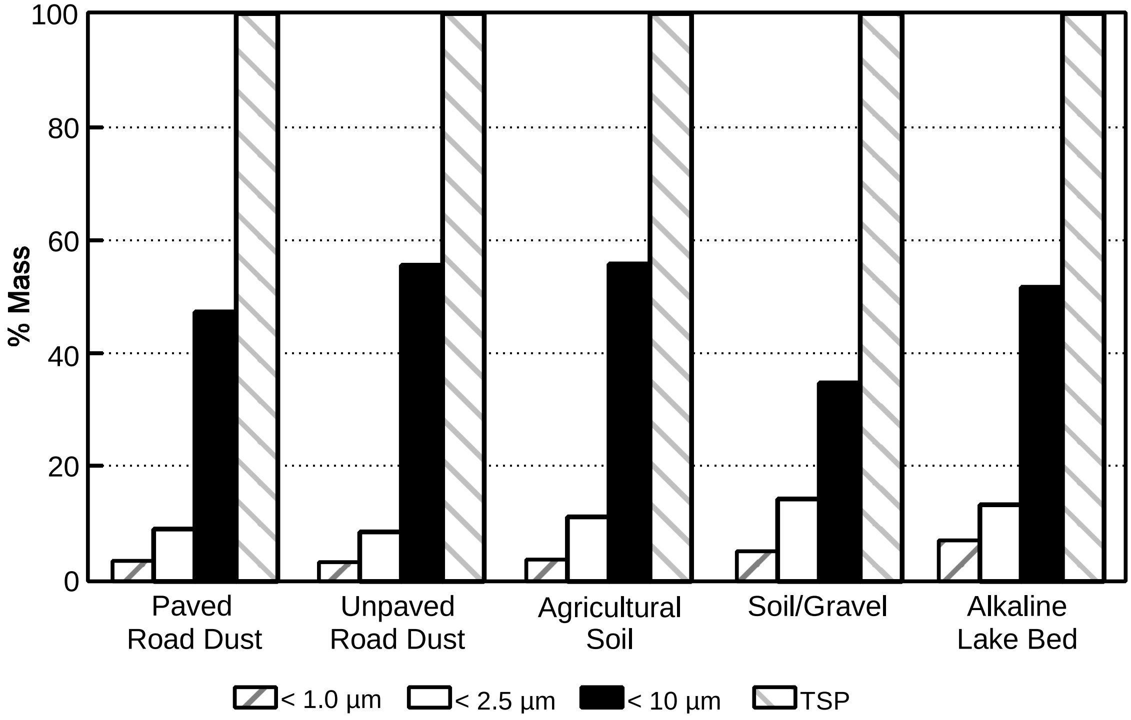

Figure 3B-1. Size distribution of particles generated in a laboratory resuspension chamber.

Source: Chow et al. (1994).

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 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 Rogge et al. (1993a) was collected in Pasadena, California during May of 1988. The sample analyzed by Schauer and Cass (2000) is a composite sample

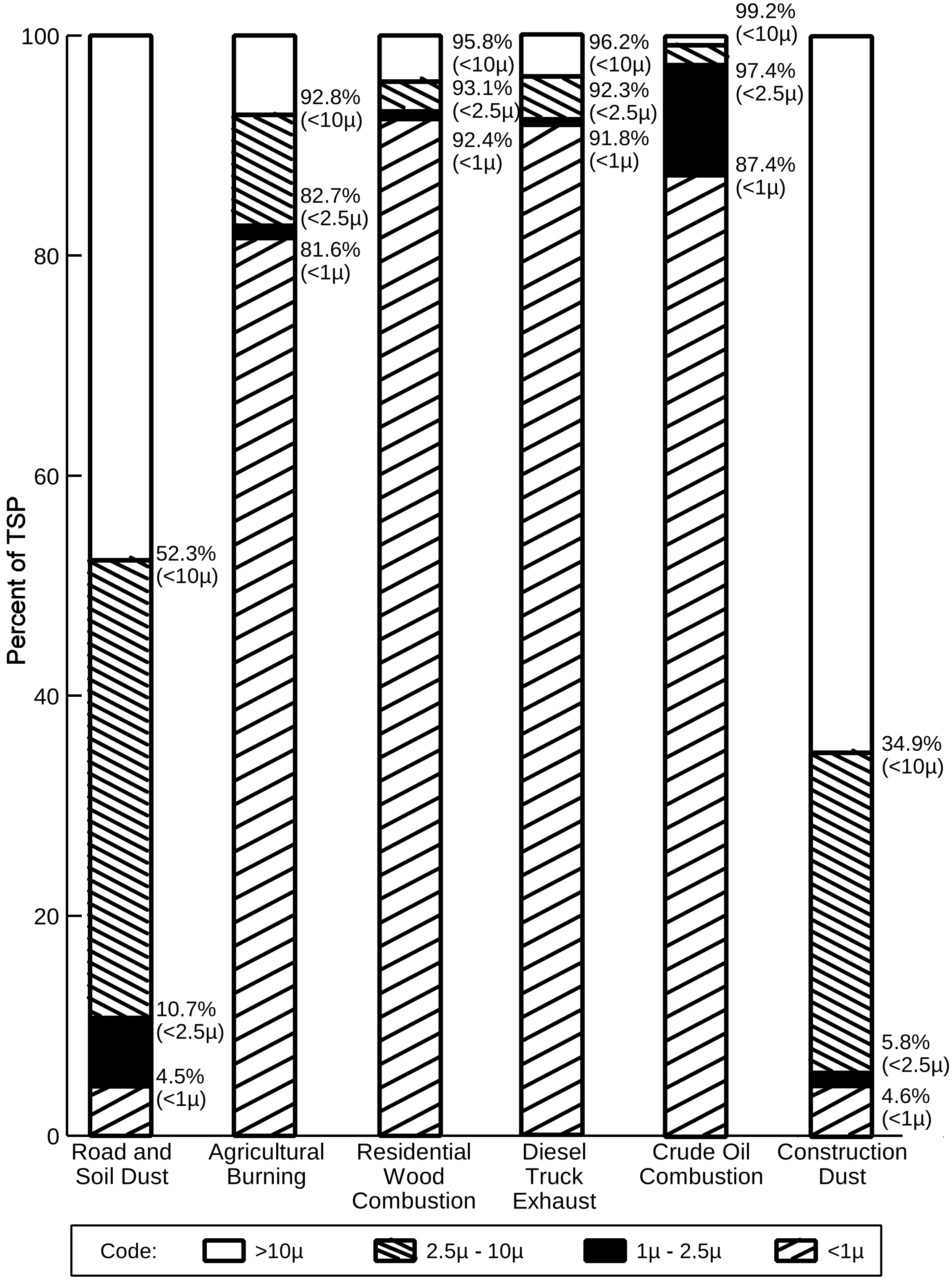

Figure 3B-2. Size distribution of California source emissions, 1986.

Source: Houck et al. (1989, 1990).

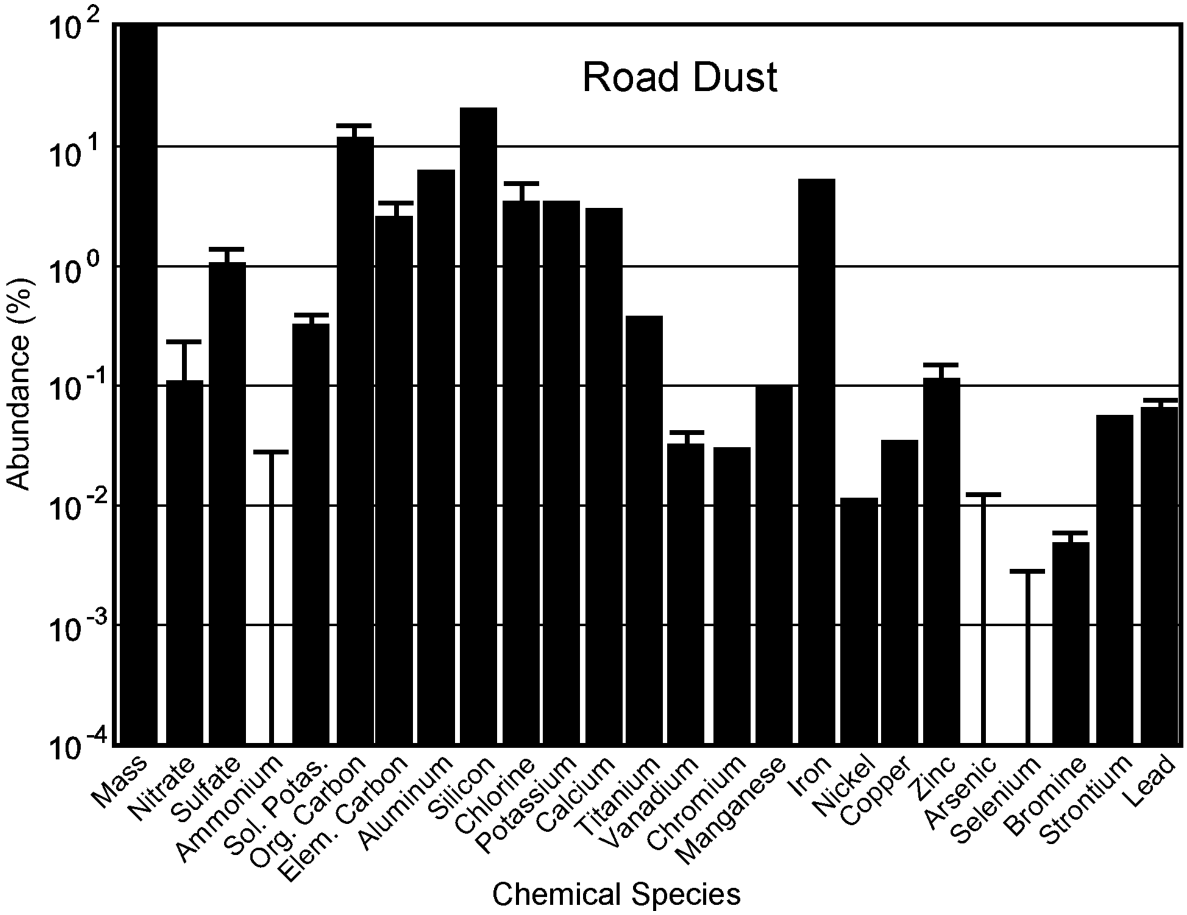

Figure 3B-3. Chemical abundances for $PM_{2.5}$ emissions from paved road dust in Denver, CO. Solid bars represent fractional abundances, and the error bars represent variability in species abundances. Error bars represent detection limits when there are no solid bars.

Source: Watson and Chow (1994).

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 3B-2 summarizes the organic compounds measured in these road dust samples.

TABLE 3B-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

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 3B-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 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 could 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

TABLE 3B-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 3B-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						
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 3B-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
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.

Source: Adapted from Olmez et al. (1988).

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 oils (RFO) in a fire tube package boiler, which 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, which 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 3B-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, and Sb are enormously enriched compared to their crustal abundances. A comparison of the trace elemental composition of incinerator emissions in Philadelphia, PA (shown in Table 3B-3), with the composition of incinerator emissions in Washington DC, and Chicago, IL (Olmez et al., 1988), shows agreement for most constituents to better 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, but 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. As a result, 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 3B-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, 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. There appears to be a tendency for emissions of elemental carbon to increase relative to emissions of organic carbon for gasoline fueled vehicles as simulated driving conditions are changed from a steady 55 km/h to the various load conditions specified in the Federal Test Procedures (FTPs). Also shown are the results of sampling from mixed vehicle types along roadsides and in tunnels.

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 lognormal 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 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

TABLE 3B-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] U.S. EPA SPECIATE database.
[c] Norbeck et al. (1998).

Source: U.S. Environmental Protection Agency (1999).

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 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, which increased to 0.18 μm for smokers and diesels. Corresponding average emissions rates of $PM_{2.5}$ found by Cadle et al. (1999) for diesels were 552 mg/mi; for smokers they were 222 mg/mi; and, for gasoline vehicles, they were 38 mg/mi. The values for smokers and for diesels appear to be somewhat lower than those given in Table 3B-5, whereas the value for 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 as part of the North Frontal Range Air Quality Study (NFRAQS), which took place in December 1997 in Colorado are shown in Table 3B-5. As can be seen from Table 3B-5, emissions of total carbon (TC), which is equal to the sum of organic carbon (OC) and elemental 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

TABLE 3B-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).

species than for OC and EC among different source profiles (e.g., SPECIATE, Lawson and Smith (1998), Norbeck et al. (1998)). They suggest that this may arise because their emissions are not related only to the combustion process, but also to their abundances in different fuels and

TABLE 3B-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).

lubricants and also to wear and tear during vehicle operation. Emissions from smokers are comparable to those from 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 also are correlated with vehicle acceleration and emissions occur predominantly during periods of heavy acceleration, even in newer vehicles (Maricq et al., 1999).

Although the data shown in Table 3B-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 particulate matter 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 3B-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 3B-6 summarizes the composition of motor vehicle exhaust measured by Fraser et al. (1999) and Schauer et al. (1999).

TABLE 3B-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) to make up from 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). Excluding these semi-volatile 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 woodstoves 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 woodstoves is shown in Figure 3B-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

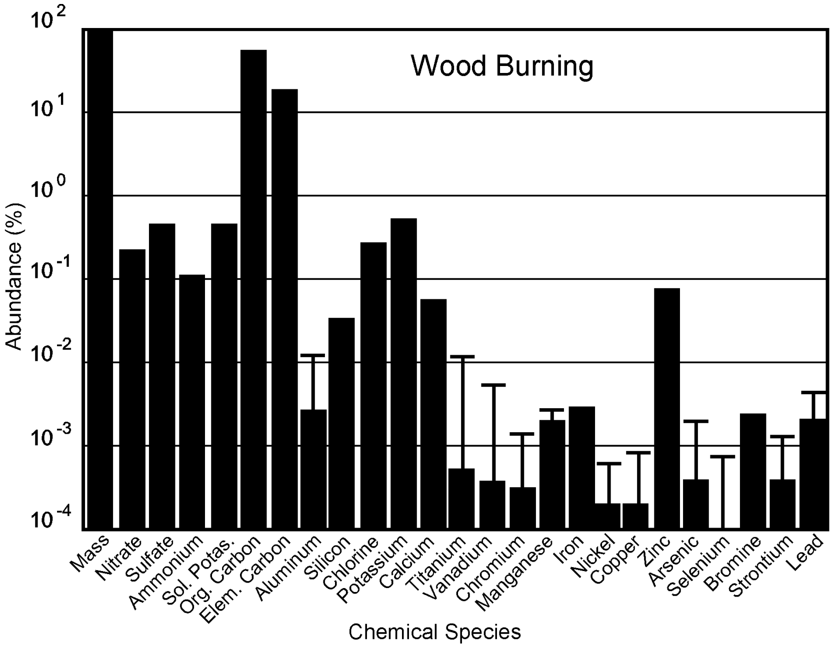

Figure 3B-4. Chemical abundances for $PM_{2.5}$ emissions from wood burning in Denver, CO. Solid bars represent fractional abundances, and the error bars represent variability in species abundances. Error bars represent detection limits when there are no solid bars.

Source: Watson and Chow (1994).

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 studies of wood burning emissions. For instance, the mass median diameter of wood-smoke 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 particulate matter ($PM_{2.5}$) 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 3B-7. It should be noted that the two methods used for the

TABLE 3B-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.

measurements shown in Table 3B-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).

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 3B-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

TABLE 3B-8. SUMMARY OF PARTICLE-PHASE ORGANIC COMPOUNDS EMITTED FROM THE COMBUSTION OF WOOD IN FIREPLACES (Measurements were made using a dilution sampler and no semi-volatile organic compound sorbent.)

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

Source: Rogge et al. (1998).

chromatography/mass spectrometry (HTGC-MS) to measure high-molecular-weight organic compounds in smoke from South American leaf and steam 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 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 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 woodstove 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 was shown in Figure 3B-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 3B-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 1988. As can be seen from a comparison of the data shown in Table 3B-9 with those shown in Figure 3B-4, there are a number of similarities and differences (especially with regard to the heavy metal content) in the abundances of many species. The

TABLE 3B-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]
$SO_4^=$	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 $\mu g/m^3$.
[b] Beneath detection limit.

Source: Pinto et al. (1998).

abundances of some crustal elements (e.g., Si, Fe) are higher in Table 3B-9 than in Figure 3B-4, perhaps reflecting additional contributions of entrained soil dust.

Limited emissions data that includes 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 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) 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, the aerosol drops are composed of this organic material in addition to sea salt (about 3.5% by weight in sea water). Na^+ (30.7%), Cl^- (55.0%), $SO_4^=$ (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 sea water (Wilson, 1975). The composition of the marine aerosol also reflects the occurrence of displacement reactions that enrich sea-salt particles in SO_4^- and NO_3^-, while depleting them of Cl^- and Br^-.

Seasalt 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.

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 not insignificant natural source for many trace elements. It should be noted though that these estimates are based on emissions estimates that have uncertainty ranges of an order of magnitude.

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4. ENVIRONMENTAL EFFECTS OF PARTICULATE MATTER

4.1 INTRODUCTION

Several later chapters (Chapters 5 through 8) of this document assess the latest available information on determinants of human exposures to particulate matter (PM); dosimetry of particle deposition, clearance, and retention in human respiratory tract; epidemiologic analyses of health effects associated with human exposures to ambient PM; and toxicologic evaluations of pathophysiologic effects of PM and underlying mechanisms of action. The human exposure and health-related findings assessed in those chapters provide key elements of the scientific bases to support upcoming decision making regarding potential retention or revision of the primary PM National Ambient Air Quality Standards (NAAQS). This chapter, in contrast, assesses information pertinent to decision making regarding secondary standards aimed at protecting against welfare effects of PM. More specifically, this chapter assesses environmental effects of atmospheric PM, including discussion of PM effects on vegetation and ecosystems, PM effects on visibility, PM effects on man-made materials, and relationships of ambient PM to global climate change processes.

4.2 EFFECTS ON VEGETATION AND ECOSYSTEMS

The Particulate Matter National Ambient Air Quality Standards (PM NAAQS) set in 1971 were specified in terms of total suspended particulates (TSP), which included both fine and coarse mode particles (the latter ranging up to 25 to 40 μm in size). The 1987 revision of the TSP NAAQS to PM_{10} standards focused attention on those particles ($\leq$10 μm mean aerometic diameter) capable of being deposited in lower (thoracic) portions of the human respiratory tract. The subsequent 1997 PM NAAQS revisions retained the PM_{10} standards and added fine particle ($PM_{2.5}$) standards (both specified in terms of mass concentrations of particles undifferentiated in terms of their specific chemical composition). The effects of PM on vegetation and ecosystems as a basis for a secondary standard were not considered as part of the 1997 PM NAAQS revisions. Vegetation and ecosystem effects of ambient PM evaluated in this chapter are dependent not so much just on PM size-related mass concentration, but rather on exposure of plants to PM components differentiated by chemical composition as well.

Particulate matter deposition to vegetation is not well understood. Unlike gaseous dry deposition, neither the solubility of the particles nor the physiological activity of the surface are likely to be of first order importance in determining deposition velocity (V_d). Factors that contribute to surface wetness and stickiness may be critical determinants of sticking efficiency. Available tabulations of deposition velocities are highly variable and suspect. High-elevation forests receive larger particulate deposition loadings than equivalent lower elevation 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 (Lovett, 1984). Recent evidence indicates that all three modes of deposition, (1) wet, (2) occult, and (3) dry, must be considered in determining inputs to watersheds or ecosystems because each may dominate over specific intervals of time or space.

Exposure to a given mass concentration of airborne PM may lead to widely differing phytotoxic responses, depending on the particular mix of deposited particles. The most common and useful subdivision of PM, derived from the typical bimodal distribution of atmospheric particles, is into fine and coarse particles (Wilson and Suh, 1997). The smallest particle at or near 1.0 to 2.5 μm generally is taken as the division between fine and coarse, although this is not an absolute and is subject to some shift (e.g., with changing ambient humidity). However, the typical the rule of thumb, as previously used in the 1996 PM Air Quality Criteria Document or "PM AQCD" (U.S. Environmental Protection Agency, 1996a), is that fine PM nominally falls in the range of 0 to 2.5 μm and coarse-mode PM, 2.5 to 10.0 μm.

In general, fine-mode PM is secondary in nature, having condensed from the vapor phase or been formed by chemical reaction from gaseous precursors in the atmosphere. These particles exist in a nucleation mode (having a mass median aerodynamic diameter or MMAD of about 0.06 μm) and may grow by coagulation of existing particles or by condensation of additional gases onto existing particles into an accumulation mode (about 0.5 μm). Sulfur and nitrogen oxides (SO_x and NO_x), as well as volatile organic gases, are common precursors for fine PM, often neutralized with ammonium cations as particulate salts. Condensation of volatilized metals and products of incomplete combustion also are common precursors. Reactions of many of these materials with an oxidizing atmosphere lead to high secondary PM concentrations during summer months in many parts of the United States.

In general, coarse-mode particles are primary in nature, having been produced and emitted from a point or area source as a fully formed particle. They range in size from ca. 2.5 to 100 μm. This material is created by abrasion and subsequent suspension by wind or mechanical means. Suspended geologic material contains the chemical and, potentially, the biological signature of the soil from which it derives (dominated by iron, silica, aluminum, and calcium). Additional anthropogenically derived coarse-mode PM derives from fly ash, automobile tires and brake linings, and industrial effluent associated with crushing and grinding operations. Coarse-mode particles also include biogenically derived organic materials (e.g., fragments of plants and insects, pollen, fungal spores, bacteria and viruses included in marine aerosols).

Atmospheric deposition of particles to ecosystems takes place via both wet and dry processes through three major routes: (1) precipitation scavenging in which particles are deposited in rain and snow; (2) fog, cloud-water, and mist interception; and (3) dry deposition, a much slower, yet more continuous removal to surfaces (Hicks, 1986).

Precipitation scavenging includes rainout involving within-cloud nucleation phenomena and washout involving below-cloud scavenging by impaction. Total inputs from wet deposition to vegetative canopies can be significant (Table 4-1), although not all wet deposition involves particle scavenging because gaseous pollutants also dissolve during precipitation.

Wet deposition is not affected by surface properties as much as is dry or occult deposition. However, forested hillsides may receive much (four- to sixfold) greater precipitation than short vegetation in nearby valleys because of a variety of orographic effects (Unsworth and Wilshaw, 1989). Additionally, closer aerodynamic coupling to the atmosphere of the tall forest canopy than of the shorter canopies in the valleys leads to more rapid foliar drying, reduced residence time of solubilized particulate materials available for foliar uptake, and, consequently, more rapid and more extreme concentration of such materials on the cuticular surface. The results of direct physical effects on leaves are not known.

Most of wet deposited particulate material passes through the plant canopy to the soil by throughfall and stemflow, causing soil-mediated ecosystem-level responses. Rainfall also removes much of the dry-deposited PM resident on foliar surfaces, reducing direct foliar effects

TABLE 4-1. 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^{-}, dry sulfur consists of vapor phase SO_2, and particulate sulfur consists of pSO_4^{--}.

(Lovett and Lindberg, 1984). This washing effect, combined with differential foliar uptake and foliar leaching (both of which depend on the physiological status of the vegetation), alters the composition of rainwater that reaches the soil. Dry deposition onto foliage and subsequent wet removal by runoff enhances soil-mediated effects of particulate deposition, both by enhancing total dry deposition relative to unvegetated surfaces nearby and by accelerating passage of deposited particles to the soil. The most significant effects of wet deposition occur through soil-mediated processes involving biogeochemcial cycling of major and minor nutrients and trace elements.

Dry deposition is more effective for coarse particles of natural origin and elements such as iron and manganese, whereas wet deposition generally is more effective for fine PM of atmospheric origin and elements such as cadmium, chromium, lead, nickel, and vanadium (Smith, 1990a). The actual importance of wet versus dry deposition, however, is highly variable, depending on ecosystem type, location, and elevation. For the Walker Branch Watershed, a deciduous forest in rural eastern Tennessee, dry deposition constituted a major fraction of total annual atmospheric input of cadmium and zinc (=20%), lead (=55%), and manganese (=90%), but wet deposition rates for single precipitation events exceeded dry deposition rates by one to four orders of magnitude (Lindberg and Harriss, 1981). Miller et al. (1993) emphasized that immersion of high-elevation forests in cloudwater for 10% or more of the year can enhance significantly overall efficiency of transfer of atmospheric particles and gases to a forest canopy.

Dry deposition of particles occurs to all vegetational surfaces exposed to the atmosphere (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. Wet deposition generally is confounded by fewer factors and has been easier to quantify (Chapter 2).

Emphasis in this and the next section is placed on discussion of PM effects on individual plants in natural habitats and terrestrial ecosystems. Except for the deposition of nitrogen and sulfur-containing compounds and their effects exerted via acidic precipitation, information concerning the effects of deposition of other specific substances as PM on crops is not readily available. The U.S. National Acid Precipitation Assessment Program (NAPAP) Biennial Report to Congress: An Integrated Assessment presents an extensive overall discussion of the effects of acidic deposition (National Science and Technology Council, 1998). The effects of gaseous sulfur oxides and nitrogen oxides on crops are discussed in detail in EPA criteria documents for those substances (U.S. Environmental Protection Agency, 1982, 1993). A detailed discussion of the ecological effects of acidic precipitation and nitrate deposition on aquatic ecosystems also can be found in the EPA Nitrogen Oxides Air Quality Criteria Document (U.S. Environmental Protection Agency, 1993). Neither nitrate or sulfate deposition on crops is discussed in this chapter, as they are added frequently in fertilizers. Also, the effects of lead on crops, vegetation, and ecosystems are discussed in the EPA document, Air Quality Criteria for Lead (U.S. Environmental Protection Agency, 1986).

The effects of deposited PM may be direct or indirect. Indirect effects are chiefly nutritional responses mediated through the soil and result from the effects of PM components on soil processes. In the following sections, the direct effects on individual plants are discussed first, followed by effects on plant species and their interactions in ecosystems.

4.2.1 Direct Effects of Particulate Matter on Individual Plant Species

Particulate matter in the atmosphere may affect vegetation directly following deposition on foliar surfaces, 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 impacts, however, are usually the most significant because they can alter nutrient cycling and inhibit plant nutrient uptake. The possible direct responses to PM deposition are considered in this section, and the indirect responses in the sections on ecosystems.

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 impacts. The effects of "inert" PM are mainly physical, whereas those of toxic particles are both chemical and physical. The chemical 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).

Studies of the direct effects of chemical additions to foliage in particulate deposition have found little or no effects of PM on foliar processes unless exposure levels were significantly higher than typically would be experienced in the ambient environment. Interpretation of the effects of atmospheric chemical deposition at the level of individual plants and ecosystems is difficult because of the complex interactions that exist among biological, physicochemical, and climatic factors. The majority of the easily identifiable direct and indirect effects, other than climate, occur in severely polluted areas around heavily industrialized point sources, such as limestone quarries, cement kilns, and smelting facilities for iron, lead, or various other metals. The diverse chemical nature and size characteristics of ambient airborne particles and the lack of any clear distinction between effects attributed to phytotoxic particles and to other forms of air pollutants confound the direct effects of PM on foliar surfaces. Most documented toxic effects of particles on vegetation reflect their acidity, trace metal content, nutrient content, surfactant properties, or salinity. These materials typically elicit similar biological effects, whether deposited as coarse or fine particles, in wet, dry, or occult form, and, frequently, whether deposited to foliage or to the soil. Studies of direct effects of particles on vegetation have not yet advanced to the stage of reproducible exposure experiments. Experimental difficulties in application of ambient particles to vegetation have been discussed by Olszyk et al. (1989).

4.2.1.1 Effects of Coarse Particles

Coarse-mode particles, ranging in size from 2.5 to 100 μm, are chemically diverse, are dominated by local sources, and are typically deposited near the source because of their sedimentation velocities. Airborne coarse particles are derived from road, cement kiln, and foundry dust; fly ash; tire particles and brake linings; soot and cooking oil droplets; biogenic materials (e.g., plant pollen, fragments of plants, fungal spores, bacteria and viruses) and sea salt. Most coarse particles in rural and some urban areas are composed of silicon, aluminum, calcium, and iron, suggesting that their main source is fugitive dust from disturbed land, roadways, agricultural tillage, or construction. Rapid sedimentation of these particles tends to restrict their direct effects on vegetation largely to roadsides and forest edges.

Physical Effects—Radiation. Dust can have both a physical and chemical impact. Deposition of inert PM on above-ground plant organs may result in an increase in radiation received, in leaf temperature and blockage of stomata. Increased leaf temperature, 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*) (Guderian, 1986) under the conditions of the experiment. Broad-leaved plants exhibited greater temperature increases because of particle loading than did the needle-like leaves of conifers. 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 fourfold increase in the absorption coefficient of leaves of *Hedera helix* (Eller, 1977; Guderian, 1986) for near infrared radiation (NIR; 750 to 1350 nm). Little change occurred in absorption 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 net energy budget 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 impact 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 as well.

Brandt and Rhoades (1973) attributed the reduction in growth of trees because of crust formation from limestone dust on the leaves. Crust formation reduced photosynthesis and formation of carbohydrate needed for normal growth, induced premature leaf-fall, destruction of leaf tissues, inhibited growth of new tissue, and reduced storage. Dust may affect 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, however, 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, which can penetrate the epidermis and enter the mesophyll, and, in some cases, the leaf surface alkalinity may reach to pH 12. Lipid hydrolysis coagulation of the protein compounds and ultimately plasmolysis of the leaf tissue result in reduction in 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.

Particulate matter in the form of sea salt enters the atmosphere from oceans following mixing of air into the water and subsequent bursting of bubbles at the surface. This process can be a significant source of sulfate, sodium chloride, and trace elements in the atmosphere over coastal vegetation, resulting in the formation of the maritime forest, a specialized ecosystem. Sea-salt particles can serve as nuclei for the adsorption and subsequent reaction of other gaseous and particulate pollutants. Both nitrate and sulfate from the atmosphere have been found to be associated 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. Salt pruning is a common phenomenon near the ocean (i.e., salt spray kills the buds on the windward side of trees and shrubs).

4.2.1.2 Effects of Fine Particles

Fine PM 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, condensation 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. The conclusion reached in the 1982 PM AQCD (U.S. Environmental Protection Agency, 1982) that sufficient data were not available for adequate quantification of dose-response functions for direct effects of fine aerosols on vegetation continues to be true today. Only a few studies have been completed on the direct effects of acid aerosols (U. S. Environmental Protection Agency, 1982). The major effects are indirect and occur through the soil (Section 4.3).

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 (e.g., 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.

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 tail 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 damage, 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. This 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. Volatilization losses of nitric acid during this process, if they occur, have not been characterized.

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 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), indicating 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 chemical 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 4.3).

Sulfur. Anthropogenic sulfur emissions are >90% as 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 sulfate/SO_2 increases with aging of the air mass and, therefore, with distance from the source. Sulfate is sufficiently hygroscopic that, in humid air, it may exist significantly in the coarse particulate fraction. As 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). 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 (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 impacts 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, respectively), or ammonium and sulfate (179 and 637 μg/m^3, respectively). 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 for 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 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. Huttunen (1994) concluded that his studies of conifers and review of the literature suggest that acidic precipitation causes direct injury to tree foliage and, also, indirect effects through the soil. The indirect effects of acidic precipitation are discussed in Section 4.3.

Based on his review of the many studies involving field and controlled laboratory experiments on crops in the literature, Cape (1993) drew a number of conclusions concerning the direct effects of acidic precipitation on crops:

- foliar injury and growth reduction occurs 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 when aerosol exposure preceded O_3 exposure. In none of the studies cited above did acid rain per se produce significant growth changes. 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 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 Chapter 2 (Tong, 1991; Youngs et al., 1993). 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. The mycelium of fungi becomes particularly abundant on leaf surfaces as the growing season progresses and is in intimate association with deposited particles (Smith, 1990b).

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 impact 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. A trace metal must be brought into solution before it 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 sulfur dioxide were present in concentrations toxic to some species near the smelter; however, toxic zinc concentrations extended beyond the detectable limits of sulfur dioxide (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 be used to 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 region showing 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 is a cause of tree injury and, therefore, contributes to forest decline in the northeastern United States (Gawel et al., 1996).

One potential direct impact 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 parasites included *Aureobasidium pullulans, Chaetomium sp., Cladosporium sp., Epicoccum sp.*, and *Philaphora verrucosa*. Those existing primarily as parasites included *Gnomonia platani, Pestalotiposis 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. Fine particles in the atmosphere reacting with volatilized chemical compounds 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 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. (1993) inventoried the organic contaminants associated with fine particles (diameter $\leq 2.0\ \mu$m) in road dust, brake lining wear particles, and tire tread debris. In excess of 100 organic compounds were identified in these samples, including n-alkanols, benzoic acids, benaldehydes, 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, POPs, or 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, deposited as a particle onto the waxy cuticle of leaves or uptake thorough 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 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 (Smith, 1990d).

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 microbial toxicity of organic contaminants to soil microorganisms is not well studied (Foster, 1991).

4.2.2 Particulate Matter Effects on Natural Ecosystems

4.2.2.1 Introduction

Human existence on this planet depends on nature and the life-support services ecosystems provide. Ecosystem services (Table 4-2) are the conditions and processes through which natural ecosystems, and the species of which they are comprised, sustain and fulfill human life (Daily, 1997). Both ecosystem structure and function play an essential role in providing societal benefits. Society derives two types of benefits from the structural aspects of an ecosystem: (1) products with market value such as fish, minerals, forage, forest products, biomass fuels, natural fiber, and many pharmaceuticals and the genetic resources of valuable species (e.g., plants for crops and timber, animals for domestication); and (2) ecosystem services (Table 4-2) include the use and appreciation of ecosystems for recreation, aesthetic enjoyment, and study (Westman, 1977; Daily, 1997). Economic benefits and values associated with ecosystem functions 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). Services usually are not considered to be items with market value.

TABLE 4-2. ECOSYSTEM SERVICES

- Purification of air and water
- Mitigation of floods and droughts
- Detoxification and decomposition of wastes
- Generation and renewal of soil and soil fertility
- Pollination of crops and natural vegetation
- Control of the vast majority of potential agricultural pests
- Dispersal of seeds and translocation of nutrients
- Maintenance of biodiversity, from which humanity has derived key elements of its agricultural, medicinal, and industrial enterprises
- Protection from the sun’s harmful rays
- Partial stabilization of climate
- Moderation of temperature extremes and the force of winds and waves
- Support of diverse human cultures
- Providing of aesthetic beauty and intellectual stimulation that lift the human spirit

Source: Daily (1997).

Ecosystems are structurally complex biotic communities consisting of populations of plants, animals, insects, and microorganisms interacting with one another and with their abiotic environment (Odum, 1993). They are dynamic, self-adjusting, self-maintaining, complex adaptive systems in which patterns at higher levels of organization emerge from localized interactions and selection processes. Macroscopic ecosystem properties such as structure, diversity-productivity relationships and patterns of nutrient flux emerge from the interactions among components and may feed back to influence subsequent development of those interactions. The relationship between structure and function is a fundamental one in ecosystem science (Levin, 1998). Structure refers to the species, their biodiversity, abundance, mass, and arrangement within an ecosystem. Ecosystem functions, energy flow, nutrient flux, and water and material flow, are characterized by the way in which ecosystem components interact. Elucidating these interactions across scales is fundamental to understanding the relationships between biodiversity and ecosystem functioning (Levin, 1998). To function properly and maintain themselves, ecosystem components must have an adequate supply of energy, chemical nutrients, and water. It is the flows of nutrients and energy, that provide the interconnectedness between ecosystem parts and transforms the community from a random collection of species into an integrated whole, an ecosystem in which the biotic and abiotic parts are interrelated (Levin, 1998).

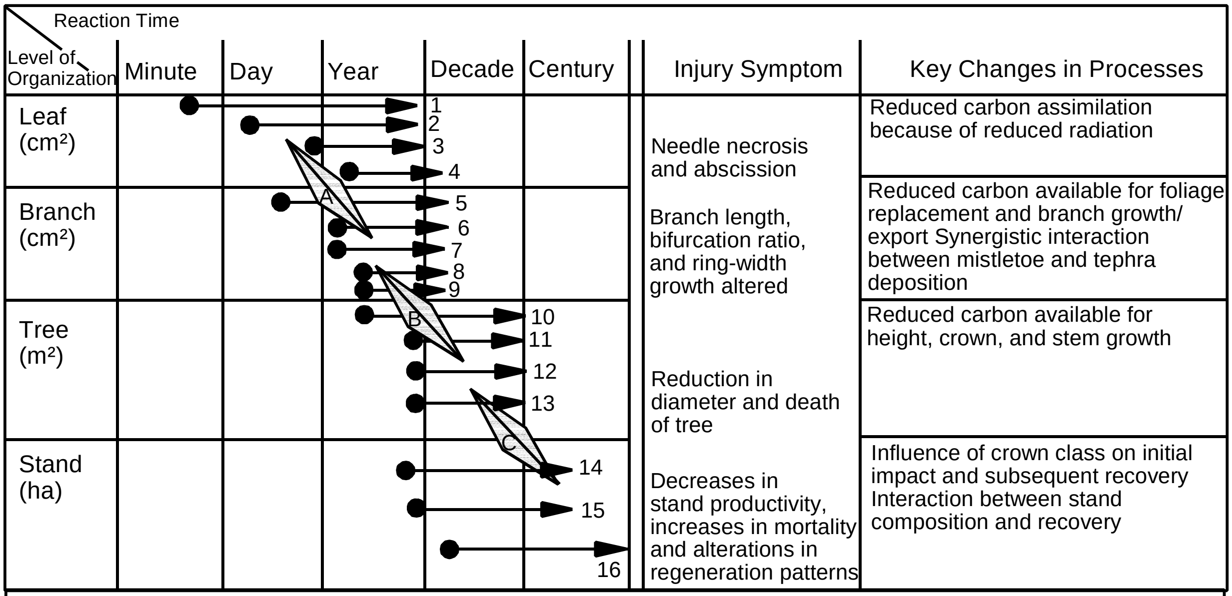
Growth of new trees and other vegetation requires energy in the form of carbon compounds. Plants accumulate, store, and use carbon compounds to build their structures and maintain physiological processes. Plants, using energy from sunlight, in their leaves combine carbon dioxide from the atmosphere and water from the soil to produce the carbon compounds (sugars) that provide the energy required by vegetation for growth and maintenance (Waring and Schlesinger, 1985). Energy is transferred through an ecosystem from organism to organism in food webs and, finally, is dissipated into the atmosphere as heat (Odum, 1993). Chemical nutrients, such as nitrogen, phosphorus, or sulfur, on the other hand, are taken up from the soil by plants and are transferred to other species through the food webs. The process is cyclic with the chemical nutrients eventually returning to the soil. This process is referred to as biogeochemical cycling (Odum, 1993). The biogeochemistry of an ecosystem is influenced by vegetation growth characteristics (Herbert et al., 1999).

Ecosystem functions are characterized by the way components interact. These are the functions that maintain clean water, pure air, a green earth, and a balance of organisms, the functions that enable humans to survive. They are the dynamics of ecosystems. 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, climate, and the fixation of solar energy (Table 4-2; Westman, 1977; Daily, 1997).

Concern has risen in recent years regarding the consequences of changing 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 causing the loss of biodiversity and altering the complexity and stability of ecosystems and producing changes in nutrient cycling (structure and function) (Pimm, 1984; Levin, 1998; Chapin et al., 1998; Peterson et al., 1998; Tilman, 1996; Tilman and Downing, 1994; Wall, 1999; Daily and Ehrlich, 1999). 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 references discussing the importance of ecosystem structure and function. Ecorisk, complexity, stability, biodiversity, resilience, sustainability, managing earth’s ecosystems, and ecosystem health are frequently discussed topics. There is a need, therefore, to understand how ecosystems respond to both natural and anthropogenic stresses and, especially, the ways that anthropogenic stresses are impacting ecosystem services and products.

4.2.2.2 Ecosystem Responses to Stress

Ecosystem responses to stresses begin at the population level. Population changes however, begin with the response of individual plants or animals. Plant responses, both structural and functional, must be scaled in both time and space and propagated from the individual to the more complex levels of community interaction to produce observable changes in an ecosystem (Figure 4-1). 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). The response of individual organisms within a population based on their genetic constitution (genotype), stage of growth at time of exposure, and the microhabitats in which they are growing

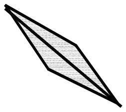


For a given level, the dot associated with a line begins with a process (e.g., photosynthesis for #1 under leaf) and ends with the associated structure (e.g., the needle).

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 4-1. 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 impacts 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).

vary in their ability to withstand the stress of environmental changes (Levin, 1998). Individual organisms within a population vary in their ability to withstand the stress of environmental changes. 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. 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). Ecosystem perturbation by natural stresses can be only a temporary setback. Extremely severe natural perturbations return succession to an earlier stage, reduce ecosystem structure (scarcity of life forms and no symbiotic interactions) and functions, 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, which 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 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 which 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) expanses 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 other sources.

4.2.2.3 Ecosystem Response to Direct Plant Effects

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 impacts are indirect. These impacts 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. Particulate matter, as considered in this chapter is a heterogeneous mixture of particles differing in size, origin, and chemical constituents and their impacts vary depending on the chemical nature of PM being deposited on vegetation or soil. Particulate inputs and ecosystem cycling of key elements are considered below.

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 reproduction of plants from particulate deposition have been reported (Saunders and Godzik, 1986). Sensitivities of individual species have been associated with changes in composition and structure 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 (Saunders and Godzik, 1986). Rapid evolution of certain populations of tolerant species at sites with heavy trace element and nitrate deposition has been observed. 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 4-3; Smith, 1974). Frequently, trace metals that penetrate the above-ground plant parts are less injurious than when taken up through the roots (Guderian, 1986).

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 it is difficult to quantify, especially

TABLE 4-3. 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).

when there are other pollutants present in the ambient air, which 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. 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 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. *Q. prinus* dominated the area, and the larger trees were 60 to 80 years old. The dusty site was dominated by white oak

(Q. alba), whereas *Q. rubra* 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 *L. tulipifera* (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 *Acer rubrum,* 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 *C. florida, Ostrya virginiana,* redbud *(Cercis canadensis),* and sugar maple *(Acer saccarum).*

Crust formation reduced photosynthesis, induced premature leaf fall, 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 a 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, *Acer saccharum* 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 *L. tulipifera, C. florida, O. virginiana,* black haw *(Viburnum prunifolium),* and *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 *A. rubrum, Q. prinus,* and *Q. rubra,* occurred in all strata. On the other hand, all of these characteristics increased in *L. tulipifera,* 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 *L. tulipifera* 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 impact ecosystems.

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). Early needle senescence and abscission in the San Bernardino Forest changed fungal microflora successional and decomposition patterns by altering the taxonomic diversity and population density of microflora that normally develop on needles while they are on the tree. Changing the fungal community on the needles weakened the decomposer community, decreasing the rate of decomposition, and altered nutrient cycling (Bruhn, 1980). Nutrient availability was influenced by accumulation of carbohydrates and mineral nutrients in the heavy litter under those stands with the most severe needle injury and defoliation (U.S. Environmental Protection Agency, 1996b). Possible impacts 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 when the leaf drops off (Hughes, 1981) and 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 Nikliňska et al. (1998) point out that heavy metals have impacts on 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. Nikliňska 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, 1990e). 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

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 noted that the chemical substances denoted by such headings are not criteria air pollutants controlled by the NAAQS under Section 109 of the Clean Air Act (CAA) (U.S. Code, 1991), but rather are controlled under Sect.112, Hazardous Air Pollutants. 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, in the atmosphere, many of the chemical compounds are partitioned between gas and particle phases. As particles, they can become airborne, be distributed over a wide area, and impact 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 through 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 also 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. 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.

Persistent polychlorinated 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 also, 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 (PCDDs) and polychlorinated dibenzofurans (PDCF/s) also 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, which directs the Environmental Protection Agency (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 and discussed below.

(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 or water discharges).

(2) A plausible link exists between emissions into the air of Great Waters toxic pollutants of concern; the atmospheric 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.

4.2.2.4 Indirect Effects of Particulate Matter In Ecosystems

The presence of PM in the atmosphere directly affects vegetation following physical contact with foliar surfaces (as discussed above in Section 4.2.2.2), but in many cases the more significant impacts are indirect. These impacts 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 in the atmosphere are considered briefly below and in greater detail later, under Section 4.5. Indirect plant responses are chiefly soil mediated and depend primarily on the chemical composition of the individual elements deposited in PM. The individual elements must be bioavailable to have an effect. 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 affect on the growth of the bacteria involved in nutrient cycling and the fungi involved in plant nutrient uptake.

Particulate Matter-Related Atmospheric Turbidity: Effects on Vegetative Processes

Photosynthetic processes underlie the contribution of vegetative surfaces to nutrient and energy cycling. Photosynthesis and the heat-driven processes of water cycling depend on net receipts and characteristics of the radiation environment. These characteristics may be altered substantially when the atmosphere becomes turbid because of particulate loading.

Specific wavelengths of interest depend on the vegetation process under consideration. Canopy temperature and water relations are particularly sensitive to long-wave, infrared radiation, whereas primary photosynthetic charge separations depend on short-wave radiation in the visible and photosynthetically active range (0.4 to 0.7 μm).

Effects of anthropogenic aerosols on the radiation environment at the Earth's surface are difficult to assess. The residence time of suspended particles varies with size and environmental conditions (seconds to months or years), and concentrations are spatially and temporally variable.

In particularly polluted urban and near-urban areas, unambiguous particulate impacts on radiation and local climate may be observed. Visibility was degraded by 50% in a large plume originating in the St. Louis urban area during the midweek, midday period (Pueschel, 1993). In contrast, visibility was reduced by only 20% on weekends, when traffic and industrial emissions were reduced. The area affected by this plume includes highly productive agricultural land.

Empirical relationships between mass of specific components of the aerosol and radiation scattering have been developed (e.g., Pueschel, 1993), from which regional visibility (or radiation attenuation) isopleths can be constructed if appropriate mass data are available. These estimates support trends observed by direct measurement of turbidity (e.g., Flowers et al., 1969; U.S. Environmental Protection Agency, 1982).

Sulfates, nitrates, and elemental carbon dominate effects on visibility, in part, because they frequently dominate the mass profiles and, in part, because they exhibit particularly large absorption coefficients (see Section 4.3). Absorption by particles containing carbon may range from 5 to 10% in rural areas to up to 50% in urban areas (U.S. Environmental Protection Agency, 1982). In west-coast cities with contrasting particulate sources and loadings, the common component that related PM to visibility degradation was sulfate between 0.65 and 3.6 μm (Barone et al., 1978). For example, in Los Angeles, sulfate and nitrate had similar effects on visibility (White, 1976), despite the dominance of nitrate from transportation sources in the aerosol, although this is changing with controls on point sources of sulfate (Farber et al., 1994).

No long-term global trend of increasing atmospheric optical depth has been documented (Bolle et al., 1986; Pueschel, 1993), although seasonal and regional impacts are substantial. The classic study by Flowers et al. (1969) demonstrated large regional distinctions in turbidity across the United States. Typically, the western deserts, plains, and Rocky Mountains exhibited low mean annual turbidity, whereas the more humid and densely vegetated eastern half of the country exhibited much greater turbidities. In the mid-1970s, visible range in the mountainous southwest exceeded 110 km and radiation attenuation was ca. 2.6%; whereas, in the east, visible range was below 24 km and radiation attenuation was ca. 10%. Visibility in the eastern United States has decreased generally since the 1940s (Flowers et al., 1969; Trijonis and Shapland, 1979; U.S. Environmental Protection Agency, 1982). Correlative trends in visibility degradation and emissions of sulfur oxides suggest that particulate sulfate may account for much of the turbidity.

These trends are typical of urban industrial areas around the world. Turbidity has increased above Mexico City (Binenko and Harshvardhan, 1993) since the 1911 to 1928 period. During this early period, a single annual peak of turbidity coincided with the end of the dry period, and natural sources dominated. By 1957 to 1962, the number of annual peaks had increased, as anthropogenic sources came to dominate. During this period, atmospheric transmission of direct-beam solar radiation decreased by about 10% (Binenko and Harshvardhan, 1993). Visibility in the Los Angeles basin has improved very slightly in the past decades (Farber et al., 1994), as sulfate emissions have been controlled by regulation. The composition of the aerosol has changed, particularly in inland areas, as the former dominance of sulfate shifts to a preponderance of secondary organics.

Particles interact with solar radiation through 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 reradiate in the infrared range, then some of this energy is lost as long-wave reradiation to space. This loss mechanism is minimized because most of the anthropogenic aerosol in the troposphere resides in the planetary boundary layer (Bolle et al., 1986), even within the lower 500 m (Binenko and Harshvardhan, 1993), where the temperature is similar to that of the surface. Some of this energy is captured at the surface as down-welling infrared radiation.

These wavelengths directly impact canopy temperatures and influence transpirational water use by vegetation. The presence of absorbing aerosols reduces the ratio of photosynthetically active radiation to total radiation received at the surface, potentially reducing photosynthetic water use 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. In general, absorption is not a dominant particulate effect.

Scattering of radiation dominates the effects of particulate loading on visibility and turbidity. Nonabsorbing, scattering aerosols raise the overall albedo of the atmosphere and reduce the amount of radiation reaching the surface by the amount reflected or backscattered to space. As atmospheric turbidity increases, so does the scattering of light, including forward scattering of photosynthetically active radiation that intercepts the Earth's surface (Hoyt, 1978).

The largest effect is described by Mie-scattering theory. Forward scattering reduces the intensity of direct radiation by disrupting the solar beam, thereby increasing the path length and probability of absorption and also increases the intensity of diffuse (sky) radiation. 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, even up to 100% of solar radiation 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.

Particle scattering is wavelength dependent, causing objects to appear blue- or red- tinged, depending on viewing and illumination angles and on the light quality, the alteration of which is a minor contributor to photosynthetic light-use efficiency. The wavelength dependence of scattering decreases rapidly from extreme sensitivity for very fine particles to little dependence at 10 μm. Equations relating scattering at a reference wavelength to scattering at wavelengths of interest are rigorously applicable only to spherical particles but may be extended to nonspherical particles of equal volume (Janzen, 1980).

World Meteorological Organization (WHO) data summarized in U.S. Environmental Protection Agency (1982) indicated that turbidity in the eastern United States commonly resulted in radiation losses of ca. 3.5% because of backscattered radiation and ca. 3.5% because of absorption, with a resulting total reduction of incident radiation to ca. 93% of total solar radiation. However, 28% of the radiation reaching the surface was converted from direct radiation to diffuse, or sky, radiation. Under more polluted conditions, losses were ca. 9% backscattered and 9% absorbed, reducing total radiation to 82% of total solar radiation and converting 72% from direct beam to diffuse radiation. Photosynthetically active radiation (0.4 to 0.7 μm) typically is enriched in diffuse radiation relative to total or direct beam radiation.

Altered Radiative Flux: Effects on Vegetative Processes

Canopy photosynthesis is typically a nearly linear function of incident radiation, overcoming saturation exhibited by individual leaves by distributing the light throughout the multilayer canopy. Light penetration into canopies limits photosynthetic productivity (Rosenberg et al., 1983). The uppermost leaves of many canopies are at or above light saturation for photosynthetic processes. The simplest radiative transfer functions describing plant canopies relate total down-welling radiation (direct plus diffuse radiation measured above the canopy) to radiation interception at each leaf level through a Beer's Law analogy. The expected exponential decline in radiation through the canopy depends only on total radiation and a bulk canopy extinction coefficient that depends on leaf size, orientation, and distribution, as well as on reflectance and absorption in wavelengths of interest. These simplified models predict radiation distribution adequately for homogeneous canopies. Turbidity affects canopy processes only by attenuating the total radiation impinging on the canopy surface.

In more complex, and more realistic, canopy-response models (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 affects 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 down-welling 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 down-welling 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. Up-welling (diffuse) radiation results from scattering and reflectance within the canopy, and by the soil, of both direct and diffuse down-welling radiation.

The effect of the altered distribution between diffuse and direct radiation impacts photosynthesis in upper, exposed leaves as a function of leaf angle and in total canopy photosynthesis as a function of penetration of radiation within the canopy. This depends on canopy structure, leaf optical properties, and leaf area density, as well as on solar angle and atmospheric turbidity. Absorption of radiation by particles heats the upper atmosphere and results in reduced vertical temperature gradients. This could reduce the intensity of atmospheric turbulent mixing. The magnitude of such potential effects on turbulent transport within canopies remains unknown, although damping of eddy transport could inhibit canopy gas exchange. Suppressed tropospheric mixing also could intensify local temperature inversions and increase the severity of pollution episodes (Pueschel, 1993), with direct inhibitory effects on photosynthetic processes.

The most significant effect of aerosols on vegetation is probably through their role as cloud condensation nuclei because clouds have substantial impact on radiation receipts at the surface.

An important characteristic of fine particles is their ability to affect the flux of solar radiation passing through the atmosphere directly, by scattering and absorbing solar radiation, and indirectly, by acting as cloud condensation nuclei which in turn influence the optical properties of clouds (Chameides et al., 1999). Regional haze has been estimated to diminish surface solar visible radiation by approximately 8%. Crop yields have been reported as being sensitive to the amount of sunlight received. The potentially significant impact 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 affects 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 optimal crop yields of approximately 70% of the crops are being depressed by at least 5 to 3% by regional scale air pollution and its associated haze (Chameides et al., 1999).

Effects of Solar Ultraviolet Radiation on Terrestrial Ecosystems

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 chlorofluorcarbons (CFCs) and other substances, such as halides, has resulted in heightened concern about potentially deleterious increases in the amount of solar UV-B (SUVB) radiation reaching the Earth's surface (see Section 4.5). One salient consideration is that, although CFC production is at a peak level now, the problem likely will continue well into the future because of the length of time it takes for molecules to reach the stratosphere (Greenberg et al, 1997).

The vulnerability of terrestrial plants to UV-B results from their requirement for sunlight for photosynthesis. Each 1% decline in ozone has been predicted to decrease crops yield by 1% (Greenberg et al., 1997). In addition to inhibiting photosynthesis, UV-B radiation triggers numerous responses in plants (e.g., membrane, protein, and DNA damage; delayed maturation; diminished growth; activation of chemical stress; flavonoid synthesis; leaf thickening) (Table 4-4). It is not known which of the injury and damage effects are most detrimental to plant growth (Table 4-4). Effects of increased UV-B on plant growth are likely to be incremental. Because plants evolved under the selective pressure of ambient UV-B radiation in sunlight, they have developed adaptive mechanisms (Greenberg et al., 1997). Although inhibition of photosynthesis is a detrimental growth effect, flavonoid synthesis represents acclimation.

TABLE 4-4. TYPES OF PLANT RESPONSES TO ULTRAVIOLET-B RADIATION[a]

Acclimation and Morphological Responses	Damage and Injury Responses
Altered biomass distribution	Altered gene expression
Altered leaf cell division	Degradation of auxin
Cotyledon curling	Degradation of chlorophyll and carotenoids
Increased DNA repair	Degradation of proteins
Increased flavonoid biosynthesis	Diminished biomass
Increased leaf thickness	Epidermal collapse
Increased leaf number	Inhibition of growth
Increased number of tillars	Inhibition of photosynthesis
Leaf wrinkling	Increased stomatal conductance
Reduced leaf area	Lower seed yield
Reduced hypocotyl growth	Oxidation of DNA
Reduced shoot height	Peroxidation of lipids
Reduced stomatal density	Prymidine dimer formation

[a] Entries in alphabetical order.

Plants growing under full light have been shown to be protected against UV-B effects but not when growing under weak visible light (Björn, 1996). A common adaptation is alteration in leaf transmission properties, which results in attenuation of UV-B in the epidermis before it can reach the leaf interior.

Plant species vary enormously in their response to UV-B exposures, and large differences in response occur among different genotypes within a species. In general, dicotyledonous plants are more sensitive than monocotyledons from similar environments. In addition, plant responses may differ depending on stage of development. Therefore, extrapolation of experimental responses from seedlings to mature plants must be taken with caution (Björn, 1996). The above facts are especially important when considering the effects of UV-B on agricultural plants. For example, among soybeans and rice, there are varieties for which growth and crop yield are severely decreased by increased UV-B radiation and other varieties that are not affected or may even be stimulated. On the other hand, the growth of the same sensitive soybeans when grown under water stress was not inhibited. Many crop plants grown in temperate regions originated in more tropical areas, hence, a gene pool for more resistant varieties is likely to exist (Björn, 1996). Crop plants, unlike forest trees and vegetation in natural ecosystems, are only exposed for one generation, and thus, it may be possible to readily change the genotype if a variety proves to be sensitive.

Trees, forests, and perennial evergreen plants are long-lived when compared to agricultural systems, making it possible for UV-B exposure impacts to accumulate with time. Saplings and young and small trees react differently when compared to mature trees; also, on evergreen trees, needles of different ages respond differently (Björn, 1996). Breeding and testing trees is a slow process, and, for this reason, much care needs to be taken when planting large areas with trees of a single species and one provenance (e.g., Stika Spruce [*Picea sitchensis*] in Britain). The response of only a few broad-leaved trees have been studied. The most investigated genus has been loblolly pine (*Pinus taeda*) (Björn, 1996).

A few studies indicate that the photomorphogenesis (changes in leaf thickness under UV-B that results in a transition from shade to sun leaves, Table 4-4) and the variable responses of native plants in ecosystems to UV-B exposures results in changes in interactions between various plants species, changes between plants and other organisms, and between plants and their abiotic environment. These preliminary studies suggest that in natural ecosystems, composed of many different plant species, with complex interactions between plants and between plants and other organisms, there may develop effects of UV-B that cannot be determined from experiments on single plant species. The effects of UV-B on natural plant systems, therefore, should be of greater concern than on agricultural crops (Björn, 1996).

Nitrogen Deposition Effects

Nitrogen has long been recognized as the nutrient most important for plant growth. Plants usually absorb nitrogen through their roots by absorbing $NH_4^{\ +}$ or $NO_3^{\ -}$ or informed by symbiotic organisms in the roots. Plants, however, vary in their ability to absorb ammonium and nitrate (Chapin et al., 1987). Nitrogen 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).

Because nitrogen is not readily available and is usually in shortest supply, it is the chief element in agricultural fertilizers. Atmospherically deposited nitrogen also can act as a fertilizer in soil low in nitrogen. Not all plants, however, are capable of utilizing extra nitrogen. Inputs of nitrogen to natural ecosystems that alleviate deficiencies and increase growth of some plants can impact competitive relationships and alter species composition and diversity (Ellenberg, 1987; Kenk and Fischer, 1988; U.S. Environmental Protection Agency, 1993).

The impact of increasing nitrogen inputs (e.g., NO_x, nitrates, nitric acid) on the nitrogen cycle and forests, wetlands, and aquatic ecosystems is discussed in detail elsewhere (U.S. Environmental Protection Agency, 1993, 1997a; Garner, 1994; World Health Organization, 1997). The most important effects of nitrogen deposition are accumulation of nitrogen compounds resulting in the enhanced availability of nitrate or ammonium, soil-mediated effects of acidification, and increased susceptibility to stress factors (Bobbink et al., 1998). A major concern is “nitrogen saturation”, the result of the deposition of large amounts of particulate nitrates. Nitrogen saturation results when additions to soil background nitrogen (nitrogen loading) exceed 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, ecosystems become unable to utilize excessive nitrogen inputs and disruptions of ecosystem functioning may result (Hornung and Langan, 1999).

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 America (Bytnerowicz and Fenn, 1996; Fenn et al., 1998). Not all forest ecosystems react in the same manner to nitrogen deposition. High-elevation alpine watersheds in the Colorado Front

Range and a deciduous forest in Ontario, Canada, also are naturally saturated even though nitrogen deposition has been moderate (≈8 kg.ha ha^{-1}.year^{-1}). 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 4-5; Fenn et al.,1998). 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 indicates that these forests have reached saturation.

Possible ecosystem responses to nitrate saturation, as postulated by Aber and coworkers (Aber et al., 1989), include a permanent increase in foliar nitrogen and reduced foliar phosphorus and lignin caused by the lower availability of carbon, phosphorus, and water; reduced productivity in conifer stands because of disruptions of physiological function; 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. 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 impact 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 4-2; Aber et al., 1989).

Subsequent studies have shown that, although initially, there was an increase in nitrogen mineralization (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. Also, studies suggest that, during saturation, soil microbial communities change from predominantly fungal (mycorrhizal) communities to those dominated by bacteria (Aber et al., 1998).

TABLE 4-5. 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 (M.E. Fenn and M.A. Poth). 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).

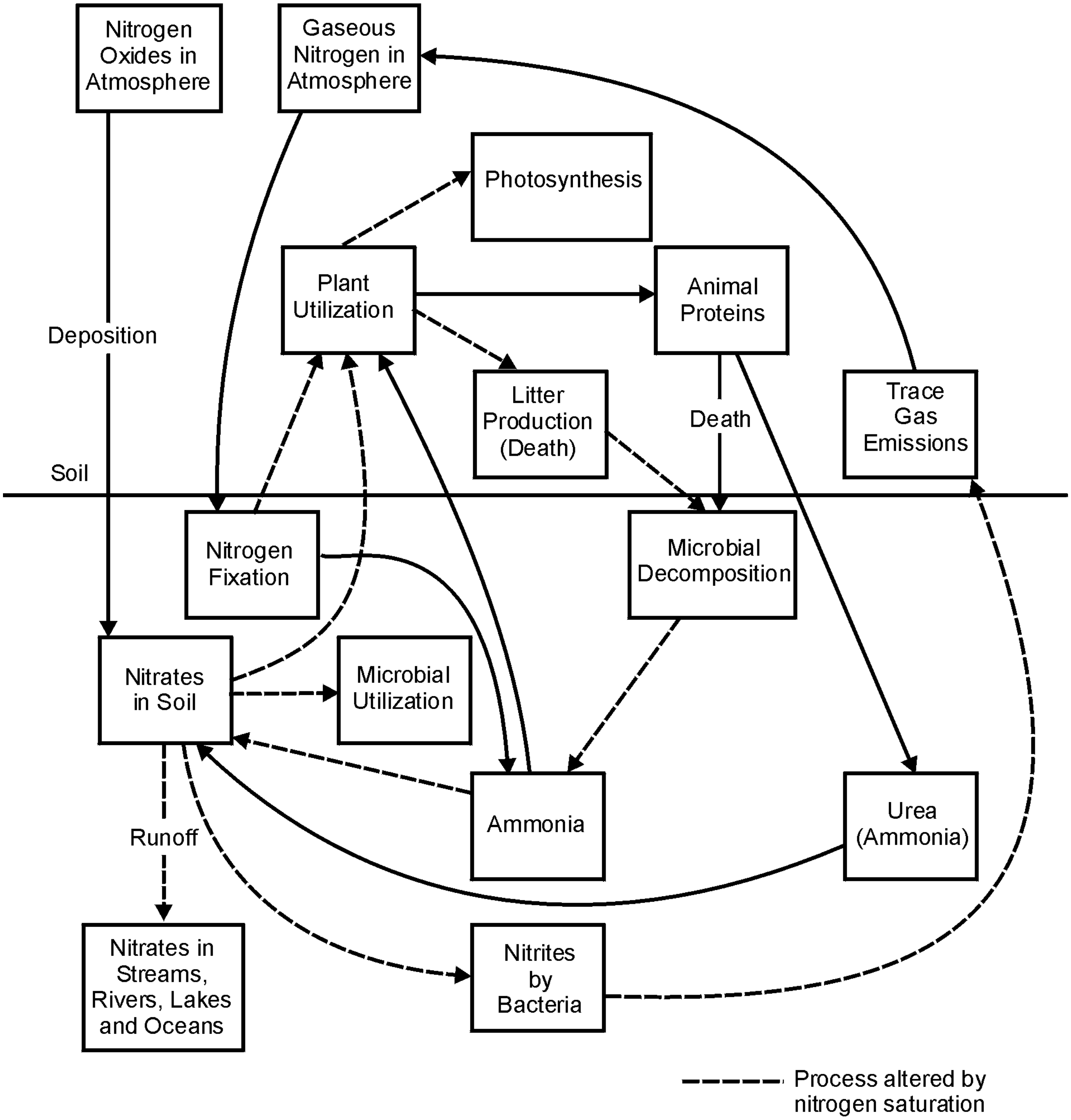


Figure 4-2. Nitrogen cycle (dotted lines indicate processes altered by nitrogen satuation).

Source: Garner (1994).

The availability of nutrients is an important factor in determining species composition, and nitrogen is usually the growth-limiting nutrient (Bobbink, 1998). Most of the plants growing in nutrient-poor habitats have become adapted to them over time and can only compete successfully on soils low in nitrogen (Bobbink, 1998; Chapin, 1991). All plants growing in low resource environments (e.g., infertile soil, shaded understory, deserts, tundra) have been observed to have certain similar characteristics: a slow growth rate, low photosynthetic rate, and low capacity for nutrient uptake. An important feature to plants adapted to low-resource environments is that they grow slowly and tend to respond less, even 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 to nitrogen increases; however, other nutrients may soon be limiting. The capacity of gymnosperms in general, and in subalpine and boreal species in particular, 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).

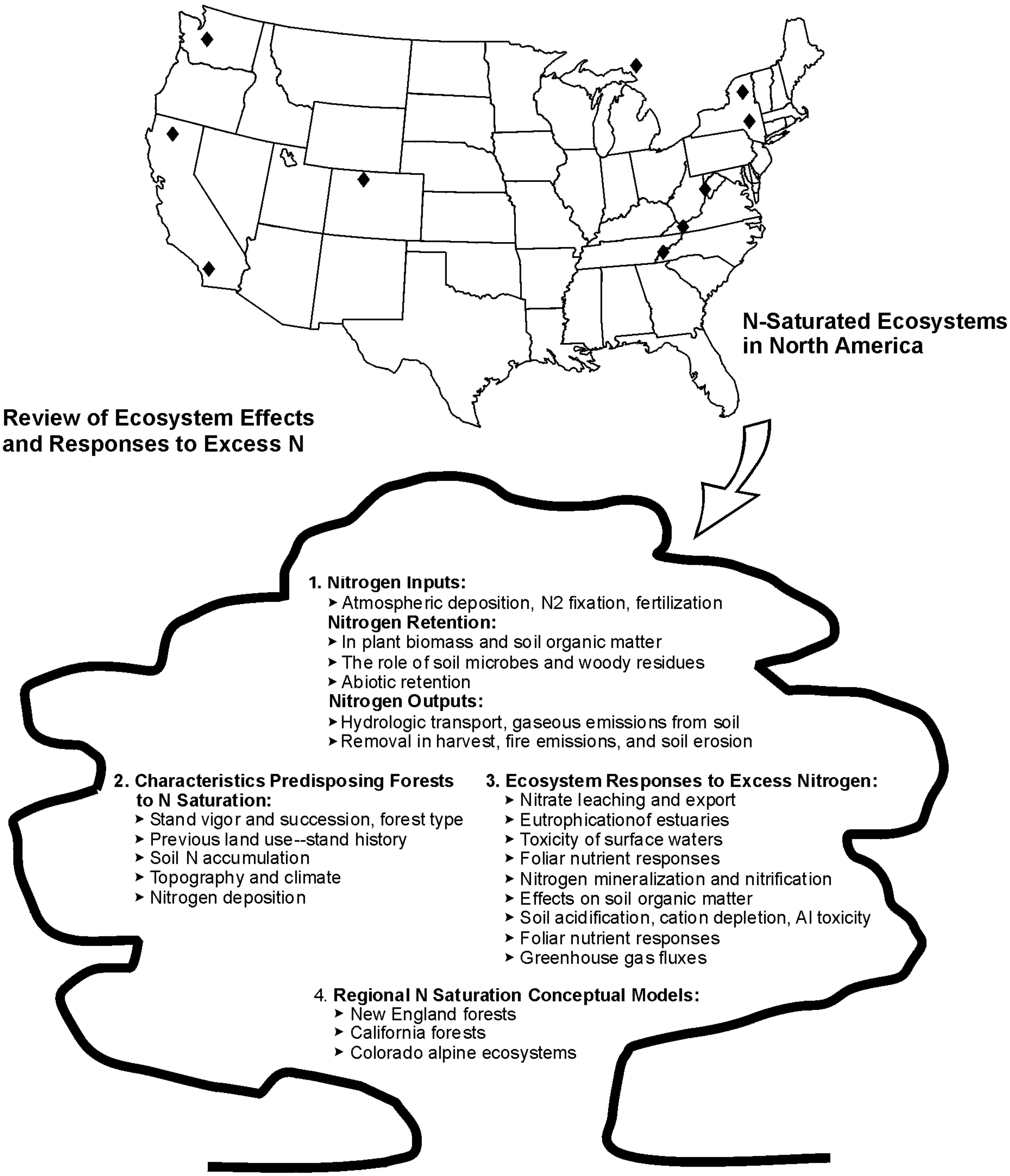
Because the competitive equilibrium of plants in any community is finely balanced, the alteration of one of a number of environmental parameters, (e.g., continued nitrogen additions), can change the vegetation structure of an ecosystem (Bobbink, 1998; Skeffington and Wilson, 1988). Increases in soil 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.

The long-term impacts of increased nitrogen deposition have been studied in several western and central European plant communities: 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 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). Falkengren-Grerup (1998), in an experimental study involving 15 herbs and 13 grasses, 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. Also, Schulze (1989), Heinsdorf (1993), and Lamersdorf and Meyer (1993) attribute magnesium deficiencies in German forests, in part, to excessive nitrogen deposition.

Plant succession patterns and biodiversity are affected significantly by chronic nitrogen additions in some North American ecosystems (Figure 4-3). Fenn et al. (1998) report 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, Vermont, 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).

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



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 4-3. Diagrammatic overview of excess nitrogen (N) in North America.

Source: Fenn et al. (1998).

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 loss of biodiversity, in addition to loss of genetic resources, loss of productivity, loss of ecosystem buffering against ecological perturbation, and loss of aesthetic and commercially valuable resources, also may alter or impair ecosystems services.

The C:N ratio of the forest floor can be changed by nitrogen deposition over time. This change appears to occur when the ecosystem becomes nitration 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 the 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 10kg 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. 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 a limiting nutrient 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 heath lands by oaks (*Quercus robur*). Soils are dynamic entities, the features of which can change like the rest of the ecosystem with age and management. The soil-forming factors under the heath have been vegetation type during the last 2000 years, whereas the invasion by oaks has been taking place for only a few decades. Clear 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).

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 have notable impacts on aquatic ecosystems as well. One illustrative example is recently reported research (summarized by Paerl et al., in press) characterizing impacts 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, and altered fish distributions, catches, and physiological states and 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).

Sulfur Deposition Effects

Sulfur is an essential plant nutrient and, as such, is a major component of plant proteins. 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 indicates that neither element can be assessed adequately without reference to the other. There is a regulatory coupling of sulfur and nitrogen metabolism. 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 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 (1988). 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 impacts 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, 1998a,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 gas pollution (SO_2), hydrogen sulfide (H_2S), and fugitive sulfur aerosol for more than 20 years. Observations under the microscope showed no sulfur deposits on the needle surfaces and led to the conclusion that the sulfur was derived from the soil. The oxidation of elemental sulfur and the generation of protons is well known for the soils of Alberta, CN. 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

Substantial and previously unsuspected changes in soils are occurring both in polluted areas of eastern North America, the United Kingdom, Sweden, and Central Europe and in less polluted regions of Australia and western North America (reviewed by Johnson et al., 1991b; see review by Huntington, 2000). In some cases, trends are toward more acidic soils (e.g., Markewitz et al., 1998), and, in others, there are 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 have occurred at many sites in the eastern United States during recent decades. Temporal trends in tree ring chemistry were examined as indicators of historical changes in the chemical environmental of red spruce. Chemical changes in tree-ring chemistry reflect changing inputs of regional pollutants to forests. If significant base cation mobilization and depletion of base cations from eastern forest soils has occurred, a temporal sequence of changes in uptake patterns and possibly in tree growth would be expected. Patterns of tree-ring chemistry principally at high-elevation sites in the eastern United States, leads to the conclusion that significant changes in soil chemistry have occurred in many of these sites during recent decades leading to changes in growth (Bondietti and McLaughlin, 1992). These changes are spatially and temporally consistent with emissions of SO_2 and NO_2 across the region, suggesting that increased acidification of forest soils has occurred.

Increases in levels of Al and Fe typically occur as base cations are removed from soils by tree uptake. A region-wide Ca increase above expected levels followed by a decrease suggests that increased mobilization began perhaps 30 to 40 years ago (Bondietti and McLaughlin, 1992). The period of Ca mobilization coincides with a region-wide increase in growth rate of red spruce, whereas the period of decreasing levels of Ca 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 Ca suggests that Ca loss may have been increased to the point at which base saturation of soils has been reduced (Bondietti and McLaughlin, 1992).

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 have not (Garner et al., 1989). Shortle and Bondietti (1992) present evidence that, from the late 1940s into the 1960s, the mor humus 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 impact 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 nutrient, 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: (1) acidification of the soil and the loss of cations K^+, Ca^{2+}, and Mg^{2+}; and (2) 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) 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 stream-water data, that large amounts of Ca and Mg 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 Ca and Mg concentrations in forest floors at Hubbard Brook over the period 1976 to 1997. They also found both gains and losses in forest floor Ca and Mg 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."

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 4-4 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, where either NH_4^+ or NO_3^- can be taken up. In that, nitrogen is a nutrient taken up in great quantities, the uncertainty in the ionic form of nitrogen taken up 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 Ca, K, and Mg 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 then available for either plant uptake or leaching (Figure 4-4). The introduction of H^+ by

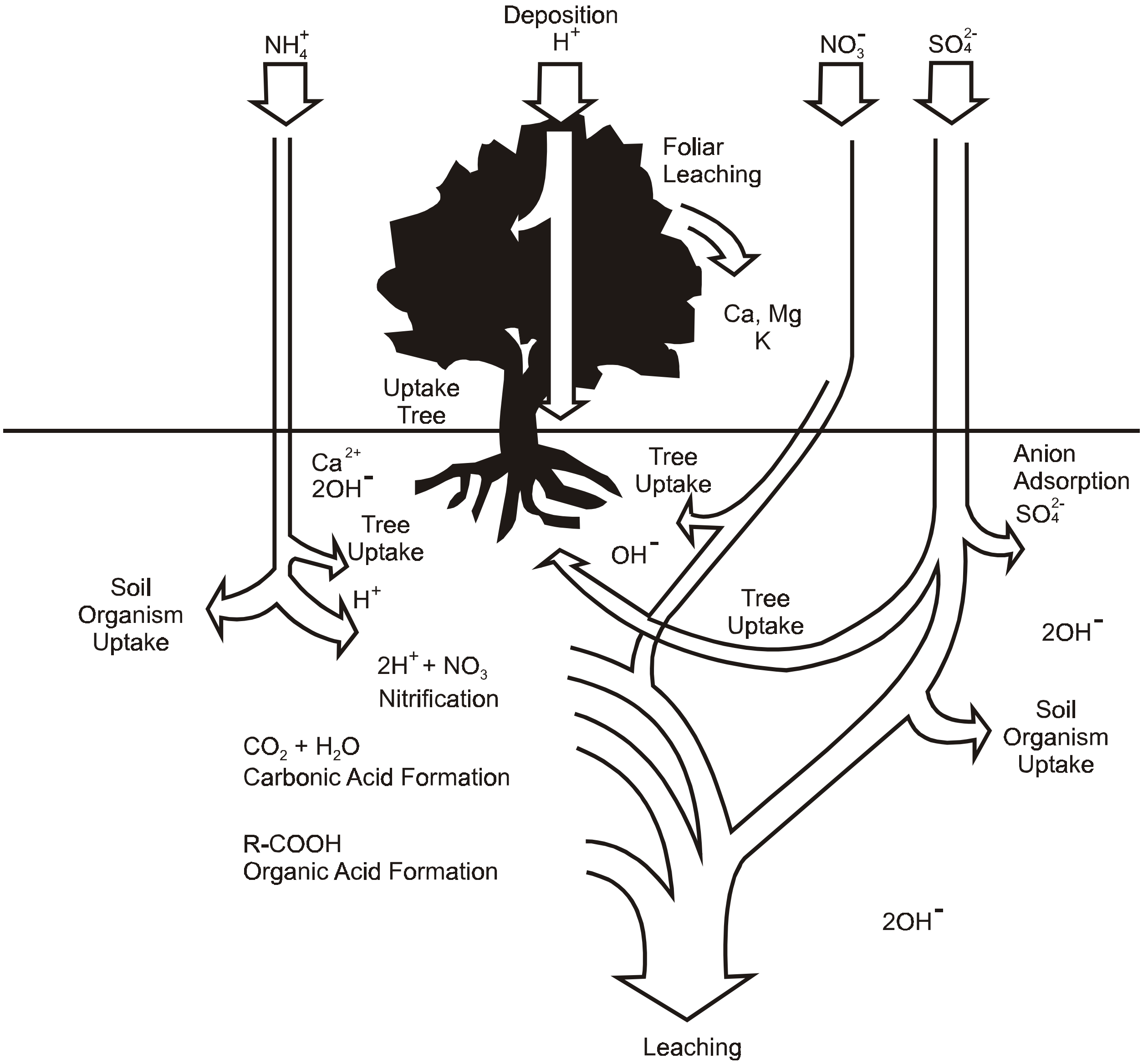


Figure 4-4. Schematic of sources and sinks of hydrogen ions in a forest (from Taylor et al., 1994).

atmospheric deposition or by internal processes will impact directly 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, 1992a).

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, 1983). Changes in intensity factors can have a rapid impact 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 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 impact 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 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 result 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).

A major concern has been that soil acidity would lead to nutrient deficiency. Calcium is essential in the formation of wood and the maintenance of cells, the primary plant tissues necessary for tree growth. Trees obtain Ca from the soil, but to be taken up by roots, the Ca (a positively charged ion) must be dissolved in soil water (Lawrence and Huntington, 1999). Tree species may be adversely affected if high Al to nutrient ratios limit uptake of Ca and Mg and create a nutrient deficiency (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. When in solution, aluminum can be taken up by roots, transported through the tree and, eventually, deposited on the forest floor in leaves and branches. Aluminum is more readily taken up than is Ca because it has a higher affinity for negatively charged surfaces than does Ca. When present in the forest floor, Al tends to displace adsorbed Ca and causes it to be more readily leached. The continued buildup of Al in the forest floor layer, where nutrient uptake is greatest, can decrease the availability of Ca to the roots (Lawrence et al., 1995) and lower the efficiency of Ca uptake because Al is more readily taken up than is Ca $^{2+}$ when the ratio of Ca to Al in soil water is less than one (Lawrence and Huntington, 1999). A 1968 Swedish report to the United Nations postulated a decrease in forest growth of ca. 1.5%/year as result of Ca $^{2+}$ loss by leaching (Johnson and Taylor, 1989). The concern that soil acidification and nutrient deficiency may result in forest decline remains extant today.

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).

Aluminum toxicity may influence forest tree growth, where acid deposition and natural acidifying processes increase soil acidity. Aluminum concentrations have been observed to exhibit a strongly descending gradient from bulk soil through the rhizosphere to the root (Smith, 1990a). Once it enters the forest tree roots, Al accumulates in root tissue (Thornton et al., 1987; Vogt et al., 1987a,b). There is abundant evidence that Al is toxic to plants. Reductions of Ca uptake by roots has been associated with increases in Al uptake (Clarkson and Sanderson, 1971). Calcium plays a major role in cell membrane integrity and cell wall structure. A number of studies have suggested 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 Ca^{2+} requirement relative to agricultural 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 the fine root environment. Aluminum in the soil solution reduces Ca uptake by competing for binding sites in the cortex of fine roots. Reduction in Ca uptake suppresses cambial growth and reduces the rate of wood formation (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 than 25% of cross-sectional stem area (Smith, 1990a).

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 acid soils, as evidenced by their presence in unpolluted, even pristine forests of the northwestern United States and Alaska (Johnson et al., 1991b). The soil becomes 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 impact on the distribution and cycling of base cations (Turner and Kelly, 1981). The presence of C. *apetalum* as a secondary tree layer beneath brush cox (*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) and Hedin et al. (1994) are especially relevant. Driscoll et al. (1989) 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, in 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 Integrated Forest Studies (IFS) supports the authors' contention that atmospheric base cation inputs may seriously affect ecosystem processes. Johnson et al. (1994a) 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 (Johnson et al., 1994b). Further, the authors suggest 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 exacerbated by sulfate leaching (U.S. Environmental Protection Agency, 1999).

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 adverse impact of acidic deposition on tree growth or nutrition:

- forests have a 50% risk of adverse impacts 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 impacts 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

(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

In Europe, the critical load concept generally has been accepted as the basis for abatement strategies to reduce or prevent injury to the functioning and vitality of forest ecosystems caused by long-range transboundary 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). A biological indicator, a chemical criterion, and a critical value are the elements used in the critical load concept. 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, which 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. 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). The physiology of carbon allocation has also been suggested as an indicator of anthropogenic stress (Andersen and Rygiewicz, 1991). 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).

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 the effects of deposition 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 the total particulate deposition, the vast majority (>90%) is >2 μm.

Figures 4-5 through 4-8 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), some sites show net annual gains of base cations (i.e., total deposition > leaching), some show losses (total deposition < leaching), and some are approximately in balance. Not all cations follow the same pattern at each site. For example, calcium shows net accumulation at the Coweeta, TN; Durham (Duke), NC; and Florida sites (Figure 4-5), potassium shows accumulation at the Duke; Florida; Douglas-fir; red alder; Thompson, WA; Huntington Forest, NY; and Whiteface Mountain, NY, sites (Figure 4-7), and magnesium accumulated only at the Florida sites (Figure 4-6). Only at the Florida site is there a clear net accumulation of total base cations (Figure 4-8).

The factors affecting net calcium accumulation or loss include the soil-exchangeable cation composition, as noted previously; 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 (an Ultic Haploquod 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

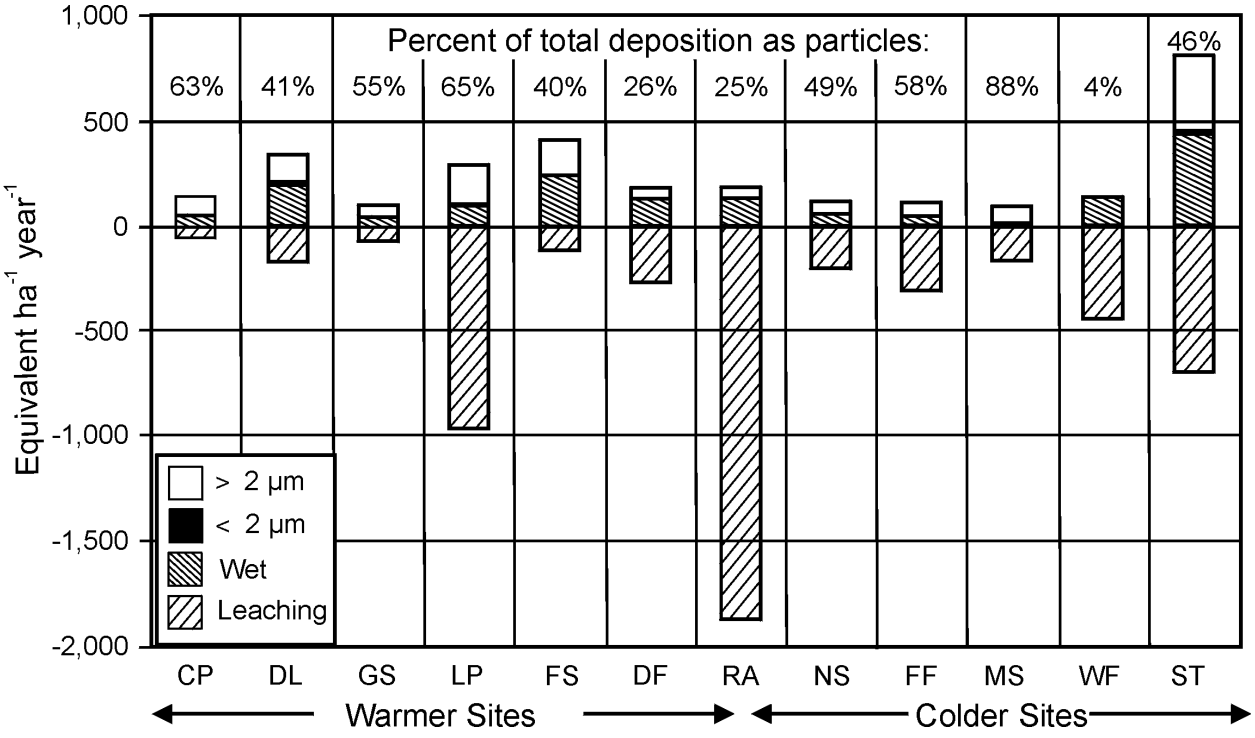


Figure 4-5. Calcium deposition in >2-μm particles, <2-μm particles, and wet forms (upper bars) and leaching (lower bars) in the Integrated Forest Study sites. CP = *Pinus strobus,* Coweeta, TN; DL = *Pinus taeda,* Durham (Duke), NC; GS = *Pinus taeda*, B. F. Grant Forest, GA; LP = *Pinus taeda*, Oak 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.

(Figure 4-9), 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 4-5 and 4-8).

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 4-5). The proportion of potassium deposition as particles ranges from 7% at the Smokies site to 77% at the Coweeta site (Figure 4-7), and the proportion of total base

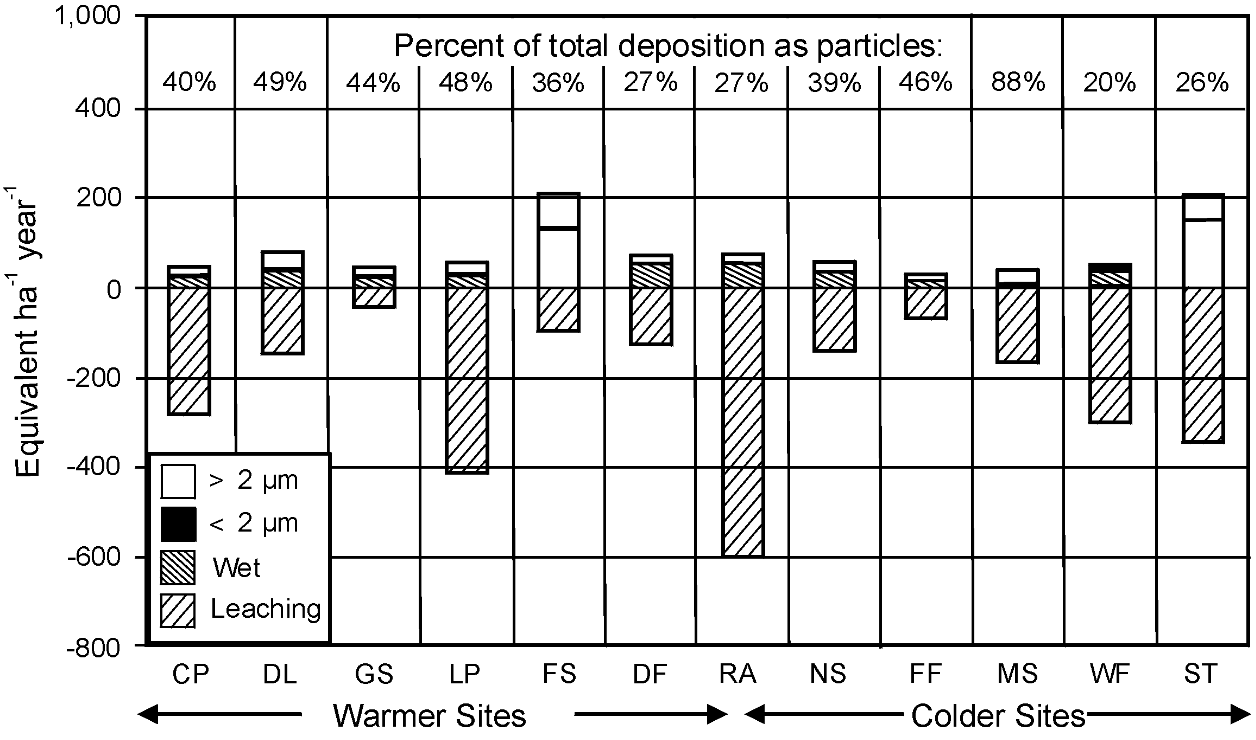


Figure 4-6. Magnesium deposition in >2-µm particles, <2-µm particles, and wet forms (upper bars) and leaching (lower bars) in the Integrated Forest Study sites. See Figure 4-5 for legend.

cation deposition ranges from 16% at the Whiteface site to 62% at the Maine site (Figure 4-8). 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 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 observed 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

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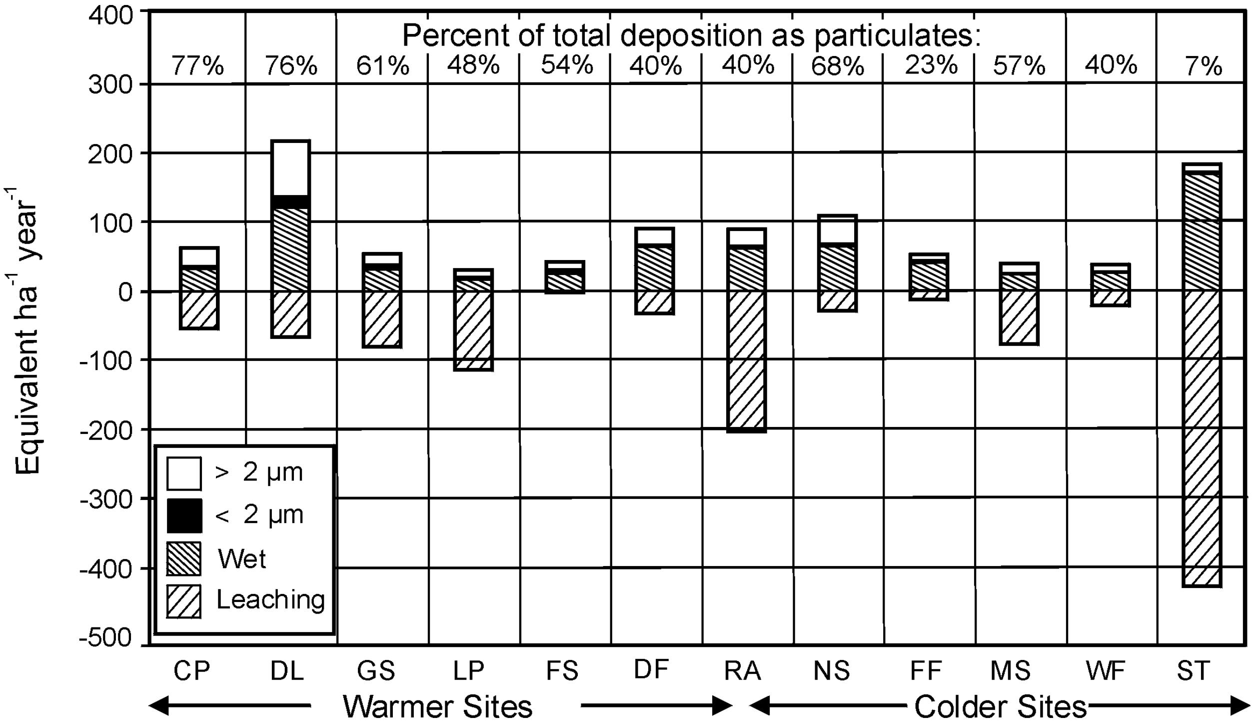

Figure 4-7. Potassium deposition in >2-μm particles, <2-μm particles, and wet forms (upper bars) and leaching (lower bars) in the Integrated Forest Study sites. See Figure 4-5 for legend.

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 4-9 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 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%) 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.

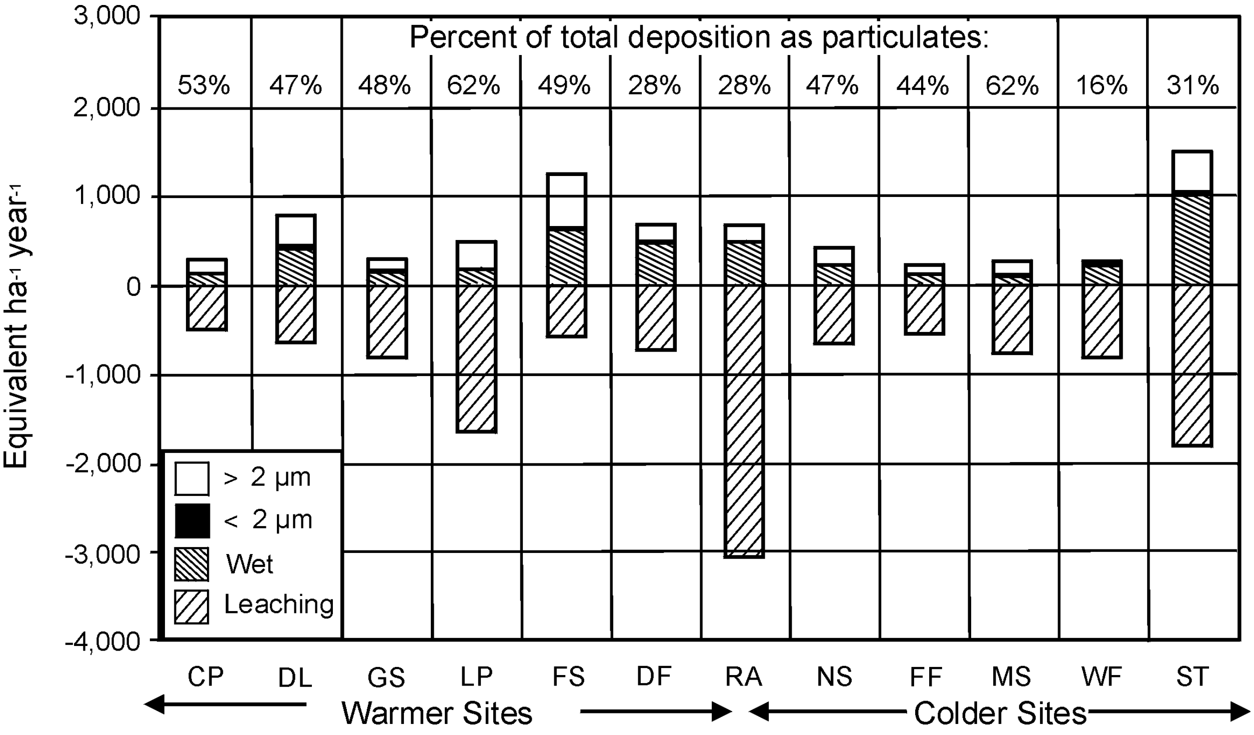

Figure 4-8. Base cation deposition in >2-*μ*m particles, <2-*μ*m particles, and wet forms (upper bars) and leaching (lower bars) in the Integrated Forest Study sites. See Figure 4-5 for legend.

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 is the case 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-*μ*m fraction was neglected.)

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 *μ*m, but only a very small fraction is <2 *μ*m. 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

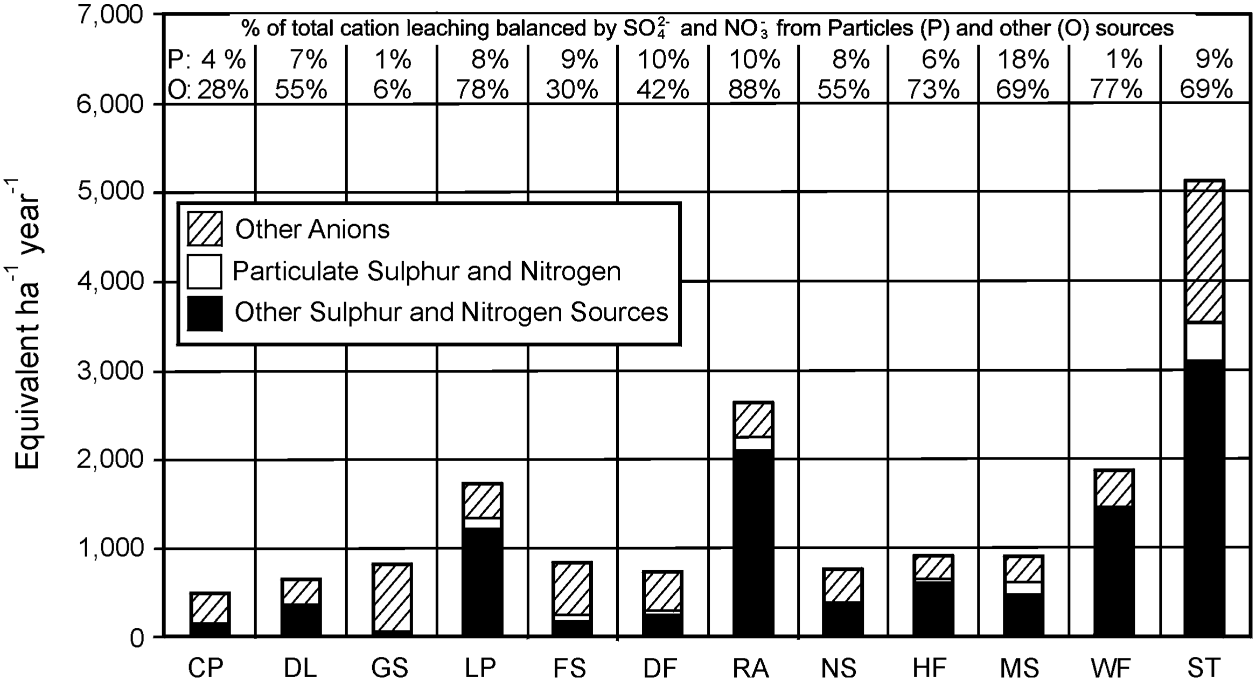

Figure 4-9. Total cation leaching (total height of bar) balanced by sulfate and nitrate estimated from particulate deposition (assuming no ecosystem retention, particulate sulfur and nitrogen) and by other sources (both deposition and internal) of sulfate and nitrate (other sulfur and nitrogen sources) and by other anions in the Integrated Forest Study sites. See Figure 4-5 for legend.

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 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 4-10 to 4-12. It readily is seen that net leaching losses of cations pose no threat in terms of depleting soil-exchangeable Ca^{2+}, K^+, or magnesium ion within 25 years at the Coweeta, Duke, Georgia,

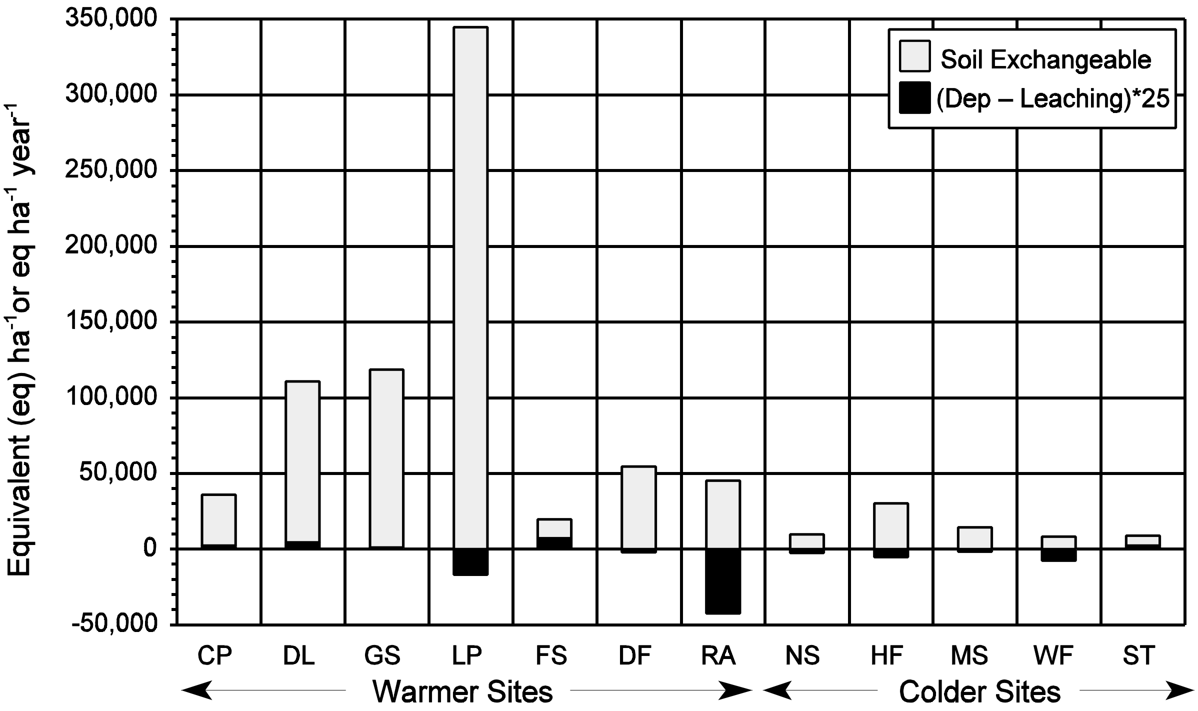

Figure 4-10. Soil exchangeable Ca^{2+} pools and net annual export of Ca^{2+} (deposition minus leaching times 25 years) in the Integrated Forest Study sites. See Figure 4-5 for legend.

Oak Ridge, or Douglas-fir sites. There, however, 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 Mountain, Smokies, and Maine red spruce sites; the Thompson red alder site; and the Huntington Forest northern hardwood site appear to be most 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

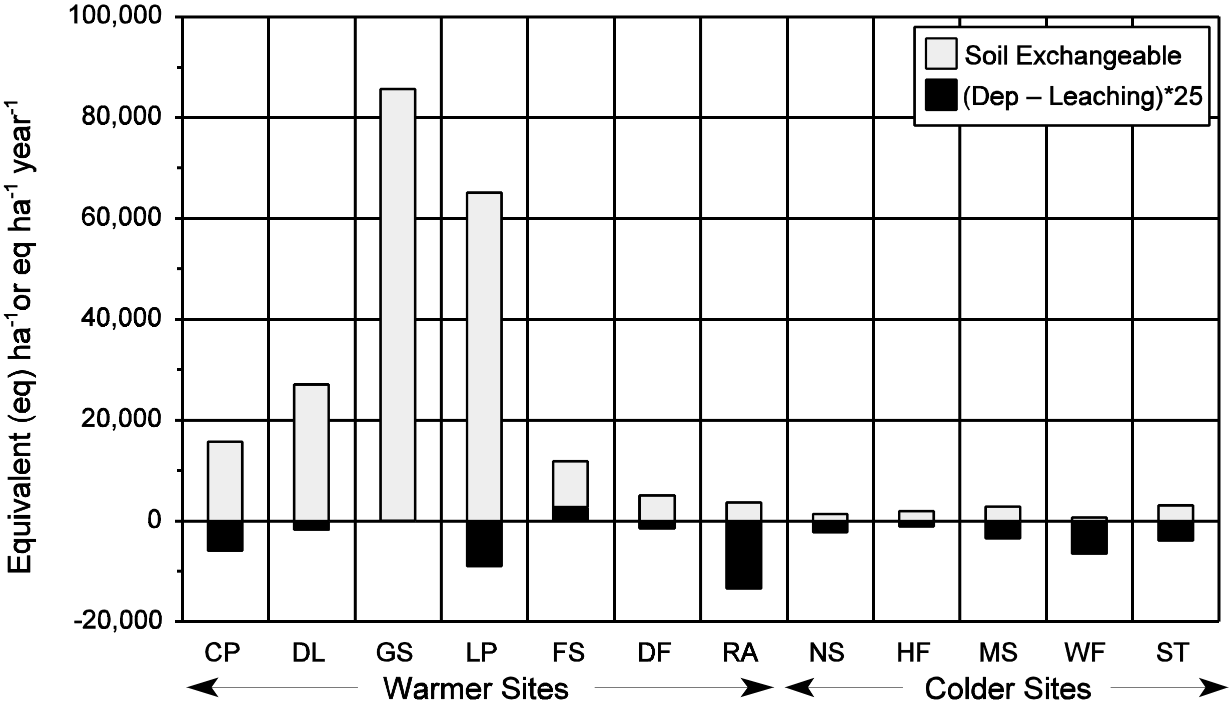

Figure 4-11. Soil exchangeable Mg^{2+} pools and net annual export of Mg^{2+} (deposition minus leaching times 25 years) in the Integrated Forest Study sites. See Figure 4-5 for legend.

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 would appear 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

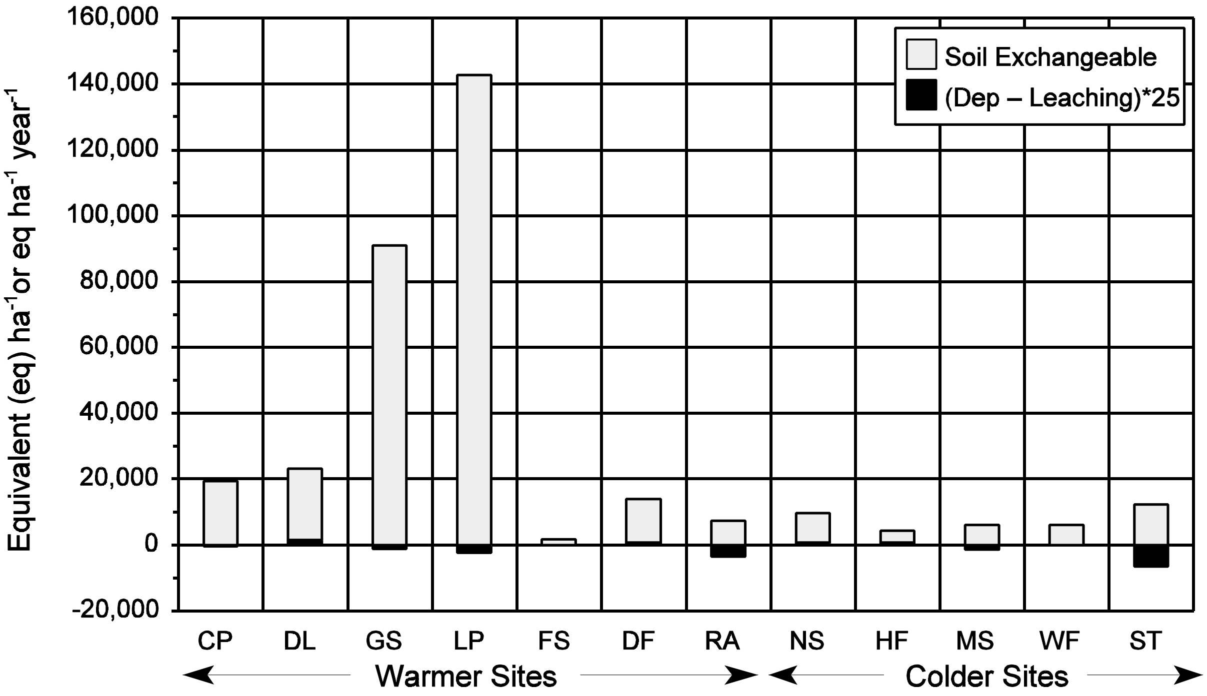

Figure 4-12. Soil exchangeable K^{2+} pools and net annual export of K^{2+} (deposition minus leaching times 25 years) in the Integrated Forest Study sites. See Figure 4-5 for legend.

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, and soil solution sulfate and base cation leaching decline accordingly, but base saturation continues to decrease. During Stage III, two alternative scenarios are introduced: (1) sulfur deposition continues to decline, whereas base cation deposition says constant; or (2) both sulfur and base cation deposition decline. Under Stage III-1, 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-2, this recovery in base saturation is over-ridden by the reduction in base cation deposition.

The IFS project, for the first time, accurately quantifies 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 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 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, soil solution levels there are lower than in the Smokies, which are in a visibly obvious state of decline (e.g., no dieback other than the fir killed by the balsam wooly adelgid, no needle yellowing, etc). 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: (1) the red spruce and (2) 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 4-13 and 4-14, which shows 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 in soil solution SO_4^{2-}, NO_3^- and, therefore, MAA concentrations, as expected, and 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 14). 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 acid Coweeta soil, base saturation was high and little affected by scenario (not shown), Al was unimportant, and S and N deposition had a much greater effect than C_B deposition in all respects (Figure 15).

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

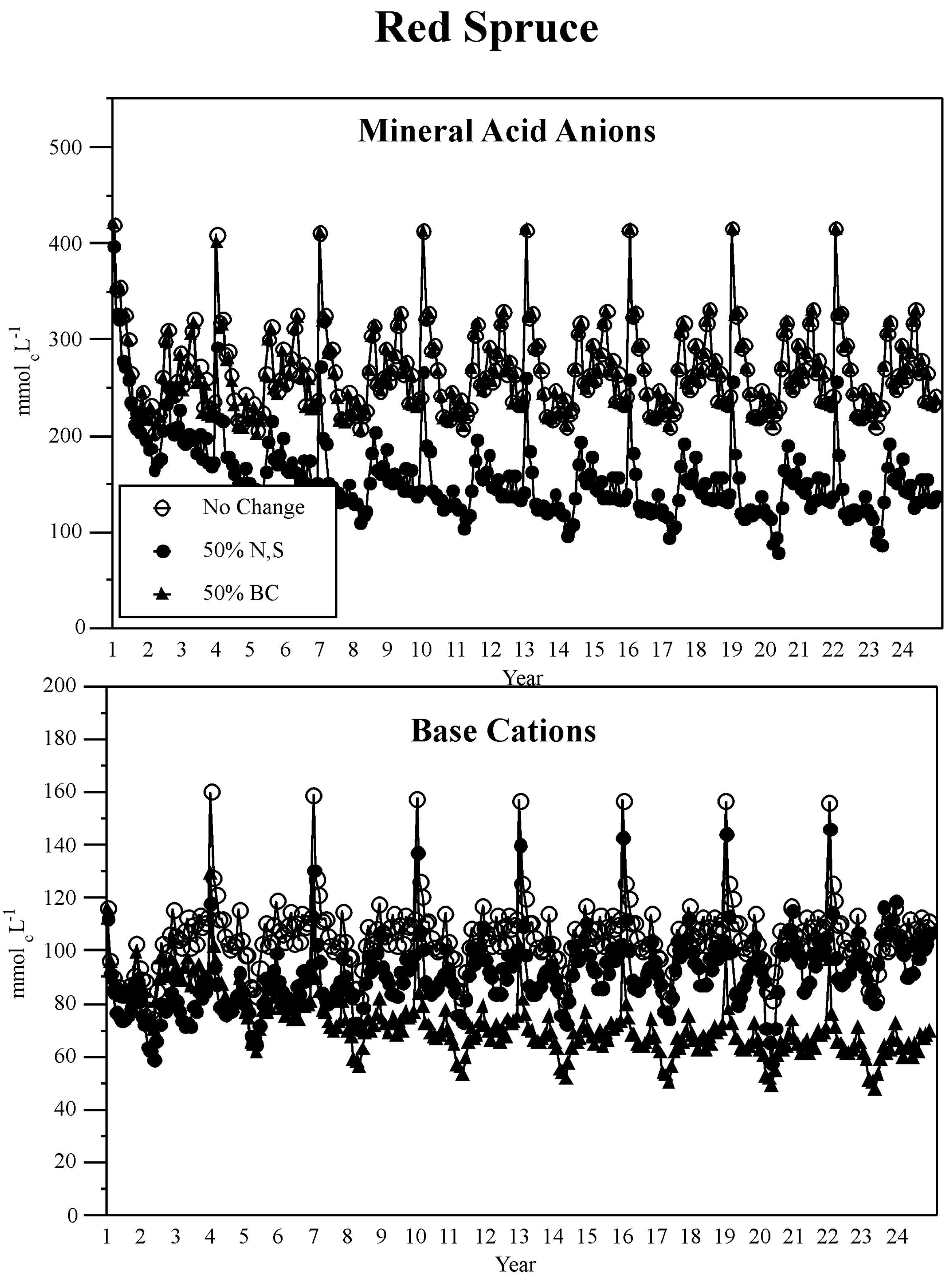

Figure 4-13. Simulated soil solution mineral acid anions and base cations in the red spruce site with no change, 50% N and S deposition, and 50% base cation deposition. Redrawn from Johnson et al. (1999).

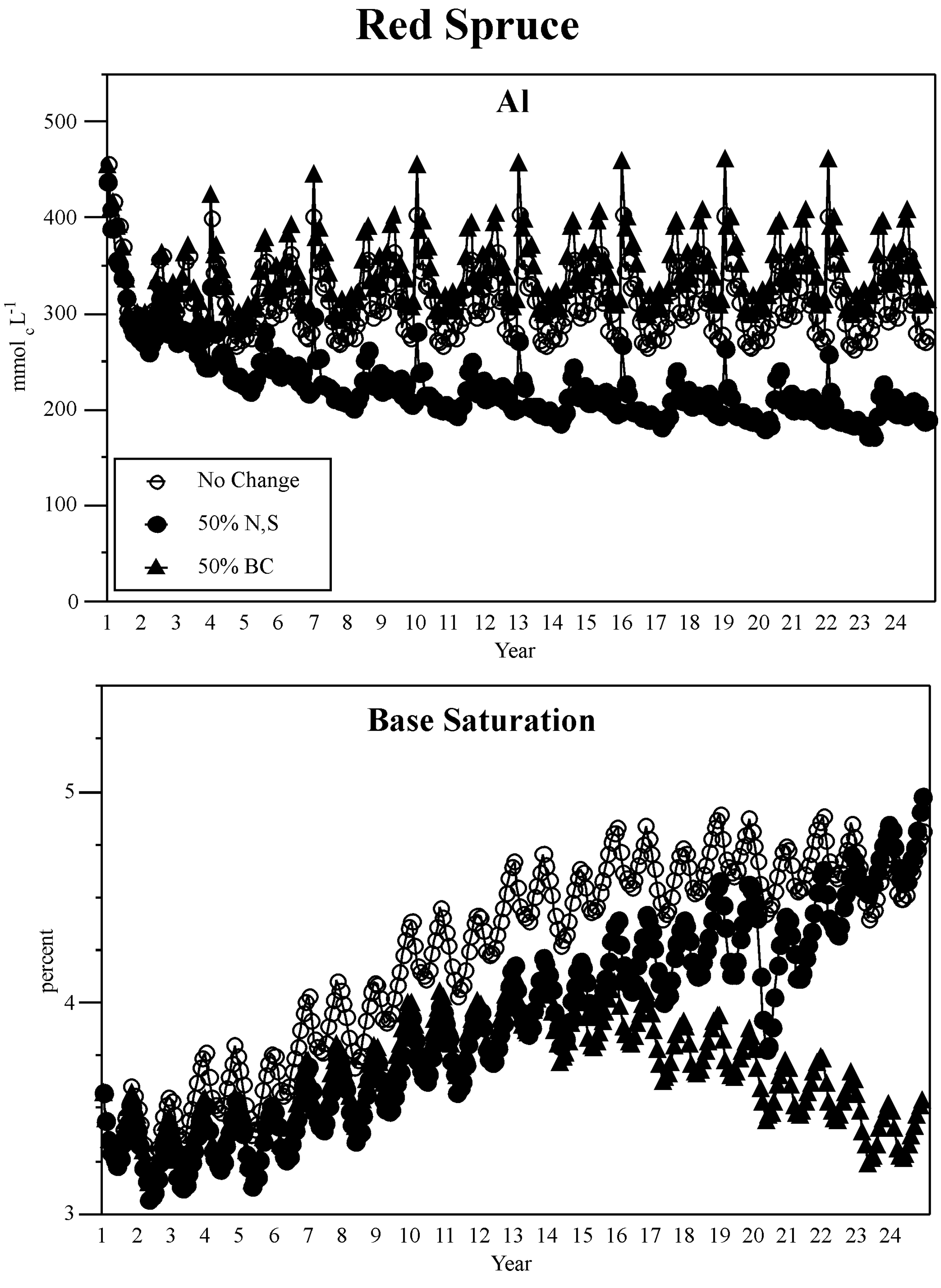

Figure 4-14. **Simulated soil solution A1 and soil base saturation in the red spruce site with no change, 50% N and S deposition, and 50% base cation deposition. Redrawn from Johnson et al. (1999).**

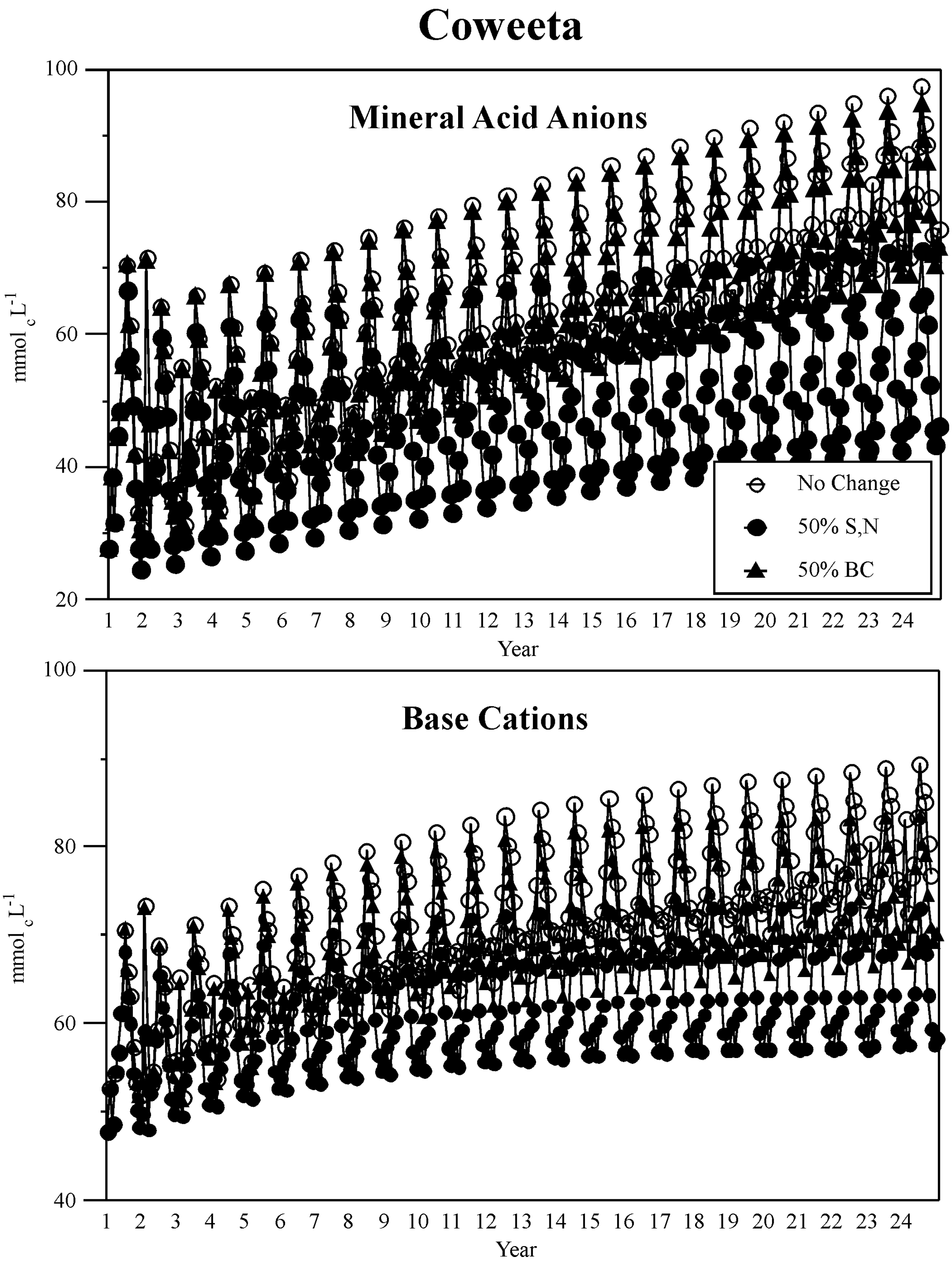

Figure 4-15. Simulated soil solution mineral acid anions and base cations in the Coweeta site with no change, 50% N and S deposition, and 50% base cation deposition. Redrawn from Johnson et al. (1999).

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.

Trace Element Effects

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 via the soil or as 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, 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 for being toxic to roots and soil organisms and interfering with nutrient cycling (Smith, 1990e). 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, 1990e). Exposures at lower concentrations have the potential, over the long-term, for interfering with the nutrient-cycling processes when they affect mycorrhizal function.

Accumulation of heavy metals in litter presents the greatest potential for interference with nutrient cycling. 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 the result of effects on the microorganismal populations. Cadmium toxicity to microbial populations was observed to decrease and prolong logarithmic rates of microbial increase, to reduce microbial respiration and fungal spore formation and germination, to inhibit bacterial transformation, and to induce abnormal morphologies. Also, 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 (1990b).

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 4-16. 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).

Trace metals deposited from the atmosphere to forests accumulate either in the richly organic forest floor or in the soil layers immediately below, layers where greatest biological activity occurs. The shallow-rooted species plant species are those most likely to take up metals from the soil (Martin and Coughtrey, 1981).

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 bioindicators of metals (e.g., Astragalius 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 the garden and comparing the results with the same plant species growing in two other 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).

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

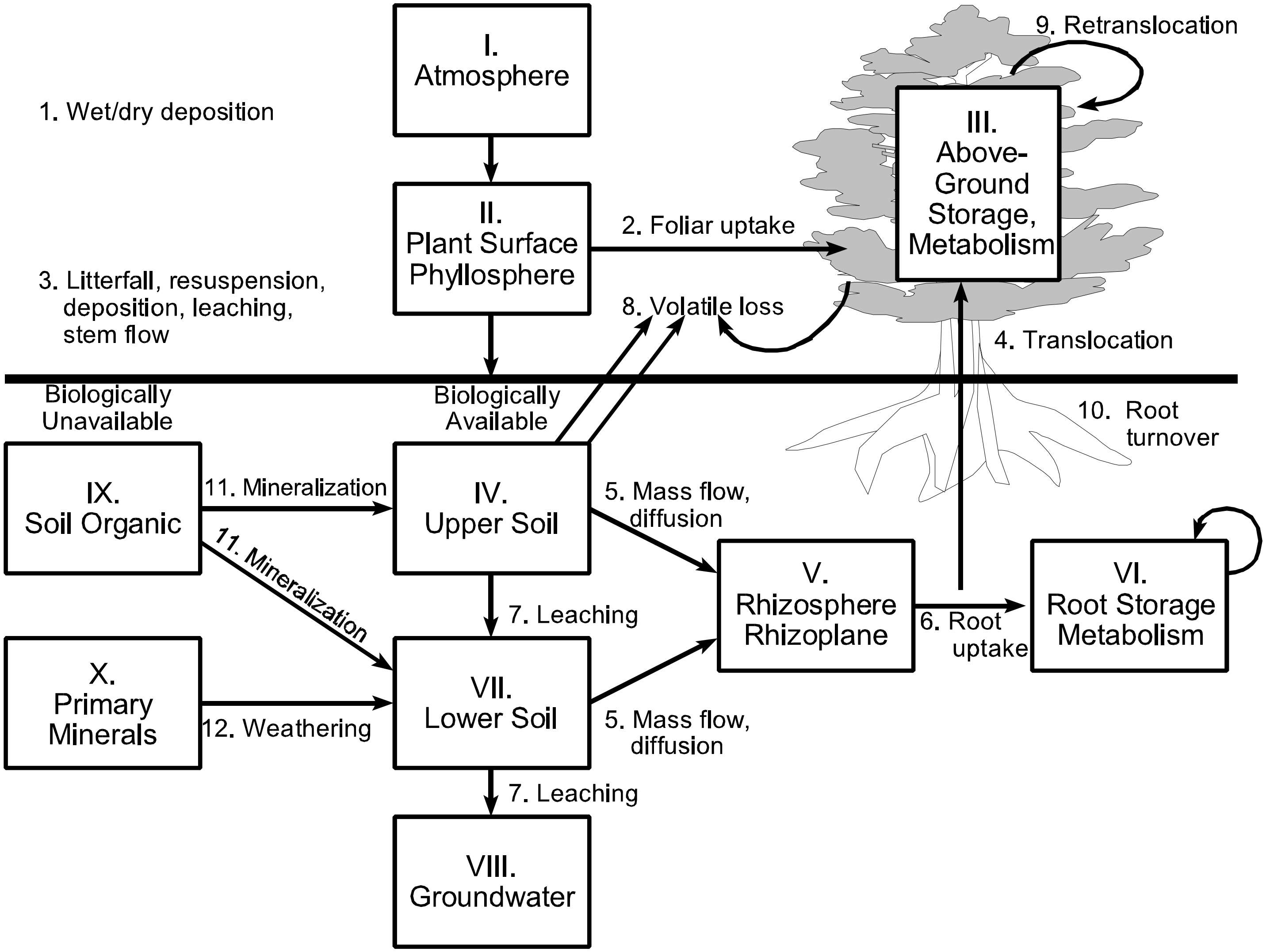

Figure 4-16. Relationship of plant nutrients and trace metals with vegetation. Compartments (roman numerals) represent potential storage sites, whereas arrows (arabic numerals) represent potential transfer routes.

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).

The effects of lead in ecosystems are discussed in the *Air Quality Criteria for Lead* (U.S. Environmental Protection Agency, 1986b). Studies have shown that there is cause for concern in three areas where 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 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, 1986b).

4.2.3 Ecosystem Goods and Services and Their Economic Valuation

Human existence on this planet depends on ecosystems and the services and products they provide. The essential services and products provided by the planet’s collective biodiversity (the earth’s flora, fauna, and microorganisms) are clean air, clean water, clean soil, and clean energy (Table 4-6). Today, governments around the world pursue a “bottom line” that driven is by an

TABLE 4-6. 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).

economy that is disconnected from the natural world and is fundamentally destructive of local ecosystems (Suzuki, 1997). For this reason, human society needs to be reconnected to the biologically diverse ecosystems and the natural world of which they are a part (Suzuki, 1997). There is a need to understand the biodiversity that encompasses all levels of biological organization, including populations, individuals, species and ecosystems (Wilson, 1997). Populations, geographical entities within a species of organisms, usually distinguished ecologically or genetically, are essential to the conservation of species diversity. Their number and size influence the probability of the future existence of the entire species (Hughes et al., 1997). The number, biodiversity, structure, and functions of ecosystem populations, provide ecosystem products (goods) and services. For any given population, the number of individuals, the genetic variation between individuals, and the area occupied affects ecosystem functioning and the delivery of ecosystem services and other benefits provided by that population (Hughes, et al., 1997). Loss of population diversity means loss of the benefits described in Table 4-6 and, in particular, with time, the loss of the life-support systems on which humanity relies (Hughes et al., 1997).

Attempts have been made to value biodiversity and the world's ecosystem services and natural capital (Pimentel et al., 1997; Costanza et al., 1997). Pimentel et al. (1997) estimated economic and environmental benefits for services contributed from all biota (biodiversity) in the United States, including their genes, at $319 billion per year. Costanza et al. (1997) have estimated the total value of ecosystem services by biome for the entire bioshere. Ecosystems provide at least $33 trillion worth of services annually. Approximately, 63% of the estimated value is contributed by marine ecosystems ($20.9 trillion per year), most of which comes from coastal ecosystems ($10.6 trillion per year). About 38% of the estimated value comes from terrestrial ecosystems, mainly from forests ($4.7 trillion per year) and wetlands ($4.9 trillion per year). Costanza et al. (1997) state that it may never be possible to make a precise estimate of the services provided by ecosystems. Their estimates, however, indicate the relative importance of ecosystem services.

Heal (2000), however, feels that attempts to value ecosystems and their services are probably 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) also deals with the need to understand human impacts 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).

The above assessment of new information leads to the clear conclusion that atmospheric PM at levels currently found in the United States has 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 4.2.1 above. The major impacts of airborne PM on ecosystems, however, are the indirect effects on plant populations that occur through the soil and affect the cycling of nutrients necessary for plant growth and vigor, as discussed in Section 4.2.2. By altering the cycling of nitrogen, nitrogen deposition changes the biodiversity of ecosystems and their functioning and, by altering the vigor of forest tree stands, alters forest succession. Also, nitrogen deposition in combination with the deposition of sulfur in the form of acid rain alters the biogeochemical cycling of soil mineral nutrients and changes the biodiversity and functioning of forest ecosystems. The changes in the ability of forest vegetation and soil microorganisms to utilize nutrients results in the leaching of nitrates and other minerals from the soils. The nitrate and mineral runoff impacts coastal and aquatic ecosystems and, thus, influences the services important to human life provided by these ecosystems as well (Table 4-6).

4.3 EFFECTS ON VISIBILITY

4.3.1 Introduction

Visibility is defined as the degree to which the atmosphere is transparent to visible light and the clarity (transparency) and color fidelity of the atmosphere (National Research Council, 1993). Visibility impairment is defined as any humanly perceptible change in visibility (light extinction, visual range, contrast, or coloration). Visual range is described as the farthest distance at which a large black object can be distinquished against the horizontal sky (U.S. Environmental Protection Agency, 1979). For regulatory purposes, visibility impairment is classified into two principal forms: (1) “reasonably attributable” impairment, attributable to a single source or small group of sources and (2) regional haze, described as any perceivable change in visibility (light extinction, visual range, contrast, or coloration) from which would have existed under natural conditions that is caused predominantly by a combination of many sources over a wide geographical area (U.S. Environmental Protection Agency, 1999).

The objective of the visibility discussion in this section is to summarize the linkage between air pollution, in particular particulate matter, and visibility. This section summarizes the information discussed in the previous 1996 PM air quality criteria document (PM AQCD) and includes additional relevant information available since publication of that document. For a more detailed discussion on visibility, the reader is referred to the earlier PM AQCD entitled, Air Quality Criteria for Particulate Matter (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), and the U.S. Environmental Protection Agency (1995a).

4.3.2 Factors Affecting Atmospheric Visibility

4.3.2.1 Anthropogenic Pollutants

Visibility impairment may be connected to air pollutant properties, including size distribution, aerosol chemical composition, and relative humidity. In the United States, visibility impairment is caused by sulfate and nitrate particles in the 0.1- to 1.0-micron (μm) range, and organic aerosols, carbon soot, and crustal dust. Generally, sulfates are responsible for most of the visibility impairment in the United States, as measured by light extinction, accounting for approximately two-thirds of the light extinction in the eastern United States. Sulfate concentrations are higher in summer months than in the wintertime (Malm et al., 1994). Exceptions to the sulfate-related effects on visibility include California, where the primary cause of visibility effects is ambient nitrate, and Alaska, where visibility impairment is caused by fine soil plus coarse mass (classified as coarse extinction) or organics, thought to be from natural sources (Sisler and Cahill, 1993).

4.3.2.2 Human Vision

Human vision is one of the factors that affects the way an object is viewed. Vision is the response to the electromagnetic radiation that enters the eye between wavelengths of 400 and 700 nm. The cones, a receptor cell in the retina, govern visibility interpretations.

The eye perceives the lightest and brightest object in a scene as white, and determines the color of other objects by comparison. The ability of the eye to perceive contrasts, the degree of color difference between the lightest and darkest object in a scene, changes in response to the illumination and setting. The effects of illumination on visibility are discussed in the following subsection. At increasing distances the brightness of a target or object will approach the brightness of the horizon making the target indistinquishable from the horizon, hence, visual range.

4.3.2.3 Characteristics of the Atmosphere

The appearance of a distant object is determined by illumination of the sight path by the direct rays of the sun, diffused skylight, light that has been reflected from the surface of the Earth (path radiance or air light), and the light reflected from the object itself. Some of the light in the sight path is absorbed or scattered towards the observer. The remaining light is absorbed or scattered in other directions. The portion of scattered light from the object being viewed that reaches the observer is the transmitted radiance. The radiance seen by the observer looking at a distant object is the sum of the transmitted radiance and the path radiance. Figure 4-17 demonstrates light being absorbed and scattered by the atmosphere and a target object.

On a clear day when the sun is high in the sky, 80 to 90% of the visible solar radiation reaches the surface of the Earth without being scattered or absorbed. Rayleigh scattering by

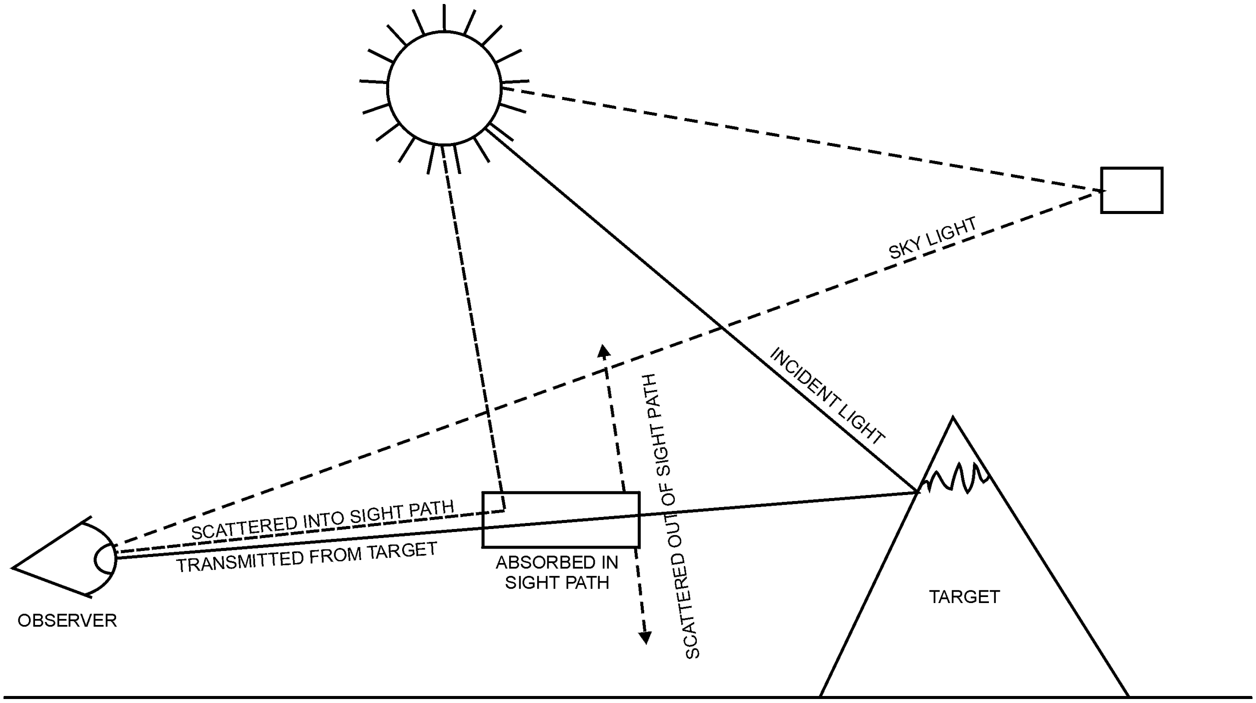

Figure 4-17. Light reflected from a target toward an observer. The intervening atmosphere scatters a portion of this light out of the sight path and scatters light from the sun into the sight path. Some particles and gases also absorb a portion of the light from the target. The light scattered into the 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).

gases is the major component of light extinction in relatively unpolluted areas. Mie scattering is the scattering of all visible wavelengths equally (Shodor Education Foundation, Inc., 1996). It is the attenuation of light in the atmosphere by scattering because of particles of a size comparable to the wavelength of the incident light (National Acid Precipitation Assessment Program, 1991). The term, multiple scattering, is used when light is scattered more than once in a turbid medium. The great majority of light absorption by particles is caused by black carbonaceous particles, assumed to be elemental carbon, that are products of incomplete combustion (Rosen et al., 1978; Japar et al., 1986; Watson and Chow, 1994). Malm et al. (1996) suggested that organic carbon also acts to scatter and absorb light. The estimated natural visibility for the east and west is 60 to 90 mi and up to 140 mi, respectively. Current visibility conditions range from 18 to 40 mi in the rural east to 35 to 90 mi in the rural west (U.S. Environmental Protection Agency, 2000b).

At the surface, a variable fraction of the solar radiation is reflected back upwards, referred to as surface reflectance or the albedo, illuminating the atmosphere from above and below. The amount of solar radiation reflected depends on the color of the terrain. Dark-colored terrain reflects less radiation than light-colored terrain.

Visibility within a sight path longer than approximately 100 km (60 mi) is affected by changes in the properties of the atmosphere over the length of the sight path. The atmosphere generally will not have uniform optical properties over distances greater than a few tens of kilometers. Air quality within a sight path can affect the illumination of the sight path by scattering or absorbing solar radiation before it reaches the Earth's surface. The light-extinction coefficient, σ_{ext}, is a measure of the fraction of light that is lost as it travels through the atmosphere. The light-extinction coefficient is the sum of the light-scattering coefficient, σ_{scat}, and the light-absorption coefficient, σ_{abs}, expressed in units of inverse lengths of the atmosphere (megameters ; Mm^{-1}). Typical extinction coefficients range from 0.01 km^{-1} (10 Mm^{-1}) in relatively clean air to ≈1000 Mm^{-1} in highly polluted areas (Watson and Chow, 1994).

The light-extinction coefficient can be divided into coefficients for the following components:

σ_{ag}, light absorption by gases,
σ_{sg}, light scattering by gases (Rayleigh scattering),
σ_{ap}, light absorption by particles, and
σ_{sp}, light scattering by particles.

Light scattering by particles, σ_{sp}, can be divided to indicate scattering by coarse and fine particles: σ_{sfp}, light scattering by fine particles and σ_{scp}, light scattering by coarse particles.

4.3.3 Optical Properties of Particles

Visibility impairment is typically caused by fine particles. Fine particles are small enough in comparison with the wavelength of visible light that their optical properties are nearly the same as those of homogeneous spheres of the same volume and average index of refraction. Accordingly, Mie equations (Mie, 1908; Kerker, 1969), for calculating the optical properties of homogeneous spheres also may be used to calculate the optical properties of fine particles with the only uncertainties being in the fine particle size distribution and index of refraction (Richards, 1973). However, within the range of indices of refraction that most commonly occur in atmospheric fine particles, the results of Mie calculations can be scaled to account for the effect of the index of refraction. Coarse particles have less of an impact on visibility than do fine particles. However, in most actual cases, the dominant uncertainty in using the optical properties for coarse particles calculated with Mie equations is the uncertainty in the particle size distribution. Uncertainties exist in the use of Mie calculations for calculating light absorption for course particles because the refractive index of the particle is generally not known, and the light-absorbing particles are not spherical in shape, making the calculated light absorption efficiency factor less reliable. Also, light absorption by elemental carbon particles can be reduced when the particle is covered by some chemical species (Dobbins et al., 1994). Conversely, light absorption by carbon particles can be enhanced when coated with a nonabsorbing refractive material such as ammonium sulfate (Fuller et al., 1999).

The output of the Mie calculations includes efficiency factors for extinction, Q_{ext}, scattering, Q_{scat}, and absorption, Q_{abs}. The Q_{ext}, Q_{scat}, and Q_{abs} give the fraction of the incident radiation falling on a circle with the same diameter as the particle that is either scattered or absorbed. The light scattering or absorption efficiency factor (in units of m^2/g) is the change in the light scattering or absorption efficiencies per unit change in mass of the fine particle constituent. The scattering and absorption efficiencies are determined by estimating the size distribution of each particle. The results of the calculations for the light absorption efficiencies contains significant uncertainties because the components of the index of refraction is generally unknown and the light-absorbing particles are frequently chained agglomerates that do not have a spherical shape. Multiplying the values of the light-scattering efficiency factor by the aerosol volume concentration (in units of $\mu m^3/cm^3$) gives the value of the light-scattering coefficient, σ_{sp}, (in units of Mm^{-1}) for these particles.

Richards et al. (1991) reported a scattering efficiency for fine particles of ammonium sulfate of 1.2 m^2/g based on Mie calculations. The value was in agreement with the value determined using the integrating nephelometer readings and the sulfate concentrations. Sulfate scattering efficiencies have been reported to increase by a factor of two when the size distribution went from 0.15 to 0.5 μm (McMurry et al., 1996). The calculated scattering efficiencies for sulfates were 4.1 m^2/g for 100% mass removal and 3.4 and 5.6 m^2/g for 25% mass removal. Calculated scattering efficiencies for carbon particles ranged from 0.9 to 8.1 m^2/g (Zhang et al., 1994; Sisler and Malm, 2000; Sloane et al., 1991). A scattering efficiency of 1.0 and 0.6 m^2/g was reported for soil and coarse mass, respectively (Trijonis et al., 1987).

Scattering efficiencies of 2.4 and 3.1 m^2/g for fine particles were reported by White et al. (1994) and Waggoner et al. (1981), using an integrating nephelometer. Coarse particle scatter less light, resulting in lower scattering efficiencies. Scattering efficiencies for coarse particles ranged from 0.4 to 0.6 m^2/g, based on integrating nephelometer readings (White et al., 1994; Trijonis et al., 1987; White and Macias, 1990; Watson et al., 1991).

Absorption efficiencies for elemental carbon particles have been reported to range from 9 to 10 m^2/g (Japar et al., 1984; Adams et al., 1989; Sloane et al., 1991). Based on a review of the available data, Horvath (1993) reported that measured light absorption efficiencies for light absorbing carbon ranges from 3.8 to 17 m^2/g. According to Horvath (1993), calculated absorption efficiencies are too high, ranging from 8 to 12 m^2/g for monodispersed carbon particles. 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 only will be greater than 10 m^2/g if the particles are internally mixed and the occluding particles are sufficiently large. Absorption values for graphitic and amorphous carbon spheres for primary sizes typical of diesel soot are around 5 m^2/g. Light absorption by aggravated carbon at visible wavelengths is enhanced by no more than 30% and diminishes if encapsulated by a nonabsorbing aerosol. Malm et al. (1996) suggested a combined scattering and absorption efficiency of 10 m^2/g for organic carbon.

Light-extinction budgets may be estimated using the light extinction efficiency and the measured species concentrations. Light-extinction budgets estimate the fraction of the total light extinction contributed by each chemical species in the sight path; however, the values obtained will depend on the assumptions used (Malm et al., 1996; Lowenthal et al., 1995; Sisler and Malm, 1994).

4.3.4 Effect of Relative Humidity on Particle Size and Light-Scattering Properties

Ambient particles contain water, even on relatively dry days. As the relative humidity increases, the particle absorbs more water and increases in size and volume. It is the increase in particle size and volume that acts to increase the light scattering properties of most particles (Malm et al., 1996).

Ambient particles are a mixture of chemical compounds. The amount of increase in particle size with increasing relative humidity is dependent on the particle composition (Zhang et al., 1993). Available data indicate that particles containing ammonium salts are in a liquid solution at relative humidities above 80%. Particles containing inorganic salts and acids are more hygroscopic than particles composed primarily of organic species (Day et al., 1996; McMurry and Stolzenburg, 1989; Saxena et al., 1995; Zhang et al., 1993, 1994; Sloane et al., 1991). Particles containing the more hygroscopic salts and acid species deliquesce and undergo changes in particle size in response to changes in relative humidity. For sulfate and nitrate aerosols, light-scattering properties are similar for all mixture types and compositions, as long as there is the same particle size distribution (Tang, 1997). Saxena et al. (1995) found that the hygroscopic properties of inorganic particles can be altered positively or negatively in the presence of organics. Based on limited data, nonurban organics were found to add to water absorption by inorganics, whereas the urban organics diminished the absorption of water by inorganic particles at relative humidities of 80 to 93%. Figure 4-18 demonstrates the humidity effect on the scattering coefficients for several internally mixed (individual particles containing one or more species) and externally mixed (species that co-exist as separate particles) aerosols. The total scattering computed for an aerosol is relatively insensitive to whether the sample is internally or externally mixed (Malm et al., 1997). Figure 4-19 demonstrates changes in the scattering coefficient ratio, $\sigma_{spw}/\sigma_{spd}$, where σ_{spw} is the scattering coefficient under humid conditions, and σ_{spd} is the scattering coefficient under dry conditions. The figure demonstrates that light scattering is a function of relative humidity and chemical composition. The monitoring data were generated as part of the Southeastern Aerosol and Visibility Study (Day et al., 2000).

There is also a relative humidity-related effect on the scattering efficiency. Ammonium sulfate fine-particle-scattering efficiency varied from 1.5 to 4.5 m^2/g, with low relative humidity and median particle sizes ranging from 0.07 to 0.66 μm (McMurry et al., 1996). Sloane et al.

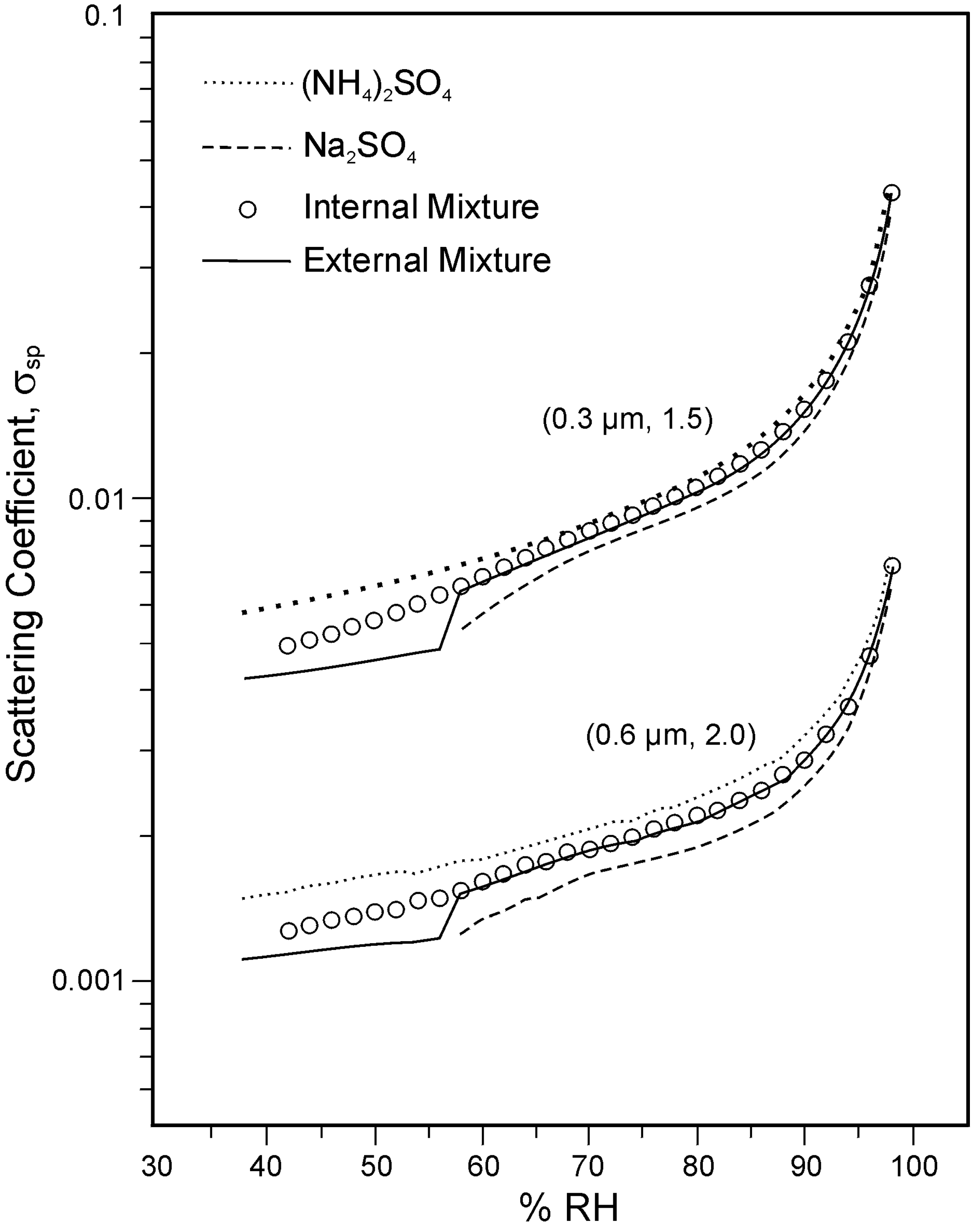

Figure 4-18. Humidity effect on scattering coefficients computed for internal and external mixtures of the mixed-salt aerosol: Na_2SO_4 (x_2 = 0.5)-$(NH_4)_2$ SO_4 (x_3 = 0.5), for two dry-salt particle size distributions, where x is the mass fraction of the dry solutes. Particle size distributions are stated in the parenthesis.

Source: Tang (1997).

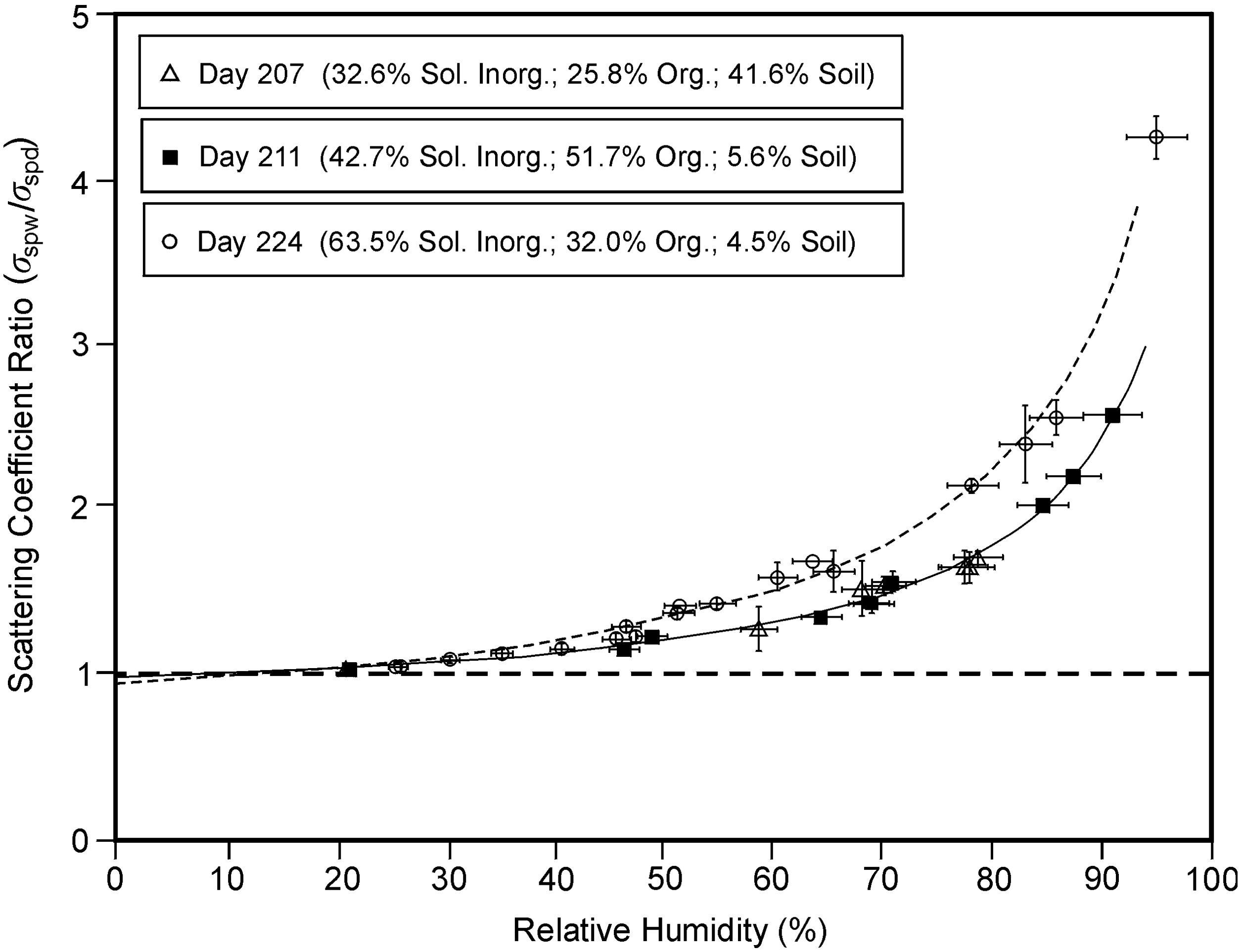

Figure 4-19. Scattering ratios, $\sigma_{spw}/\sigma_{spd}$, for different chemical compositions as a function of relative humidity.

Source: Day et al. (2000).

(1991) reported scattering efficiencies of 7.1 to 8.2 m^2/g for sulfate at 74% relative humidity and 2.1 to 2.9 m^2/g at 38% relative humidity. Average dry scattering efficiencies for sulfate ranged from 2.03 to 2.23 m^2/g for two western sites and one eastern site (Malm and Pitchford, 1997). The dry scattering efficiency increased with increasing particle size. Dry specific scattering efficiencies of 3 m^2/g were reported for sulfates and nitrates (Sisler and Malm, 2000). Omar et al. (1999) reported a calculated scattering efficiency range of 1.23 m^2/g for sulfate when the relative humidity was <63% to 5.78 m^2/g when the relative humidity was >75%. The calculated scattering efficiencies for organic carbon ranged from 3.81 m^2/g when the relative humidity was

<63% to 6.9 m^2/g at relative humidities above 75% (Omar et al., 1999). A more detailed discussion of the effects of relative humidity on the size distribution of ambient particles appears in Chapter 2 of this document.

4.3.5 Measures of Visibility

4.3.5.1 Human Observations

The National Weather Service has in recent decades recorded hourly visibility readings at all major airports in the United States based on human observations of the most distant targeted object's perceivability. Human observation of visibility, although providing a historical record of visibility readings in the United States, are dependent on the individual and the availability of a target and generally are related poorly to air quality.

4.3.5.2 Light-Extinction Coefficient and Parameters Related to the Light-Extinction Coefficient

The most frequently used indicator for visibility characterization for air quality is the light-extinction coefficient because it is closely linked to air quality (U.S. Environmental Protection Agency, 1996a). Various meteorological conditions (moisture and cloud cover) can affect the light-extinction coefficient; however, these effects can be minimized (Husar et al., 1994; Blandford, 1994; Mercer, 1994). The light-extinction coefficient can be measured directly using a transmissometer (Molenar et al., 1990, 1992) or can be estimated by measuring the components of light extinction (scattering and absorption) and calculating the sum (Malm et al., 1994).

The light-extinction coefficient is the quantitative measure of haziness, defined as σ_{ext} = K/visual range, where K is the Koschmieder constant. The value of K is determined both by the threshold sensitivity of the human eye and the initial contrast of the visible object against the horizon sky.

The visual range may be calculated from the light-extinction coefficient using the Koschmieder equation by assuming the atmosphere and the illumination over a sight path in the daytime is uniform, and that the threshold contrast is 2% (Katsev and Zege, 1994; Koschmieder, 1924). These assumptions are, however, invalid for visual ranges greater than 100 km (U.S. Environmental Protection Agency, 1996a). Visual range is an understandable, and for most purposes, an appropriate measure of the optical environment. It has the disadvantage of being related inversely to aerosol concentration.

$$Visual\ Range = 3.91/\sigma_{ext}$$

The deciview index is an atmospheric haze index that expresses uniform changes in haziness in common increments from pristine conditions to extremely visibility impaired environments. The deciview scale is linear with perceived visual changes, starting near zero for a pristine atmosphere (particle-free) at a 1.8-km elevation, and increases with increasing haziness. The deciview index may be calculated from the light-extinction coefficient for green light. For consistency, a Rayleigh scattering value of 10 Mm^{-1} is used.

$$dv = 10 \log_{10} (\sigma_{ext} /10\ Mm^{-1})$$

Under ideal conditions, a just noticeable change in the light-extinction coefficient should represent a one or two deciview change in the deciview scale, about a 10 to 20% change in the extinction coefficient. Any change in the deciview scale should have a change of similar magnitude in the visual appearance of the scene in cases where the assumptions used to develop the deciview scale are met (Pitchford and Malm, 1994; Sisler and Malm, 2000). Figure 4-20 illustrates the relationship of light extinction in Mn^{-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).

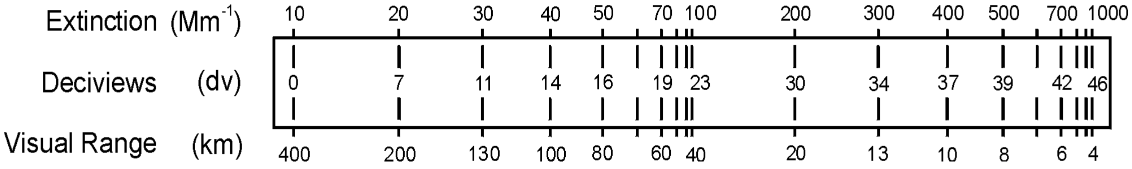

Figure 4-20. Comparison of extinction (Mn^{-1}) and visual range (km).

Source: Fox et al. (1999).

Figures 4-21a,b illustrate a change in deciview scale based on reconstructed extinction coefficients for the Great Plains Region (Badlands) using data from the Interagency Monitoring of Protected Visual Environments Network (IMPROVE). Details about the IMPROVE network appears in Section 4.5.6. The data are sorted by year into three groups based on the cumulative frequency of occurrence of $PM_{2.5}$: best visibility days (10th percentile), median (50th percentile), and worst visibility days (90th percentile) (Sisler and Malm, 2000).

Richards (1999) suggests that the deciview index may not be a good tool for measuring visibility impairment in areas restricted by boundaries. The deciview index is, however, suitable for measuring visibility conditions over a broad geographic region, which is consistent with the definition of regional haze, uniform haze caused by pollutant sources over broad areas (U.S. Environmental Protection Agency, 1999).

4.3.5.3 Light-Scattering Coefficient

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). The light-scattering coefficient is closely linked to fine particle concentrations, making it a good tool for determining small particle-related effects on visibility. When the light-scattering coefficient is increased, visibility is impaired because the transmitted radiance is decreased and the path radiance is increased. (See discussion in the previous sections on transmitted radiance and path radiance.) The light-scattering coefficient can be measured directly with an open and enclosed integrating nephelometer and a forward scatter visibility monitor (Molenar et al., 1992; National Oceanic and Atmospheric Administration, 1992). The light-scattering coefficient also may be calculated using analytical approximations of the particle size distributions, log normal size distributions, or sectional particle size distributions. In the sectional approach, the size composition distribution is represented by a set of particle size sections. The chemical composition of each size section is assumed to be the same (Wu et al., 1996).

4.3.5.4 Fine Particulate Matter Concentrations

The influence of particles on visibility degradation is dependent on the particle composition, solubility, and size (Pryor and Steyn, 1994). Fine particle species have been classified into five major types: (1) sulfates, (2) nitrates, (3) organics, (4) light absorbing carbon,

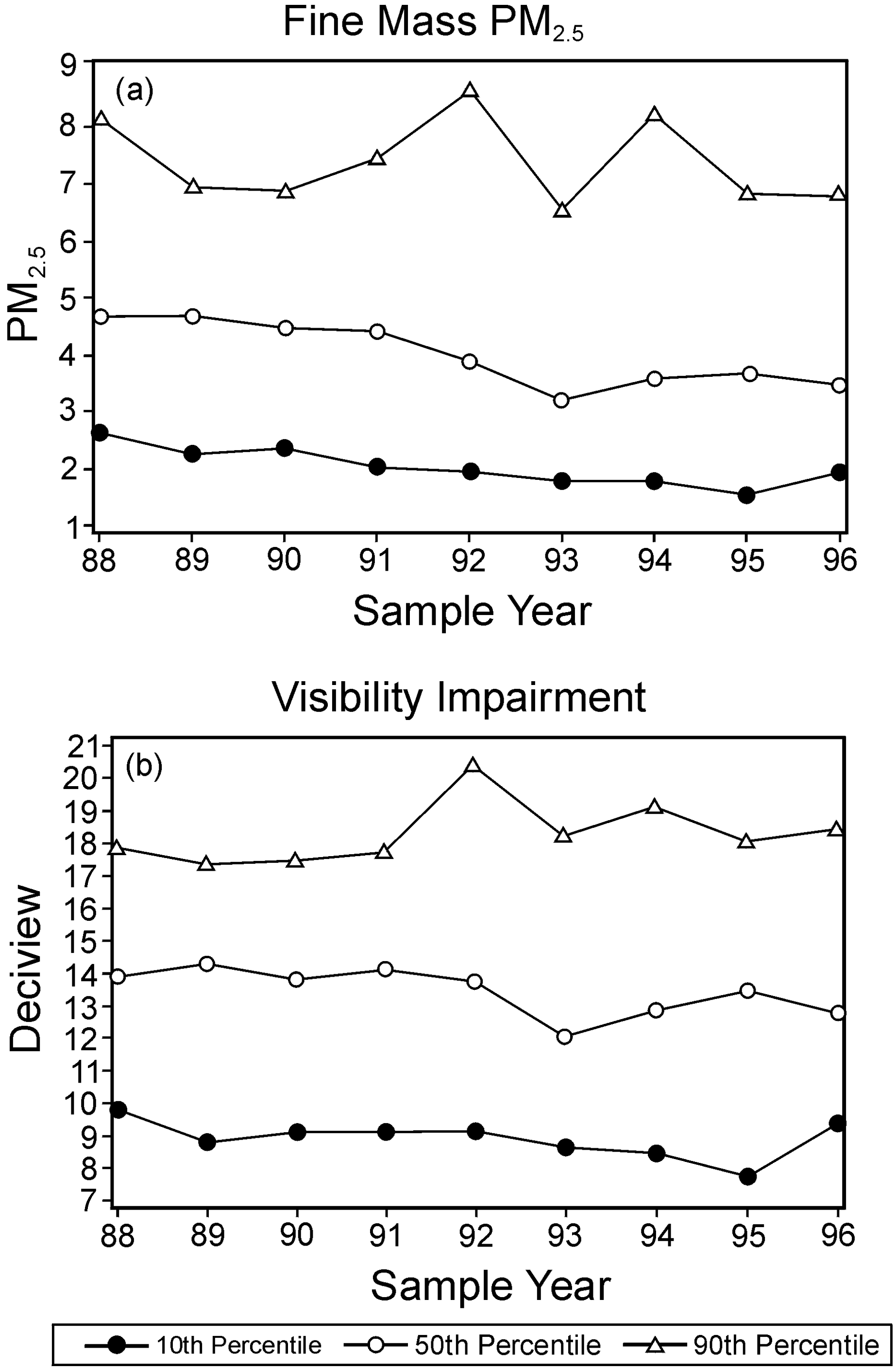

Figure 4-21a,b. Plots of the 10th, 50th, and 90th percentile groups for $PM_{2.5}$ and deciview at the Badlands National Park. The sample year began in March of each year.

Source: Sisler and Malm (2000).

and (5) soil (Malm et al., 1994). The coefficient of light-scattering by fine particles is primarily responsible for visibility impairment making fine particle concentration a suitable indicator of particle related effects on visibility. Several studies have demonstrated a relationship between the coefficient for light-scattering by particles, measured using an integrating nephelometer, and fine particle concentrations (Dattner, 1995; Waggoner and Weiss, 1980; Waggoner et al., 1981; White et al., 1994). Figure 4-22 demonstrates visual range based on particle concentrations and extinction efficiencies for road dust and sulfate.

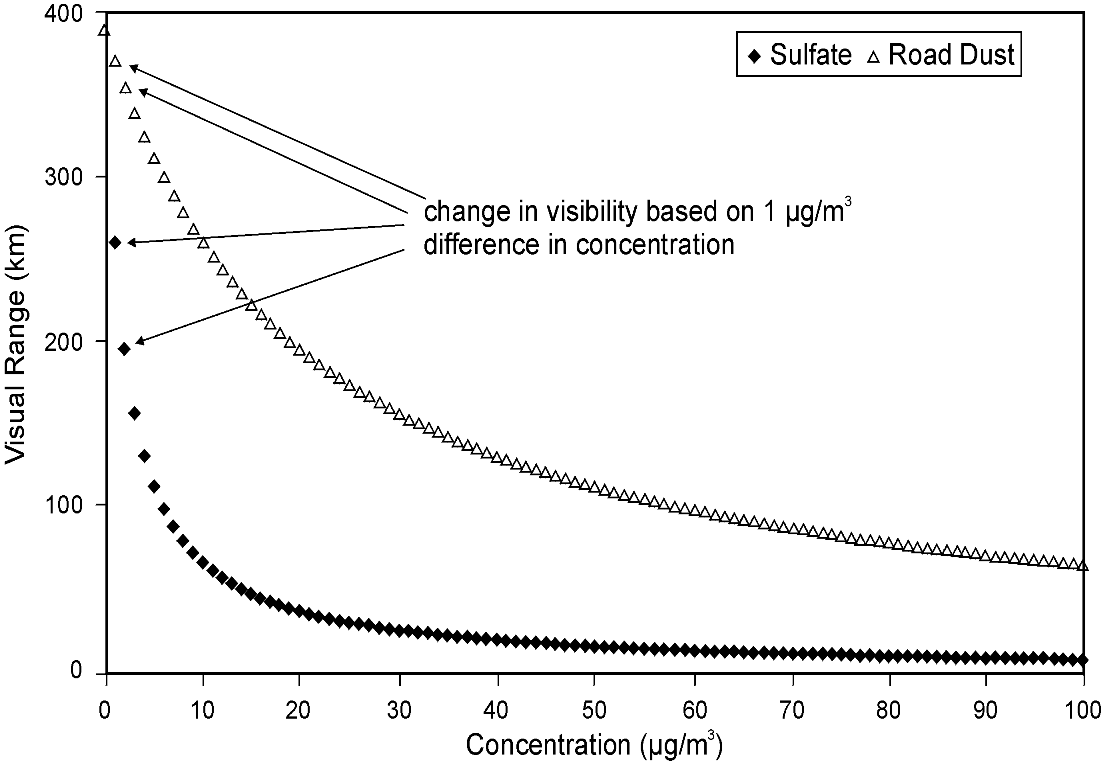

Figure 4-22. Reduction in visual range as a function of increasing fine (sulfate) and coarse (dust) particle concentrations.

Source: Watson and Chow (1994).

4.3.5.5 Discoloration

Discoloration may be used as a quantitative measurement of atmospheric color changes in urban hazes. Atmospheric color changes is a component of plume visibility models. The color of haze will primarily depend on the scene used and human vision. For plume visibility, the threshold for perception of color differences depend on the apparent width of the plume and is greater for color patches separated by sharp edges. Methods for specifying the colors of hazes include the CIE XYZ system of color matching, the Hunt94 color-appearance model, and the visual colorimeter, VISUAL colorimeter for Atmospheric Research (Trijonis et al., 1991; Mahadev and Henry, 1999).

4.3.6 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 designed to provide real-time data for runway visibility to aid in controlling airport operations.

An automated observing system, Automated Surface Observing System (ASOS), is being placed at airports around the country. This monitoring network is sponsored by the National Weather Service, the Federal Aviation Administration, and the Department of Defense. More than 500 airports are currently commissioned and an additional 500 are expected to come online in the next few years.

The visibility sensor, instead of measuring how far one can see, measures the clarity of the air using a forward scatter visibility meter. The forward scatter meter was found to correlate fairly well with extinction coefficient measurements from the Optec Transmissometer. 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 sensor transmits an average 1-min value for a 10-min period. The sensor only samples 0.75 ft of the atmosphere. An algorithm processes the air passing through the sensor over the 10-min measurement period to provide a generally accurate visibility measurement for within 2 to 3 mi of the site. Moisture, dust, snow, rain, or particles in the light beam affect the amount of light scattered (National Weather Service, 1998).

Visibility data from the ASOS network is typically reported in small increments, up to 10 mi, for the purposes of airport operations. However, beginning in 1998, the raw visibility data, including light extinction measurements equaling to visual ranges exceeding 10 mi, have been archived in databases available from the National Climatic Data Center. Data for visibility at larger distances from ASOS sites are available at the sensors for only a short period of time. The data can be directly downloaded from the site. The ASOS data may be useful for characterizing visibility in urban and suburban areas across the country. It also may be used in future analyses to better understand the effects of fine PM on visibility in non-class I areas.

The largest monitoring network that includes both visibility and air quality measurements is the Interagency Monitoring of Protected Visual Environments (IMPROVE) network. The IMPROVE network was formed as a collaborative effort between the EPA and federal land management agencies (National Park Service, U.S. Forest Service, Bureau of Land Management, and Fish and Wildlife Service) responsible for Class I areas and the land around them (National Park Service, 1998; Malm et al., 1994; Sisler et al., 1993; U.S. Environmental Protection Agency, 1995a; Eldred et al., 1997; Perry et al., 1997). The primary monitoring objectives of the IMPROVE program are to establish visibility levels, identify anthropogenic sources of impairment, document progress towards elimination of visibility impairment in protected areas from anthropogenic sources, and promote the development of visibility monitoring equipment and the collection of comparable visibility data (National Park Service, 1998; Evans and Pitchford, 1991). Presently over 70 sites employ the IMPROVE program monitoring methods. It is anticipated that an additional 80 sites will be added in 2000.

Table 4-7 contains $PM_{2.5}$ monitoring data from 30 IMPROVE sites for the years 1988 to 1996. The data includes averaged $PM_{2.5}$ mass and specific species contributions. The data are divided into eastern and western regions. The eastern regions, in addition to Washington, DC, include Acadia National Park and Appalachia and consist of data from Shenandoah and the Great Smoky Mountains National Parks. The western regions include the Northern Great Plains, West Texas, Sonora, the Colorado Plateau, Central Rockies, Cascade, Sierra Humbolt, West Coast, Sierra Nevada, Southern California, and Alaska (Sisler and Malm, 2000).

TABLE 4-7. AVERAGED REGIONAL $PM_{2.5}$ MASS AND EXTINCTION SUMMARIES FOR THE YEARS 1988 TO 1996[a]

Region	$PM_{2.5}$	Sulfate	Nitrate Organics	Organics	Fine Soil	Elemental Carbon
Alaska	1.71 (11.9)	0.55 (5.1)	0.06 (0.06)	0.77 (3.1)	0.22 (1.0)	0.10 (2.2)
Appalachia	10.81 (97.6)	6.53 (71.7)	0.60 (6.9)	2.73 (10.9)	0.52 (4.3)	0.43 (3.8)
Cascades	4.67 (50.6)	1.30 (29.1)	0.23 (5.0)	2.51 (10.0)	0.22 (4.1)	0.41 (2.3)
Colorado Plateau	3.15 (17.3)	1.06 (6.7)	0.21 (1.3)	1.08 (4.3)	0.64 (1.7)	0.17 (3.3)
Central Rockies	2.87 (15.8)	0.80 (5.5)	0.18 (1.2)	1.11 (4.4)	0.64 (1.4)	0.14 (3.2)
Coastal	4.40 (43.5)	1.35 (18.4)	0.90 (10.9)	1.65 (6.6)	0.25 (2.5)	0.25 (5.1)
Northeast	6.13 (59.3)	3.32 (40.6)	0.40 (4.8)	1.84 (7.3)	0.23 (3.4)	0.34 (3.0)
Northern Great Plains	4.26 (30.3)	1.61 (14.6)	0.51 (4.7)	1.35 (5.4)	0.63 (1.6)	0.16 (4.0)
Northern Rockies	5.15 (39.5)	0.98 (15.0)	0.31 (4.7)	2.88 (11.5)	0.57 (4.1)	0.41 (4.1)
Southern California	8.64 (51.7)	1.45 (9.3)	3.53 (22.6)	2.29 (9.2)	0.94 (4.2)	0.42 (6.3)
Sonora	4.09 (21.3)	1.52 (8.3)	0.24 (1.3)	1.28 (5.1)	0.84 (2.0)	0.20 (4.6)
Sierra Nevada	4.40 (25.2)	0.96 (7.0)	0.47 (3.5)	2.16 (8.6)	0.55 (2.6)	0.26 (3.5)
Sierra Humbolt	2.67 (16.7)	0.52 (5.2)	0.16 (1.5)	1.36 (5.5)	0.42 (2.0)	0.20 (2.5)
Washington, DC	16.90 (132.8)	7.91 (73.2)	2.16 (19.9)	4.44 (17.8)	0.82 (15.6)	1.56 (6.3)
West Texas	5.11 (27.0)	2.13 (12.9)	0.25 (1.5)	1.29 (5.2)	1.27 (1.7)	0.17 (5.7)

[a] Mass is in $\mu g/m^3$. Extinction summaries in parenthesis are in Mm.

Adapted: Sisler and Malm (2000).

The U.S. Environmental Protection Agency is currently in the process of establishing a national $PM_{2.5}$ monitoring network of approximately 1,700 monitors at over 1,100 sites. The $PM_{2.5}$ monitoring effort will be coordinated with visibility monitoring efforts currently in place, such as IMPROVE, to maximize benefits of both programs. The monitoring network is expected to be fully implemented by the end of 2000 or shortly thereafter (U.S. Environmental Protection Agency, 1997b; U.S. Environmental Protection Agency, 2000b).

4.3.7 Visibility Modeling

There are several types of models available for the evaluation of pollution-related effects on visibility. Plume visibility models and regional haze models are source models that simulate the transport, dispersion, and transformation of chemical species in the atmosphere. Plume models use the resulting air quality data to calculate the values of parameters related to human perception, such as contrast and color differences. Regional haze models calculate aerosol species concentrations and the light-extinction coefficient. Models for the photographic representation of haze use air quality data as an input and perform the optical calculations required to create images that represent the visual effects of the air quality.

4.3.7.1 Regional Haze

Regional haze models may be used to assess the impact of pollutant sources on an identified area or region, in most cases identified class I wilderness areas, or to evaluate the impact of new or existing air quality regulations. Light extinction by fine particles is used to determine the effect of anthropogenic pollutants on regional visibility degradation (regional haze). In the United States, these anthropogenic particles are composed primarily of sulfate compounds, organic compounds, and, to a much lesser extent, nitrate compounds, with the exception of California, where nitrates are the largest single contributor to light extinction. The contribution to light extinction by these compounds will vary based on the particle composition and size distribution. Once the particles are formed, their size can change, resulting in a change in their light extinction efficiency. Model calculations take into consideration the mass of the particulate constituents and the relative humidity.

The model requirements for regional-scale, multiple-source haze models are nearly identical to the model requirements for simulations of regional-scale, multiple-source fine-particle impacts. Hence, the Eulerian-based grid models currently under development to support fine particle impact assessments will be relied on to provide a means for assessing large-scale, multiple-source haze impacts.

Middleton (1997) described the findings of a Eulerian-based grid model, the Denver Air Quality Model (DAQM). The DAQM is the principal component of the Brown Cloud II study that is part of earlier work investigating visibility in Denver over the last 20 years. The DAQM is derived from the Regional Acid Deposition Model (RADM) and includes aerosol processes, meteorological modeling analysis, and visibility analysis procedures. The DAQM has been used to determine the relationship between emissions and concentrations of fine and coarse particles and all major gaseous pollutants under various emission scenarios and meteorological conditions. The results of the study demonstrated an association between visibility and air quality issues in the Colorado Front Range area.

Neff (1997), in his evaluation of the DAQM model, suggested that the meteorological model does not address adequately mesoscale structures responsible for the initiation and maintenance of the brown cloud episodes or cloud systems and surface moisture fluxes. Given these model uncertainties, it was suggested that there may be errors in the quantification of emissions and in the calculated optical extinction and scattering.

The Visibility Assessment Scoping Model (VASM) uses Monte Carlo techniques to generate multiple realizations of daily concentrations of sulfates, nitrates, elemental carbon, organic carbon, fine and coarse dust, and the relative humidity to determine particle effects on regional haze. Species-specific light attenuation is calculated based on particle concentration and relative humidity, producing short-term haze intensity or visual range information (Shannon et al., 1997).

The Elastic Light Scattering and Interactive Efficiency (ELSIE) model was used by Omar et al. (1999) to determine the species concentrations and to relate apportionment to the extinction coefficient in an aerosol mixture. The model assumes the aerosol is an internal inhomogeneous mixture of chemical species and size distributions. Model input parameters included the size distributions, prevailing relative humidity, refractive indices of the constituents, percent solubility of the aerosol components, and the growth function of the aerosol particles. The model assumes that the particles grow with increasing relative humidity according to a predetermined growth function.

Several source-oriented models have been developed to evaluate the effects of pollutants on regional haze. The U.S. Environmental Protection Agency, in cooperation with the U.S. Forest Service, the Fish and Wildlife Service, and the National Park Service (the Interagency Workgroup for Air Quality Modeling), developed the MESOPUFF II system of assessing regional haze impacts. The MESOPUFF II system uses the light extinction for sulfates and nitrates for an estimated 3- to 24-h average concentration (U.S. Environmental Protection Agency, 1995b). The CALPUFF modeling system can process mesoscale meteorological data and address dispersive processes of a regional nature. Simulated long-range pollutant trajectories have been compared successfully to results from a field study involving transport to 1000 km downwind (U.S. Environmental Protection Agency, 1995c). However, Lagrangian puff dispersion modeling involving transport of 200 km or more tend to underestimate the horizontal extent of the dispersion, causing the surface concentration to be overestimated (Moran and Pielke, 1994). Another source-oriented Lagrangian trajectory model capable of computing light extinction and scattering and estimating visual range from gas phase and primary particle phase air pollutant emissions directly from sources was reported by Eldering and Cass (1996). The model is comprised of several modules that take into consideration particle size distribution and chemical composition, the speciation of organic vapor emissions, atmospheric chemical reactions, transport of condensible material between the gas and particle phase, fog chemistry, dry deposition, and light scattering and absorption. The model is, however, not suitable for predicting visibility over great distances through nonuniform hazes and for visualization of pollutant effects of isolated major point source plumes. Single line Lagrangian trajectory models cannot represent horizontal turbulent diffusion, the effects of wind shear, and advection by turbulent wind components. Error in transport calculations have been reported of up to ± 50% (Eldering and Cass, 1996).

Gray and Cass (1998) developed a lagrangian particle-in-cell model for predicting source class contributions of fine particle total carbon and elemental carbon. The model simulates the motion and deposition of pollutants in an air basin with varying meteorological conditions. The model also takes into consideration the vertical mixing characteristics of pollutants in areas located near the source. The model is useful in determining changes in long-term average pollutant concentrations from implementing specific emission control measures.

The Regional Particulate Model (RPM) simulates secondary fine particulate matter ($PM_{2.5}$) formation and long-range transport. The RPM is used with the Regional Acid Deposition Model (RADM), a comprehensive acid rain model. Predictions from the RADM are used to simulate the formation of sulfate and nitrate, ammonium particles, and secondary organic aerosols. The external RADM includes particle physics from the RPM and operates at an 80- and 20-km resolution. Additional work currently is being done that will incorporate the RADM/RPM and external RADM models into a more comprehensive air quality modeling system, Models-3/Community Multi-Scale Air Quality (CMAQ). This modeling system simulates the processes involved in primary and secondary PM_{10} and $PM_{2.5}$ and ozone formation, regional haze, acid deposition, and nutrient deposition. The modeling system includes a mesoscale meteorological model, emission model, and a version of the CMAQ.

The Regulatory Modeling System for Aerosols and Deposition (REMSAD) also simulates $PM_{2.5}$ formation. The REMSAD was derived from the Urban Airshed Model Version V (UAM-V) for primary and secondary $PM_{2.5}$ and PM_{10} formation, and acid nutrient and toxic deposition. The REMSAD system consists of a meteorological data preprocessor, the core aerosol and toxic deposition model (ATDM), and postprocessing programs. The ATDM is a three-dimensional Eulerian grid model designed to calculate the concentrations of both inert and chemically reactive pollutants by simulating the physical and chemical processes in the atmosphere that affect pollutant concentrations. The basis for the model is the atmospheric diffusion or species continuity equation. This equation represents a mass balance in which all of the relevant emissions, transport, diffusion, chemical reactions, and removal processes are expressed in mathematical terms (Systems Applications International, Inc., 1998).

Zannetti et al. (1990, 1993) and Fox et al. (1997) described a semi-empirical model that could be used to estimate the visibility impact on one region resulting from sulfur dioxide emission controls in a different region. The model combined four different input parameters: (1) chemical transport; (2) possible nonlinearity of pollutant chemical transformation; (3) sulfate fraction of fine particulate matter, including the amount of water absorbed by the fine particles; and (4) the fraction of light extinction caused by fine particles. The model uses physically realistic concepts of atmospheric transport, chemical transformation, and physical effects. However, actual data sets, mathematical constructs, or expert opinions also may be used. Models also have been developed that predict the downwind concentration of smoke particulate and other combustion products from the burning of crude oil from accidental spills (McGrattan et al., 1995, 1996).

4.3.7.2 Plume Models

Several plume visibility models are currently available. Plume visibility models estimate the value of optical parameters related to human perception, such as contrast and color differences, and compare these values with perception thresholds to determine whether the plume is likely to be perceptible under various simulated conditions (U.S. Environmental Protection Agency, 1988; Latimer, 1988). An empirical algorithm, Probability of Detection Algorithm (PROBDET), allows the prediction of the lower limit of plume contrast that can be detected visually. The PROBDET can be used to estimate the detection level for plumes that fall within the bounds defined by the full-length, oval, and circular plume stimuli (Ross et al., 1997).

A simplified dispersion model using a second-order turbulence closure scheme to account for averaging time effects on the dispersion rate was described by Sykes and Gabruk (1997). The lateral and vertical spread is estimated using a Gaussian plume framework. A simplified representation of the turbulence spectrum is used to predict the reduced spread rate for short averaging times.

Earlier plume models included PLUVUE I and II, used during the preparation of a permit application to determine whether or not a proposed new facility would cause visibility impairment in a Class I area (Latimer et al., 1978; Johnson et al., 1980; White et al., 1985; U.S. Environmental Protection Agency, 1992). Seigneur et al. (1997) developed a plume visibility model, the Reactive and Optics Model Emissions (ROME), that improves on the existing plume visibility models. The model simulates the momentum and buoyancy forces of the plume rise, the dispersion and chemistry, and condensation and evaporation of the aqueous phase.
A second-order closure algorithm is used to estimate instantaneous plume concentrations, or the time-averaged plume concentration may be estimated using a first-order closure algorithm.
A comprehensive chemical kinetic mechanism simulates chemical transformation processes in the gas, aqueous, and particle phases. Particle dynamics and chemical composition is based on sectional representation of the particle size distribution. The model includes a radioactive transfer module that provides optical properties using sectional particle size distributions.
Deposition velocities based on atmospheric stability, surface type, chemical type, and particle

size are derived using a resistance-based, dry deposition algorithm. The ROME can be used with other models to estimate a stack plume opacity, the percentage of light intensity attenuated by the plume near the stack after any condensed water has evaporated (Meng et al., 2000). When compared with the PLUVUE II, the ROME, with the second-order dispersion algorithm, was found to present a more accurate estimate of plume height, width, nitrogen oxide concentration, nitrogen dioxide/nitrogen oxide ratio, and visibility. Error, bias, correlation coefficients, and simulations were within a factor of two of that observed (Gabruk et al., 1999).

4.3.7.3 Photographs

Computer-generated photographs are sometimes used to illustrate the effects of pollution on visibility. To begin, a photograph is taken on a very clean, cloud-free day to serve as the initial scene image. As previously indicated, the appearance of an object is determined by the path radiance and the transmitted radiance. To determine the transmitted radiance, an estimate of the light-extinction coefficient from the photograph is used to determine the initial radiance for each element in the scene. The transmitted radiance is equal to the initial radiance of the element in the scene multiplied by the transmittance of the atmosphere in the sight path. Because the path radiance changes over the distance of the sight path, the source function, the rate of change over the distance of the sight path, also must be determined.

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 size distribution and chemical composition of atmospheric aerosols, NO_2 concentration, temperature, and relative humidity for a clear day, for comparison purposes. 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. The WinHaze visual air quality modeling system is one tool that has been developed using techniques to simulate changes in visibility due to changes in air quality.

One of the limitations 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. Photographs are also expensive to produce. More detailed information on the use of photographic representation of haze may be found in the U.S. Environmental Protection Agency (1996b), Trijonis et al. (1991), Molenar et al. (1994), and Eldering et al. (1993).

4.3.8 Trends in Visibility Impairment

Trends in visibility impairment or haziness, visual range, often are associated with fine mass concentrations ($\leq 2.5\ \mu g/m^3$). 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 any parameter related to air pollution. After some manipulation, 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 Husar et al. (1994), Husar and Wilson (1993), and Husar et al. (1981).

Generally, visibility impairment is greatest in the eastern United States and southern California. Haziness in the southeastern United States is greatest in the humid summer months because of its affinity to atmospheric water vapor, followed by the spring and fall, and winter. Summer haziness in the southeastern United States has increased by approximately 80% since the 1950s (Husar and Wilson, 1993) because of increased sulfate from increased SO_2 emissions (Husar et al., 1994). The resulting sulfate, considered to be ammonium sulfate, accounts for 40 to 70% of the fine particle mass (Husar and Wilson, 1993). Sulfate-related effects on visibility in the southeast is a factor of 20 higher than the Great Basin area and 10 higher than the desert southwest, central Rocky Mountains, and Sierra Mountains (Malm et al., 1994). For most rural eastern sites, sulfates accounts for >60% of the annual average light extinction on the best days and >75% of the light extinction on the worst days. 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). The increase was largest in the summer and decreased in the winter. The majority of the southwest showed decreasing sulfur (Eldred et al., 1993; Eldred and Cahill, 1994). White (1997) suggested that the increase in fine-particle sulfur may be the result of the measurement method and not an upward trend in fine particle concentrations in those Class I areas. However, Iyer et al. (2000), using the Spearman correlation of trend, reported an increased trend in hazy days during the summer months in Shenandoah and the Great Smoky Mountains based on monitoring data for the period 1979 to 1996 showing high sulfur concentrations.

Sulfates also may be a significant contributor to total light extinction in the rural western United States, accounting for 30 to 40% of the total light extinction on the best days and 35 to 45% of the total light extinction on the haziest days. In several areas of the west, sulfates account for over 50% of the annual average aerosol extinction (U.S. Environmental Protection Agency, 2000b).

Organics are the second largest contributor to light extinction in most areas in the United States. Extinction caused by organic carbon is greatest in the Pacific Northwest, Oregon, Idaho, and Montana, accounting for 40 to 45% of the total extinction. Organic carbon can contribute between 20 to 30% to the total extinction in most of the western United States and 10 to 15% 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 (up to 6%) (Malm et al., 1994; U.S. Environmental Protection Agency, 2000b).

Some of the visibility impairment in northern California and Nevada, including Oregon, southern Idaho and western Wyoming, results from coarse mass and soil, primarily considered natural extinction. In some areas of the United States, extinction from coarse mass is almost negligible because the overall extinction is so high. High dust concentrations from southern California have contributed to regional haze in the Grand Canyon and other class I areas in the southwestern United States (Vasconcelos et al., 1996). White et al. (1999) reported that some of the worst haze near the Grand Canyon is associated with pollutant transport from southern California and the subtropics.

Visibility impairment in southern California is primarily caused by light extinction by nitrates. Nitrates contribute about 40% to the total light extinction in Southern California and 10 to 20% of the total extinction in other areas of the United States.

The average haze patterns across the continental United States, for five-season averages for the years 1980 to 1985 and 1990 to 1995 are shown in Figure 4-23. Haze is indicated by the 75th percentile of the extinction coefficient that is calculated from the visual range, corrected to 60% relative humidity by the Koschmeider relationship.

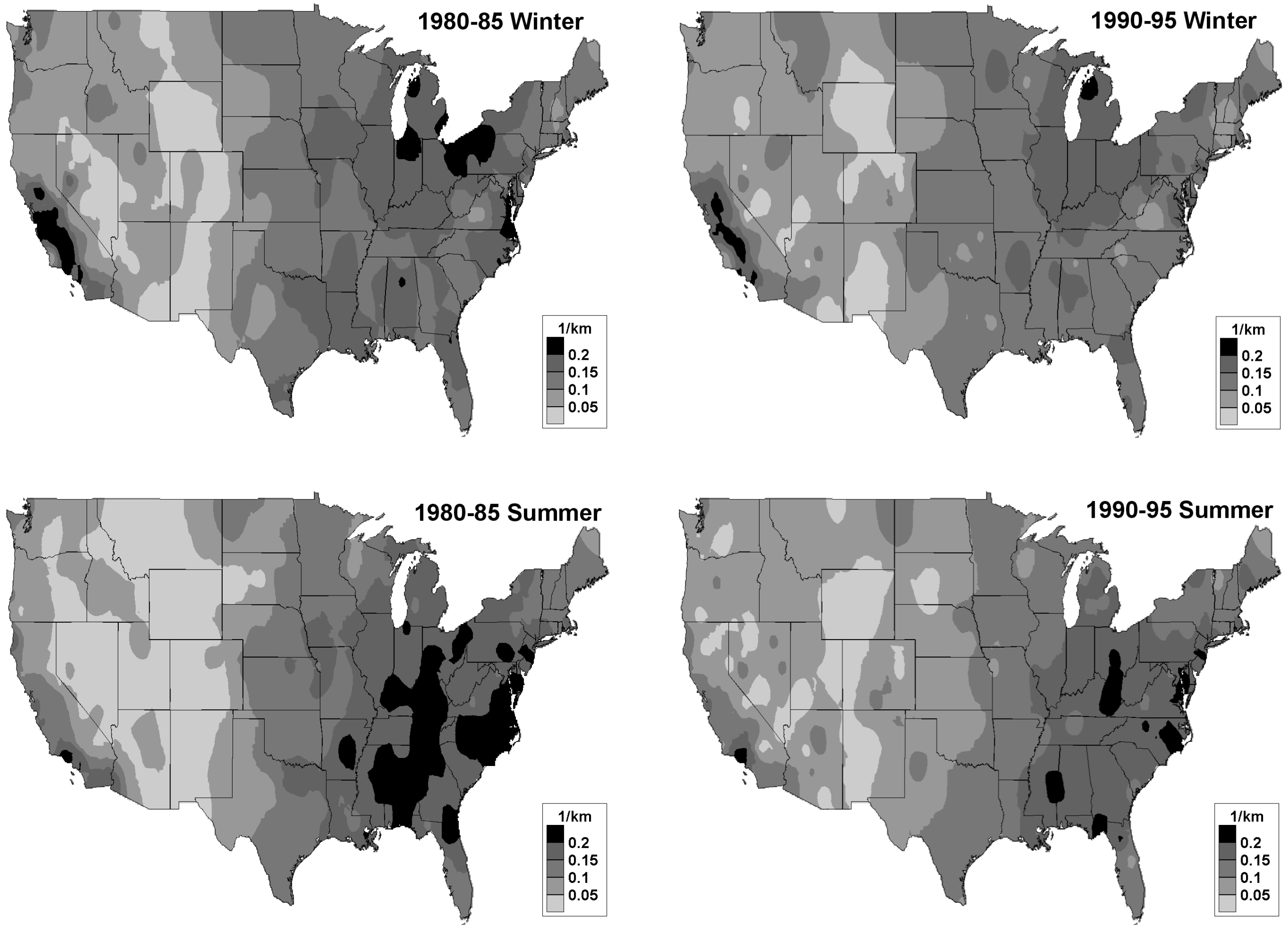

Figure 4-23. Five-season average haze patterns (75th percentile of the extinction coefficient) for the periods 1980 to 1985 and 1990 to 1995. The relationship between haze, expressed as extinction coefficient (corrected to 60% relative humidity) is 1.9/extinction coefficient in km^{-1} = visual range in km (i.e., the intensity of shading increases as visual range decreases: 0.2 km^{-1} = 9.5 km, 0.17 km^{-1} = 11.2 km, 0.14 km^{-1} = 13.6 km, 0.11 km^{-1} = 17.3 km, 0.08 km^{-1} = 23.8 km, and 0.05 km^{-1} = 38.0 km). Winter = Dec., Jan., Feb.; Summer = June, July, Aug).

Source: Husar et al., 2000.

The trends graphs in Figure 4-24 for regions in the United States represent the 75th percentile of the light extinction coefficient for the stations located within the designated region over a 30-year period (1940 to 1990). The trends are presented for quarters 1 (winter) and 3 (summer). The northeastern United States exhibited an increase in haze during quarter 3 between 1960 and 1970 and a steady decline between 1973 (0.22 km^{-1}) and 1992 (0.12 km^{-1}). In quarter 1 the haziness steadily declined from 0.15 to 0.10 km^{-1} in the 30-year period. The Mid-Atlantic region, the Virginias and Carolinas, shows a strong increase in haziness in quarter 3 between 1960 and 1973, followed by a decline. The winter haze was virtually unchanged over the 30-year period. The haziness over the Gulf states increased between 1960 and 1970 and remained virtually unchanged since then. The central Midwest, including Missouri and Arkansas, exhibit virtually no change during the winter season and a slight increase in the summer (1960 to 1970). The upper Midwest shows an opposing trend for summer and winter. Although summer haze has increased, mostly from 1960 to 1973, the winter haze has declined.

Based on $PM_{2.5}$ concentrations and changes in the deciview scale, calculated from reconstructed extinction coefficients, Sisler and Malm (2000) reported no significant deterioration in air quality and visibility conditions at 30 IMPROVE network sites for the years 1988 to 1996. The sites were divided into eastern and western regions. Averaged $PM_{2.5}$ mass and extinction summaries for the sites appear in Table 4-7. The annual best visibility (10th percentile) and median visibility days (50th percentile) are improving at approximately 70% of the sites. However, several sites are not showing steady improvements in either visibility or $PM_{2.5}$, particularly in the number of worst visibility days (90th percentile). The sites included the Badlands, Big Bend, Crater Lake, Great Smoky Mountains, Mesa Verde, Shenandoah and Yosemite National Parks, Chiricahua National Monument, and the District of Columbia.

4.3.9 Economics of Particulate Matter Visibility Effects

Given the evidence of potential economically significant effects of visibility impairment, economic analysis proceeds by quantifying in monetary terms the costs associated with different ambient levels of PM. Where possible, direct economic valuation can take place using prices that are determined in the marketplace. There are a variety of ways to estimate costs/benefits. Avoided cost methods estimate the costs of pollution by using the expenditures that are made necessary by pollution damage. For example, if ambient levels of particulate matter results in

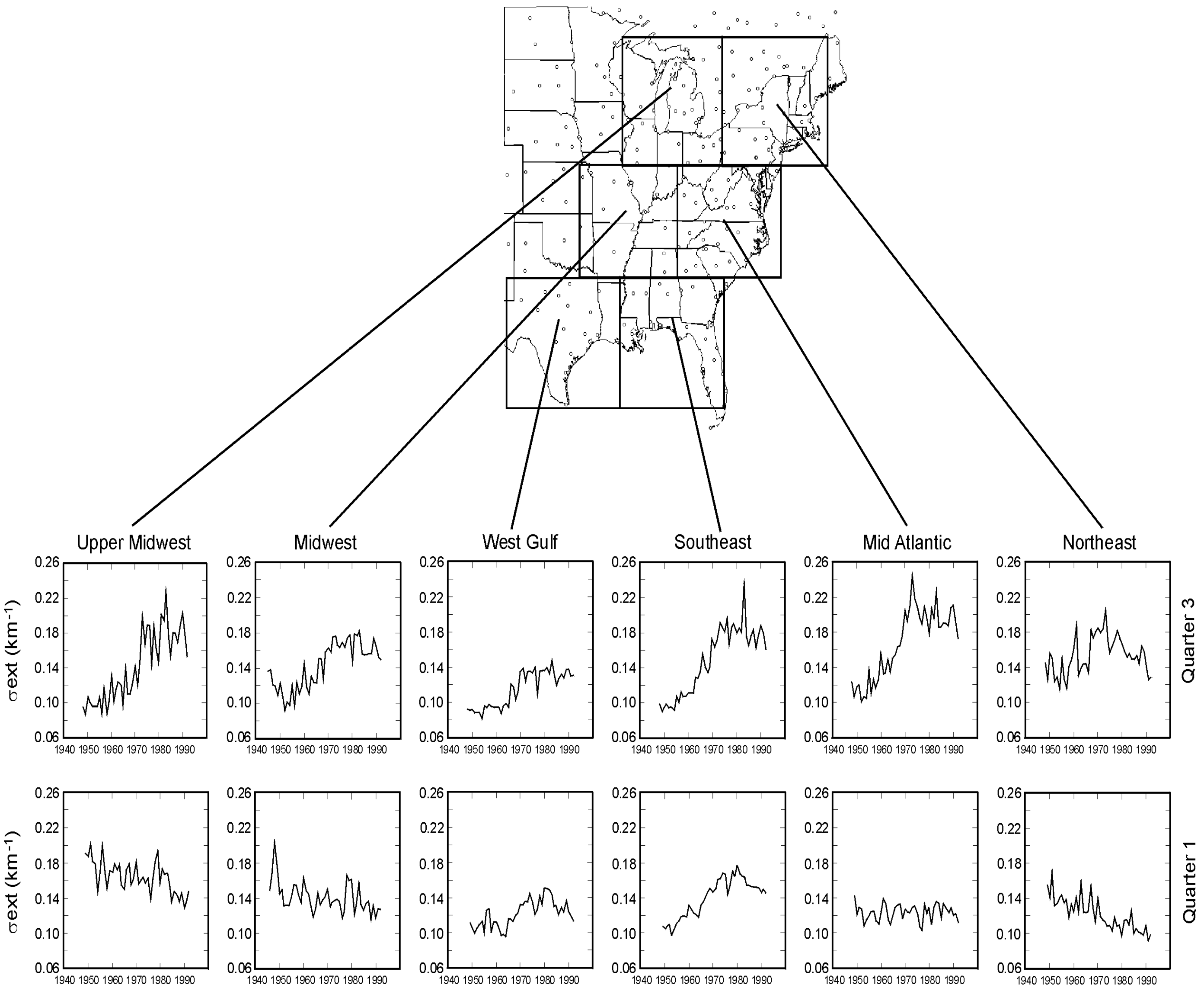

Figure 4-24. Secular haze trends for 1940 to 1990 for six regions, summer (Quarter 1) and winter (Quarter 3) in the 75th percentile.

increased frequency of building cleaning or repainting, then the appropriately calculated increase in these costs is a reasonable estimate of true economic damage. Benefits associated with reductions in the pollution levels then are represented by the avoided costs of these damages.

Estimating benefits for visibility is a more difficult and less precise exercise because the effects are not valued in the marketplace. There are several methods that economists have developed to estimate changes in environmental effects that are not valued in the marketplace (Freeman, 1993). These include hedonic price analysis, stated preference models (including contingent valuation, contingent choice, and contingent ranking), and travel cost models. Hedonic price analysis works by analyzing the way that market prices change when an associated environmental effect changes. Part of the economic costs imposed by the reduced visibility caused by PM 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) has been used to determine estimated value changes in both visibility and ecosystem functions (Hanley and Spash, 1993; Chestnut, 1997). The CVM determines pollutant-related effects by using carefully structured surveys to estimate the amount of compensation equivalent to a given change in environmental quality or equivalently, how much they would be willing to pay to obtain a given change in environmental quality. There is an extensive scientific literature and body of practice on both this theory and technique.

Other valuation methods include stated preference models, including contingent choice and contingent ranking (also known as conjoint analysis), as well as travel cost models (Johnson and Desvousges, 1997; Hanley and Spash, 1993). However, the primary methods used to date for valuation of visibility have been the hedonic price and contingent valuation methods (Hanley and Spash, 1993).

The effects of PM on visibility may differ widely between urban residential and recreational areas. Separate estimates are needed to account for welfare changes associated with improvements in visibility in class I areas. Chestnut and Dennis (1997) developed a method for estimating the value to the public of visibility improvements in class I areas using the results of a 1990 cooperative agreement project jointly funded by the EPA and the National Park Service: “Preservation Values For Visibility Protection at the National Parks.” Using the contingent valuation method, Chestnut and Davis calculated a household willingness to pay for visibility improvements in class I areas, capturing both use and nonuse recreational values. This analysis also accounts for geographic variations in the willingness to pay. The results indicate a willingness to pay per deciview improvement in visibility of between \$5 and \$17 per household.

4.4 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.

Limited new studies have been published that better define the role of air pollution in materials damage. This section briefly summarizes information on particle and sulfur-containing pollutants (formed by the chemical reactions of SO_2 with other atmospheric pollutants) exposure-related effects on materials 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 manmade building materials and naturally occurring cultural materials was discussed in the criteria document on nitrogen oxides (U.S. Environmental Protection Agency, 1993).

4.4.1 Effects of Particles and Sulfur Dioxide on Man-Made Surfaces

4.4.1.1 Metals

Metals under go natural weathering processes in the absence of environmental pollutants. The additive effect of pollutants on the natural weathering processes will depend on the nature of the pollutant and 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 affect of pollutant exposure on metal surfaces.

Several studies demonstrate the importance of time 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 time 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 affect on the rate of corrosion. 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 the time of wetness on the rate of corrosion. Although the model does not characterize specifically particle effects, the contribution of particulate sulfate was considered in model development.

Whether suspended particles actually impact on 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 on copper (protective covering) can take as long as 5 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 recent 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 4-8.

4.4.1.2 Painted Finishes

Exposure to air pollutants affect 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,

TABLE 4-8. CORROSIVE EFFECTS OF PARTICULATE MATTER AND SULFUR DIOXIDE ON METALS

Metal	Exposure Conditions	Comments	Bibliography
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 4-8 (cont'd). CORROSIVE EFFECTS OF PARTICULATE MATTER AND SULFUR DIOXIDE ON METALS

Metal	Exposure Conditions	Comments	Bibliography
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 $\mu g/m^3$) and 1.0 ppm (2,618.7 $\mu g/m^3$) 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 $\mu g/m^3$) 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)

1954) or by staining and pitting of the painted surfaces (Fochtman and Langer, 1957; Wolff et al., 1990).

The erosion rate of oil-base 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-base 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-base 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).

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 have 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 4-9. 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

TABLE 4-9. EFFECTS OF PARTICULATE MATTER AND SULFUR DIOXIDE ON STONE

Stone	Exposure Conditions	Comments	Bibliography
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 $\mu g/m^3$) SO_2; 4.1 to 41.1 ppb NO_x; 2.4 to 17.4 ppb (4.5 to 32.7 $\mu g/m^3$) NO_2; 10.1 to 25.6 ppb (19.8 to 50.2 $\mu g/m^3$) 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 sulphation of the calcitic layer by atmospheric pollutants or dry or wet deposition of atmospheric dust.	Garcia-Vallès et al. (1998)

TABLE 4-9 (cont'd). EFFECTS OF PARTICULATE MATTER AND SULFUR DIOXIDE ON STONE

Stone	Exposure Conditions	Comments	Bibliography
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)
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 $\mu g/m^3$ 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 $\mu g/m^3$ (site 1) and 88 to 189.8 $\mu g/m^3$ (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 $\mu g/m^3$ 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 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)

TABLE 4-9 (cont'd). EFFECTS OF PARTICULATE MATTER AND SULFUR DIOXIDE ON STONE

Stone	Exposure Conditions	Comments	Bibliography
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)
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)
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)

TABLE 4-9 (cont'd). EFFECTS OF PARTICULATE MATTER AND SULFUR DIOXIDE ON STONE

Stone	Exposure Conditions	Comments	Bibliography
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)

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%). Approximately 99% of the sulfur in gypsum is sulfate because of the sulphation process caused by the deposition of SO_2 aerosol. Sulphites also are present in the gypsum layer as an intermediate product (Sabbioni et al., 1996l; 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.

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), 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 runoffs 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 in 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 nonflat 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 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, in particular dry deposition of $SO_{2,}$ 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 the transformation of SO_2 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 transmissions 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; however, soiling is dependent on the particle concentration in the ambient environment, particle size distribution, and 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. A recent study suggest that it would take a 12% surface coverage by black particles before there is 100% accuracy in identifying soiling (Bellan et al., 2000). 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 have concentrated on gaseous pollutants. The deposition of the sulfur-containing pollutants are associated with the formation of gypsum on the stone (see Section 4.4.1.3). 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) found 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. 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 on 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. Studies describing the effects of particles on stone surfaces are discussed in Table 4-9.

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). 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 and oriented horizontally and 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 EFFECTS OF ATMOSPHERIC PARTICULATE MATTER ON CLIMATE CHANGE PROCESSES AND THEIR POTENTIAL HUMAN HEALTH AND ENVIRONMENTAL IMPACTS

Global climate change processes and their potential human health and environmental impacts have been accorded extensive attention during the past several decades, and they still continue to be of broad national and international concern. This is reflected by extensive research and assessment efforts undertaken since the mid-1970s by U.S. Federal Government Agencies (e.g., NOAA, EPA, CDC, etc.) or via U.S. Federal Interagency programs (e.g., the U.S. Global Climate Change Research Program [USGCRP]) and by analogous extensive research and assessment efforts undertaken by numerous other national governments or international collaborative activities (e.g., those coordinated by the Intergovernmental Panel on Climate Change [IPCC], established in the 1980s under the joint auspices of the World Meteorological Organization [WMO], and the United Nations Environment Programme [UNEP]).

Atmospheric particles play important roles in two key types of global climate change processes or phenomena: (1) alterations in the amount of solar radiation in the ultraviolet range (especially UV-B) penetrating through the Earth's atmosphere and reaching its surface, where it can exert a variety of effects on human health, plant and animal biota, and other environmental components; and (2) alterations in the amount of solar radiation in the visible range being transmitted through Earth's atmosphere and either being reflected back into space or absorbed (together with trapping of infrared radiation emitted by the Earth's surface by certain gases), which enhances heating of the Earth's surface and lower atmosphere (i.e., the widely-known "greenhouse effect") and leads to consequent "global warming" impacts on human health and the environment. Atmospheric particles also play a lesser role by absorbing infrared radiation emitted by the Earth's surface.

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 the radiative properties (extinction efficiency, single scattering albedo, and asymmetry parameter) of the particles, which are, in turn, dependent 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 6 of the 1996 PM AQCD and recapitulated in Chapter 2 of this document (e.g., fine particles mainly consisting of nitrate, sulfate, mineral dust, elemental carbon, organic carbon compounds [e.g., PAHs], and metals derived from high temperature combustion or smelting processes). The major sources of these components are shown in Table 2.1 of Chapter 2 in this document.

Knowledge of the factors controlling the transfer of solar radiation in the ultraviolet spectral region is needed for assessing the potential biological and environmental impacts associated with exposure to UV-B radiation (290 to 315 nm). Knowledge of the effects of PM on the transfer of radiation in the visible and infrared spectral regions is needed for assessing the relation between particles and global warming and its environmental and biological impacts. Key information regarding important conceptual aspects and factors related to solar ultraviolet radiation processes and effects is summarized first below and atmospheric PM roles noted, followed by summarization of global warming processes, their potential human health and environmental impacts, and potential relationships to atmospheric PM.

4.5.1 Solar Ultraviolet Radiation Transmission Impacts on Human Health and the Environment: Atmospheric Particulate Matter Effects

4.5.1.1 Bases for Concern Regarding 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 over 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, 1993; Van der Leun et al., 1995, 1998) of salient points related to stratospheric ozone depletion processes and bases for concern provide a concise introduction to the subject, as does Figure 4-25. As shown to the left in the figure, stratophospheric ozone depletion results from: (a) anthropogenic production and associated emission into the lower atmosphere 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) photodissociation processes release Cl and Br, that (especially under very cold subzero upper atmospheric conditions) catalyze ozone reduction; leading to (d) stratospheric ozone depletion that is most marked over Antarctica during Southern Hemisphere wintertime, to a less marked but still significant extent over the Arctic Polar Region during Northern Hemisphere wintertime, and to a lesser extent over mid-latitude regions during any season.

Given the long time 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

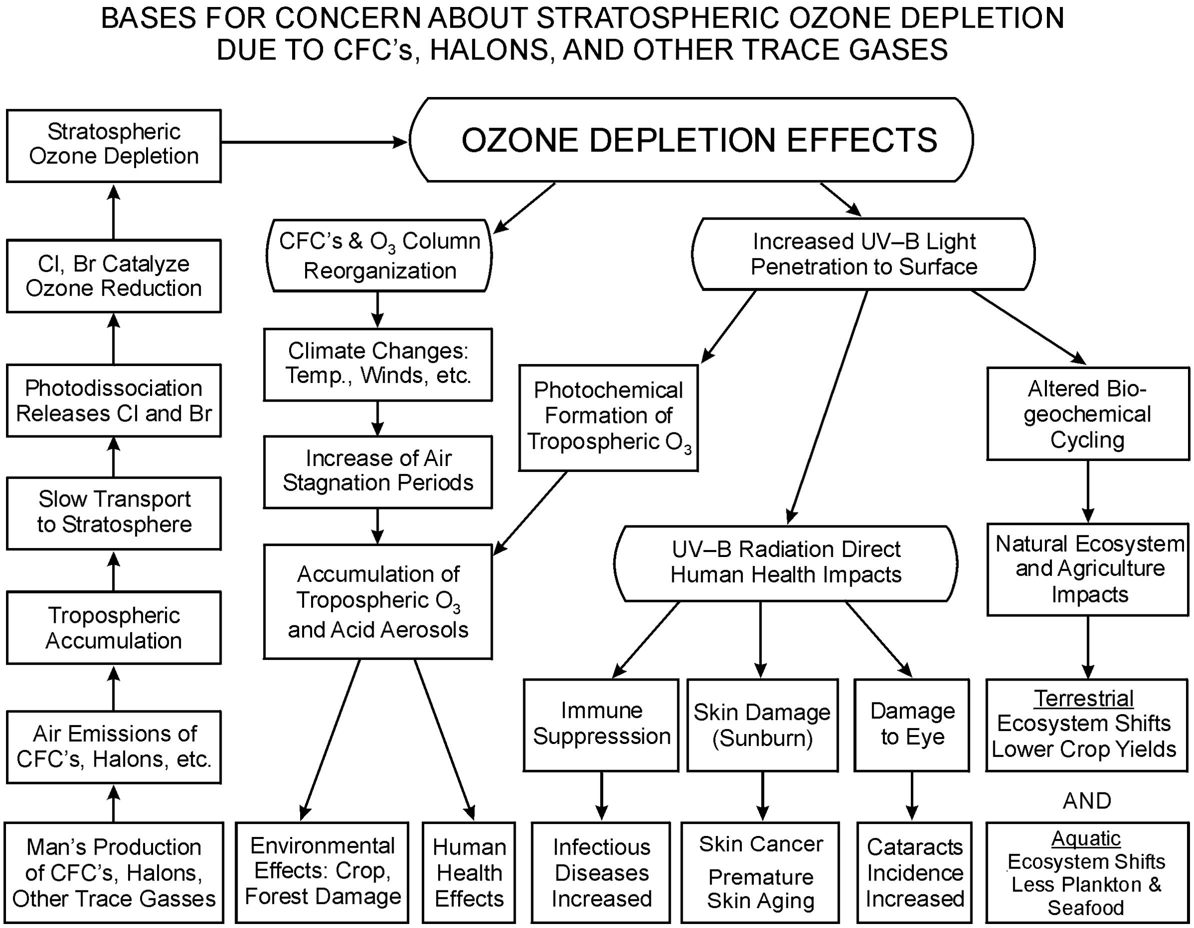

Figure 4-25. Processes involved in stratospheric ozone depletion because of man's production of CFCs, halons, and other trace gases are shown to the left. The types of effects caused by stratospheric ozone depletion and consequent increased UV-B penetration to the Earth's surface are hypothesized to include both direct effects on human health (e.g., increased cancer rates, immune suppression, etc.) and other terrestrial and aquatic ecological effects resulting from increased UV-B alterations of biogeochemical cycles.

Source: Adapted from Grant (1989).

atmospheric loadings of trace gases from anthropogenic emissions several decades ago, and those gases already in the atmosphere may continue to exert stratospheric ozone depletion effects well into the 21st century. Shorter lived gases, such as CH_3Br, also exert significant ozone depletion effects.

The main types of 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 or decreasing effectiveness of vacinations).

(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. The reader is referred for more detailed up-to-date information to the two most recently completed international assessments of processes contributing to stratospheric ozone depletion and the status of progress towards ameliorating the problem (WMO, 1999) and revised qualitative and quantitative projections of likely consequent human health and environmental effects (UNEP, 1998). (See Appendices 4A and 4B for synopses of key points abstracted from the executive summaries of these assessments).

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, and earlier discussions in this chapter [Sections 4.2.2.1 and 4.2.2.2]). As noted in the Zepp et al. 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. Also, studies of natural acquatic ecosystems indicate that organic matter is the primary determinant of UV-B penetration through water. Organic matter changes, caused by enhanced UV-B penetration and augmented by acidification and climate change, contribute to clarification of water and changes in light quality that broadly impact the effects of UV-B on aquatic biogeochemical cycles. Enhanced UV-B levels have both positive and negative impacts on aquatic ecosystem microbial activities 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.

As noted in the above detailed assessments, since the signing of the Montreal Protocol, much progress has been made in reducing emissions of ozone depleting gases, leading to estimates of the maximum extent of stratospheric ozone depletion as likely having been reached in the year 2000, 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. The role of atmospheric particles, discussed below, is one of numerous salient factors complicating modeling efforts.

4.5.1.2 Airborne Particle Impacts on Atmospheric Ultraviolet Radiation Transmission

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 (Bruehl 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 30^o to about 60^o, 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 Koschmeider'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 $\mu g/m^3$ for the polluted case. Estupinan 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. Also, 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,

$$\ln(\text{ SUVB transmission at solar noon}) = -0.1422\ \tau_{312\ \text{nm}} - 0.138,\ R^2 = 0.90,$$

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.

Liu et al. (1991) estimated, roughly, overall effects of increases of anthropogenic airborne particles that have occurred since the beginning of the industrial revolution on atmospheric transmission of SUVB. 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 the 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 also will be location-specific.

Also 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). Varying estimations of atmospheric transmission of UV and visible spectrum light are obtained for cloudy atmospheres, depending on presence of aerosols 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).

Given the above considerations, quantitation of projected effects of variations in atmospheric PM on human health or the environment because of particle impacts on transmission of solar UV-B would require location-specific evaluations, taking into account composition, concentration, and internal structure of the particles; temporal variations in atmospheric mixing heights and depths of layers containing the particles; and consequent impacts on surface-level exposures of humans, ecosystem constituents, or man-made materials. 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 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 PAH in certain freshwater lakes and coastal areas, and the adverse effects of solar UV are enhanced by uptake of PAH 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).

4.5.2 Global Warming Processes, Human Health and Environmental Impacts, and Atmospheric Particle Roles

4.5.2.1 Bases for Concern Regarding Global Warming and Climate Change

Various trace gases emitted because of man’s activities, including several noted above as contributing to stratospheric ozone depletion, can act as “greenhouse gases” (GHG). That is, as their tropospheric concentrations increase, they retard the escape of infrared radiation from the earth’s surface and thereby contribute to the trapping of heat near the surface (the “greenhouse effect”) and, ultimately, to consequent global warming and climate change. Much concern has evolved with regard to increases in the naturally very low concentrations in the atmosphere of some of these gases, especially carbon dioxide (CO_2), nitrous oxide (N_2O), methane (CH_4), chloroflurocarbons (CFCs), and tropospheric ozone (O_3).

Atmospheric processes involved in mediating global warming and its likely consequent effects have been reviewed extensively previously (United Nations Environment Programme, 1986; World Meteorological Organization, 1988; U.S. Environmental Protection Agency, 1987;

IPCC, 1996, 1998; US GCRP, 2000) and more concisely summarized by others (e.g., Grant 1989; Patz et al., 2000a; Patz et al., 2000b). The main focus here is (a) to provide first a very brief summary of key points regarding processes involved and types of effects projected as likely to be associated with global warming and climate change and, then, (b) to undertake discussion of salient considerations regarding potential impacts of atmospheric PM on such processes and effects.

All of the above noted assessments and summaries emphasize that estimating likely future global warming trends and associated climate change caused by greenhouse gases is extremely complex, with modeling results being highly dependent on key assumptions about the rates of future increases in various gases and numerous other factors (including particle effects). Modeling of the magnitude of the warming directly associated with radiative forcing by greenhouse gases (without feedback enhancement) projects temperature increases, for example, of about l.2 °C for a doubling of CO_2; another 0.45 °C for a simultaneous doubling of N_2O and CH_4; and an additional 0.15 °C from a uniform l-ppb increase in atmospheric concentrations of CFC-ll and CFC-12. Indirect effects (feedbacks) that likely would increase temperatures further are expected to occur. Increased water vapor (trapping heat) and snow and ice melting (reducing reflection of radiation back into space) are two examples of such feedback factors expected to increase temperatures. However, major uncertainties exist with regard to feedbacks between global warming and clouds, which could either amplify or, perhaps, reduce a temperature rise. Taking assumptions about rates of increase (or decrease) in GHG concentrations, consequent initial warming effects, feedback effects, and accompanying uncertainties into account, numerous modeling efforts have attempted to project likely future trends in global warming. Despite the complexity and uncertainties inherent in such modeling efforts, all typically agree that some global warming has occurred and will continue to occur during the coming decades, but the ranges of quantitative estimates vary considerably depending on specific assumptions incorporated into the models. Thus, for example, “low” scenarios assuming stabilization or reductions in GHG emissions (resulting from implementation of the 1987 Montréal Protocol) project lower temperature changes than other scenarios assuming higher rates of increase in GHG emissions or differing feedback-effect patterns.

Given the wide range of estimates of global warming trends and patterns of associated climate change emerging from modeling efforts, the estimation of likely human health and ecological effects associated with global warming on any quantitative basis is extremely difficult. The onset of any notable global warming effect is also important, with various analyses indicating that global temperatures for the past century have been rising (and now appear to be beyond average levels within the range of variation seen with cycles of global warming or cooling over the past several centuries before marked anthropogenic emissions of greenhouse gases occurred). Also posing difficulties for the quantitative estimation of human health and other effects are expected wide regional variations in temperature and climate characteristics (e.g., rain and snowfall amounts) that may be projected reasonably to result from various global warming trend scenarios. Lastly, it should be noted that, despite general warming trends in long-term average temperatures, wide extremes in both high *and* low temperatures also are expected to occur more frequently in some areas.

A Special Report of the IPCC Working Group II on Regional Impacts of Climate Change: An Assessment of Vulnerabilities (IPCC, 1998) assesses global warming processes and identifies several types of vulnerabilities likely to occur because of climate change resulting from global warming. Such general types of vulnerabilities include impacts on terrestrial and aquatic ecosystems, hydrology and water resources, food and fiber production, coastal systems, and human health. Appendix 4C provides excerpts of materials from the executive summary of the IPCC (1998) report that comprise a helpful overview of key points regarding projected global warming processes, likely climate change patterns, and their consequent impacts in terms of the types of vulnerabilities noted above.

The IPCC (1998) report notes that human activities resulting in emissions of long-lived GHCs are projected by General Circulation Models (GCMs) to lead to global and regional changes in temperature, precipitation and other climate variables—resulting in increases in global mean sea level; prospects for more extreme weather events, floods, and droughts in some areas; and consequent changes in soil moisture. Based on various scenarios of current and plausible future emissions of GHGs and aerosols and the range of sensitivities of climate change to atmospheric levels (and residence time) of GHGs, GCMs project mean annual global surface temperature increases in the range of 1 to 3.5 °C by 2100, a global mean sea level rise of 15 to 95 cm, and significant changes in spatial and temporal patterns of precipitation. The average rate of warming will be more rapid than any seen in the past 10,000 years, although regional changes could differ substantially from mean global rates.

Human health, ecosystems, and socioeconomic sectors (e.g., hydrology and water resources, food and fiber production, etc.) are projected to be vulnerable to the magnitude and rate of climate change, as well as increased climate variability. Wide variations in the courses and net impacts of climate change in different geographic areas can be expected, and, 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. 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. Appendix 4C also includes excerpts from the executive summary of the IPCC 1998 special report regarding the assessment of different types of vulnerabilities to climate change projected for each of 10 different geographic regions of the Earth, with emphasis being placed in Appendix 4C on those projected for two regions (North America and Polar) of most relevance to the continental United States and Alaska.

Appendix 4C notes that (a) the characteristics of subregions and sectors of North America suggest that neither impacts of climate change nor response options will be uniform, and (b) many systems of North America are moderately to highly sensitive to climate change, with the range of estimated effects including the potential for substantial damage or, conversely, the potential for some beneficial outcomes. The most vulnerable continental United States sectors and regions include long-lived natural forest ecosystems in the East and interior West, water resources in the southern plains, agriculture in the Southeast and southern plains, northern ecosystems and habitats, estuaries and beaches in developed areas, and low-latitude cool and cold water fisheries. Other 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 norther channels and ports; and agriculture in the northern latitudes, the interior West, and the west coast). For Alaska, substantial shifts in ecosystems (with possible major declines or loss of some sensitive species like bear and caribou or of other ice-dependent animals) may occur in parallel to beneficial effects such as opening of ice-bound water transportation routes or possible expanded agricultural viability secondary to longer growing seasons. On the other hand, for North America, the potential for mainly deleterious direct or indirect effects on human health is likely to increase (e.g., increased mortality directly linked to temperature extremes, increases in incidence and spread of vector-borne infectious diseases, impacts secondary to sea-level rise, and impacts secondary to increased tropospheric air pollution [as depicted in Figure 4-26]).

More detailed evaluations of possible global climate change impacts on various U.S. geographic areas are being conducted by the United States Global Change Research Program (USGCRP). An overview report on the assessment results and key findings from a series of workshops convened by the USGCRP National Assessment Synthesis team (NAST) has been prepared (USGCRP, 2000). Selected highly salient key points from the report and subsidiary regional assessments are presented in Appendix 4D. Overall key findings from the USGCRP (2000) report are noted below.

(1) *Increased Warming*. Assuming continued growth in world GHG emissions, the primary climate models used in the USGCRP assessment project that temperatures in the United States will rise by 5 to 10 °F (3 to 6 °C) on average during the next 100 years.

(2) *Differing Regional Impacts*. Climate change will vary widely across the United States. Temperature increases will vary somewhat from region to region. Heavy and extreme precipitation events are likely to become more frequent, yet some regions will get drier. The potential impacts of climate change will vary widely across the nation.

(3) *Vulnerable Ecosystems*. Many ecosystems are highly vulnerable to the projected rate and magnitude of climate change. A few, such as alpine meadows in the Rocky Mountains and some barrier islands, are likely to disappear entirely in some areas, with others, such as some forests of the Southeast, being likely to experience major species shifts or break up. Goods and services lost through disappearance or fragmentation of certain ecosystems are likely to be costly or impossible to replace.

(4) *Widespread Water Concerns*. Water is an issue in every region, but the nature of the vulnerabilities varies, with different nuances in each. Drought is an important concern in every region. Floods and water quality are concerns in many regions. Snowpack changes are especially important in the West, the Pacific Northwest, and Alaska.

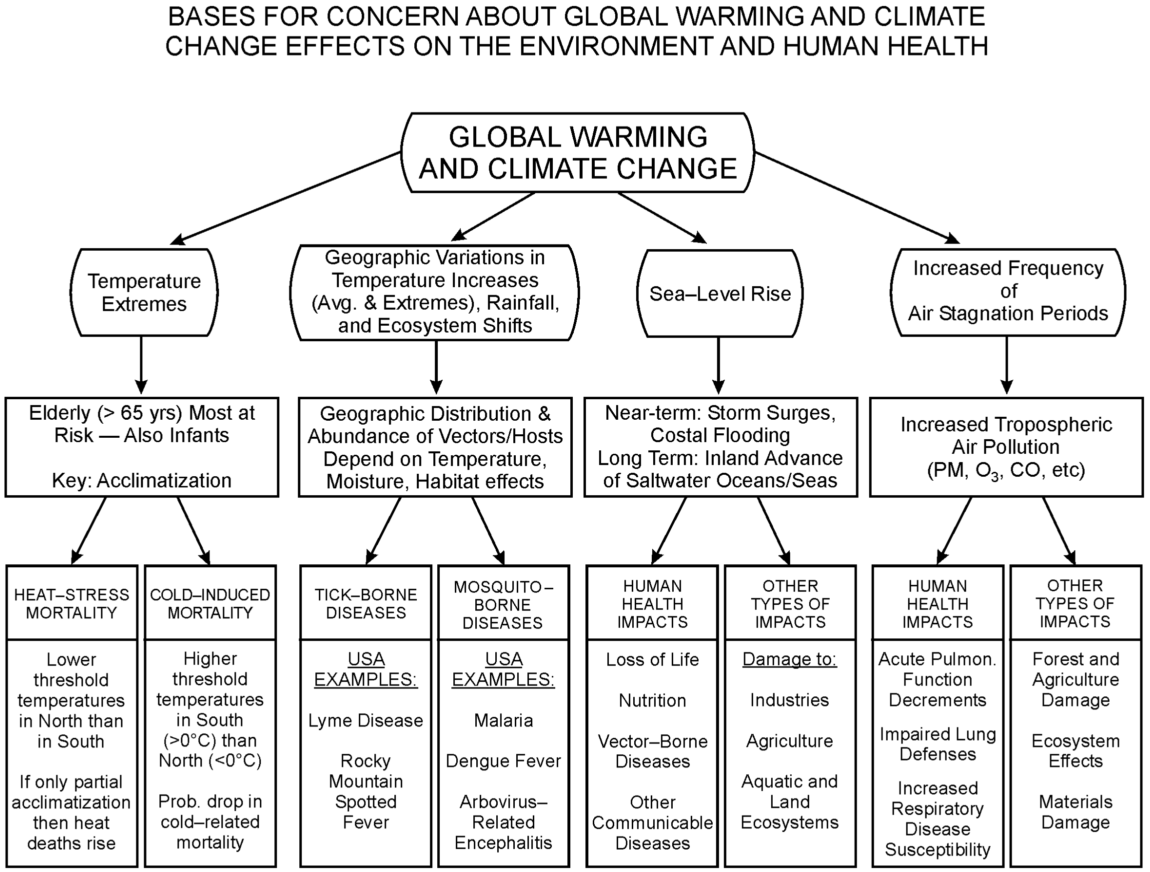

Figure 4-26. Bases for concern about global warming and climate change effects on the environment and human health. Types of hypothesized likely human health effects include (1) increases in mortality directly linked to temperature extremes, (2) increases in incidence and spread of vector-borne infectious diseases, (3) impacts secondary to projected sea-level rise, and (4) impacts secondary to increased tropospheric air pollution. Additional impacts can be expected because of shifting agricultural sustainability in various U.S. regions consequent to extreme weather patterns leading to inland flooding or droughts.

Source: Adapted from Grant (1989).

(5) *Secure Food Supply*. At the national level, the U.S. agriculture sector is likely to be able to adapt to climate change. Overall, U.S. crop productivity is very likely to increase over the next few decades, but the gains will not be uniform across the nation. Falling prices and competitive pressures are very likely to stress some farmers, while benefiting consumers.

(6) *Near-Term Increases in Forest Growth*. Forest productivity is likely to increase over the next several decades in some areas as trees respond to higher CO_2 levels. Over the longer term, changes in larger scale processes such as fire, insects, droughts, and disease will possibly decrease forest productivity. Also, climate change is likely to cause long-term shifts in forest species (e.g., distribution of sugar maple stands more northward, out of the United States).

(7) *Increased Damage in Coastal and Permafrost Areas*. Climate change and the resulting rise in sea level are likely to exacerbate threats to building, roads, powerlines, and other infrastructure in climatically sensitive places, such as low-lying coastlines and the permafrost regions of Alaska.

(8) *Other Stresses Magnified by Climate Change*. Climate change will very likely magnify the cumulative impacts of other stresses, such as air and water pollution and habitat destruction caused by human development patterns. For some systems, such as coral reefs, the combined effects of climate change and other stresses are very likely to exceed a critical threshold, bringing large, possibly irreversible impacts.

(9) *Surprises Expected*. It is likely that some aspects and impacts of climate change will be totally unanticipated as complex systems respond to ongoing climate change in unforeseeable ways.

(10) *Uncertainties Remain*. Significant uncertainties remain in the science underlying regional climate changes and their impacts. Further research is needed to improve understanding and predictive ability about societal and ecosystem impacts and to provide the public with additional useful information about adaptation strategies.

The selected findings highlighted in Appendix 4D from the USGCRP (2000) report and subsidiary regional reports illustrate well the considerable uncertainties and difficulties in projecting likely climate change impacts on regional or local scales. The findings presented in Appendix 4D also reflect well 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 assessing regional-specific potential impacts also can be illustrated by discussion below of determinants of the potential extent of direct or indirect impacts of global warming on human health, as abstracted from various published assessments cited above or alluded to in Appendices 4C, 4D, and 4E.

Modeling efforts and published analyses by Kalkstein and others have helped to identify important factors that affect the magnitude of temperature-dependent mortality and provide bases for projecting future temperature-related mortality trends (see Appendix 4E for recently published projections for U.S. cities by Kalkstein and Greene, 1997). Examples of key determinants of temperature-related mortality include (1) weather-sensitive mortality occurs mainly as a function of extremes of temperature beyond certain threshold points (for increasing or decreasing temperatures) that are characteristic of any particular city; (2) the extent of the mortality is generally more dependent on the duration of the periods (days) during which threshold points are exceeded than on maximum temperatures and also varies as a function of combined relative humidity, temperature, and barometric pressure conditions that constitute “oppressive” weather events that vary for different locales; and (3) the major population segment typically most severely affected are the elderly ($\geq$65 years old).

Threshold temperature findings for summer and winter in U.S. cities suggest that weather effects on mortality are relative (i.e., they vary in relation to the typical conditions to which local residents have become acclimatized). Thus, the highest summer threshold temperatures for mortality are found for the South and Southeast and the lowest in the Pacific and Northeast U.S. regions. Conversely, lowest threshold temperatures for winter mortality are found for cities in the coldest regions, whereas notably higher thresholds for cold-associated deaths occur for warmer region cities, with threshold values for some being well above the freezing point. Also, the total accumulated times of occurrence in the season of particular oppressive weather events are important determinants of mortality levels (e.g., hot conditions early in the spring and summer have a larger impact than similar conditions later in the summer, and length of a heat-stress period also has a larger impact than maximum temperatures reached).

Acclimatization is a key determinant of weather-related mortality, and the greatest initial increases in heat-related mortality might be expected in cities where temperatures are normally cooler or in areas where global-warming-induced climate changes lead to increased frequency and durations of high-temperature episodes. Eventual acclimatization may occur over the years, however, when higher-than-usual temperatures become the new norm for cities in currently cooler, more northern regions. As for cold-associated deaths, if average winter temperatures were not to drop as low as usual in various regions, then winter mortality might generally decrease because of fewer days falling below existing winter threshold levels for many cities.

But, if acclimatization occurs to higher average winter temperatures and wider variations in temperature extremes occur in some areas because of global-warming-induced weather changes, then those periods of lower maximum temperatures (especially of several days duration) could cause even higher than past mortality rates previously observed with comparable winter conditions. More sophisticated modeling also is needed to take into account combined effects of temperature extremes and weather-related increases in air pollutants as possible mortality determinants; for example, increased mortality or morbidity effects because of temperature extremes may be exacerbated or added to by higher surface level atmospheric PM derived from increased coal or oil combustion to generate more heat (in winter) or electricity (in summer for air conditioning) during extreme temperature periods.

In addition to concern about possible mortality increases because of temperature extremes, global warming, and consequent climate change also may impact human health through increases in some infectious diseases. For many parts of the world, infectious diseases remain among the leading causes of death, as occurred earlier in industrialized or “developed” countries (where diseases such as influenza, pneumonia, and tuberculosis were among the leading causes of death in 1900). Since then, the incidence and associated mortality for these and other infectious diseases such as diphtheria, typhus, and polio have been reduced dramatically in industrialized countries. In developed countries, it is not clear to what extent global-warming-induced climate change may cause general increases in the incidence of such diseases, unless serious disruptions of social structures occur or, in some coastal areas, breakdowns in sanitation systems happen as a consequence of sea-level rise. The spread of infectious diseases is likely of greater concern for many less developed countries, where inadequate medical care systems, immunization programs, housing conditions, and nutrition make them more vulnerable to the spreading of such diseases.

Of particular shared concern for both developed and less developed countries with regard to potential global warming impacts are infectious diseases spread by climate-dependent vectors. Vector-borne diseases are those for which the infectious microbial agent is transmitted to humans via another agent (the vector), such as the flea, tick, or mosquito. Well known examples of vector-borne diseases are malaria (transmitted to humans via mosquitos) and bubonic plague (transmitted via fleas or, at times, via animals directly to man as a respiratory disease). Climate change can affect vector-borne diseases by various direct impacts on the infectious agent, the vector, or intermediate hosts through variations in temperature, humidity, rainfall, or storm patterns that alter (1) the multiplication rates of the infectious agent or the vector, (2) the biting rate of the vector, (3) the geographic distribution of the intermediate animal hosts, or (4) the amount of time that intermediate hosts or human hosts are exposed to the vector. Climate change also can affect indirectly the rates or incidences of vector-borne diseases via impacts on agricultural practices, ecosystem mixes (of grasses, trees, underbrush, etc.), surface water levels, or other factors that determine intermediate host or vector distribution or survival. The variety of vector-borne diseases is considerable, with some being of more concern than others for particular countries, depending on specific climatic conditions and existing pools of infected hosts (both human and intermediate animal hosts). Examples of vector-borne diseases illustrative of concerns that apply to the United States for potential spread of vector-borne diseases include Lyme disease, Rocky Mountain spotted fever, dengue fever, malaria, and viral encephalitis.

Lyme disease (initially recognized in Lyme, CT) is an inflammatory disease caused by a spirochete, *Borrelia burgdorferi*, transmitted by several subspecies of *Ixodes racinus* ticks. Numerous species of birds and mammals can be hosts for various subspecies of the tick vector, with varying geographic distributions. Lyme disease has four major U.S. foci, is spreading rapidly, and has been found in Europe (Germany, Switzerland, France, and Austria). The U.S. distribution of human cases of the disease tends to match areas where the tick vector is abundant, and deer populations, along with factors such as temperature, humidity and local vegetation, represent key determinants of tick abundance. The precise impact of global warming and climate change on the distribution of Lyme disease is difficult to estimate. Lengthening of warm weather periods and shortening of winter weather could enhance tick vector abundance and its potential spread into adjoining areas if the weather changes (temperature, precipitation, etc.) were to favor wider distribution of deer or other animal or bird hosts. Shifts of human populations into or out of affected areas in response to changes in local climate also would help determine location-specific alterations in Lyme disease rates.

Rocky Mountain spotted fever (initially identified in western mountain areas but actually much more prevalent in southeastern U.S. states) is a highly fatal disease if not promptly diagnosed and treated. Caused by the occobacillus, *Rickettsiae rickettsii*, the disease is spread by ticks and is also known as tick fever, with analogous diseases occurring in many other countries. The main North America vectors are the dog tick, *D. variabilis*, and the wood ticks, *D. andersoni* and *D. occidentalis*, with varying geographic distributions. Geographic tick distributions parallel closely the typical U.S. distribution of disease cases (highest incidence across the South). Crucial for the spread of Rocky Mountain spotted fever is the wide variety of intermediate hosts available to the ticks (i.e., many woodland mammals and birds) and temperature. Certain optimum ranges of high temperatures (24 to 30 °C) likely speed the rickettsial growth in the ticks, and ambient temperatures are important in determining tick breeding season length and cycles, as well as their activity levels and biting rates. Each are enhanced by higher temperatures, and the abundance of the vector is held in check, in part, by frequency and length of time that winter temperatures drop well below freezing, thus killing overwintering adults. Lastly, relative humidity conditions and rainfall are important as well, in that hot dry weather results in desiccation of ticks and their eggs, reducing reproduction rates. Global warming-induced climate change might increase the range of Rocky Mountain spotted fever tick vectors into more northward U.S. areas and, possibly, into Canada, assuming the climate change includes sufficient rainfall to sustain adequate habitats for host species and adequate moisture for survival of ticks and eggs. Hot, dry periods caused by any prolonged drought conditions in the United States or Canada predicted by some global warming scenarios, conversely, would not be conducive to increased incidence of the disease in drought-affected areas.

Malaria, once widespread in the southern United States, remains endemic in many areas of the world and is caused by four agents: (1) *Plasmodium vivax*, (2) *P. malariae*, (3) *P. ovale*, and (4) *P. falciparum*. The agents cause clinical syndromes of varying severity, the most serious being caused by *P. falciparum*, which can progress to death (>10% fatality in untreated children and nonimmune adults). The other forms, although less severe, are still debilitating and are typified by recurring episodes of fever, chills, and sweating. Malarial agents are transmitted from infected humans, as the main host pool, by the bite of various subspecies of anopheles mosquitos. Ambient temperatures of at least 15 to 18 °C are crucial for development of the malarial agents within the mosquitos, and ambient temperature levels determine breeding season length and survival rates (higher tropical temperatures being most favorable). Man’s agricultural activities, in providing irrigation ditches and more stagnant water habitats, has contributed to spread and abundance of the anopheles mosquito in many areas of the world. Malaria is now rarely endogenously transmitted in the United States, the pool of infected humans as hosts having been reduced very substantially, owing to mosquito eradication programs. Prior to such programs, the disease was endemic in widespread southern U.S. areas up to the 1940s, but, since then, outbreaks mainly have occurred because of infected immigrants entering the country or U.S. military veterans returning from overseas endemic areas. Global warming leading to higher temperatures in more northerly U.S. areas and Europe could enhance conditions for the spread of the disease. Both the range and abundance of competent vectors (various anopheles subspecies) likely would be increased, especially if increased irrigation were required to support agriculture, owing to higher temperatures. Also, higher temperatures in more northerly areas could extend the range of adequate temperatures (>15 to 18 °C) needed for development of malarial agents in the mosquitos. The remaining key factor in determining the likelihood of the spread of malaria, however, is the infected host pool, with numbers of infected human hosts moving into or out of areas of enhanced vulnerability being of crucial importance, as emphasized by Longstreth (1999).

Dengue fever, another mosquito-borne disease, is caused by four serotypes of a Group B arbovirus. Fever, general muscle ache, severe headache, and retroorbital pain typify dengue fever (usually not fatal); but it can progress to dengue haemorrhagic fever or dengue shock syndrome (often fatal). Once endemic along the U.S. Gulf and South Atlantic coasts, dengue fever is now rarely endogenously transmitted in the United States. The *Aedis aegypti* mosquito is the primary vector, with wide southern U.S. distribution. The breeding season of the *A. aegypti* mosquito is temperature-dependent, with breeding year-round in southern Florida, nearly year-round elsewhere in Florida and along the Gulf Coast, and much shorter for successively more northward bands of geographic distribution. Another potential vector, *Aedes triseriatus*, is endogenous to states east of the Mississippi, and *Aedes albopictus*, a proven dengue vector introduced from northern Asia, has been found in scattered U.S. sites. Higher temperatures are also crucial for dengue transmission; transmission of dengue occurred experimentally only if *A. aegypti* mosquitos were kept at 30 °C, and the incubation period for the virus to develop in the mosquitos was shortened at 32 to 35 °C. Consistent with this, cases of dengue haemorrhagic fever increased at non-U.S. sites when daily mean temperatures were 28 to 30 °C during hot seasons, but decreased at the sites during cooler seasons with 25 to 28 °C temperatures. Temperature increases in temperate ozone areas with *A. Aegypti* or *A. albopictus* present would tend to expand the range of these dengue fever vectors, including potential spread especially of *A. albopictus* farther north in the United States and, perhaps, into Canada, in view of its adaptation to cold weather as well. Whether or not increases in dengue will actually occur, however, likely will depend on the distribution of rainfall and moisture content, the effects of agricultural practices (e.g., increased irrigation), and movements of infected human hosts into or out of areas with increased vector density.

Arbovirus-induced encephalitis syndromes vary in severity but include several that can be highly fatal and are related to several other types of arbovirus-related syndromes (e.g., yellow fever, dengue and other haemorrhagic fevers, hepatitis, arthritis, rashes, various tropical fevers). Different types of mosquitos that serve as competent vectors for various types of arbovirus-induced encephalitis of concern for the United States display different patterns of distribution and differentially infect other hosts besides man (e.g., birds and large vertebrates [horses, etc.] for some, birds and swine for another, and small woodland animals for others). All have temperature-dependent components involved in development or transmission of the viruses, but specific effects vary for different types. For example, the maximum temperatures allowing the western equine encephalitis (WEE) vector to transmit the virus effectively are below 25 °C, and this allows for earlier spread of the disease in warm periods and the possible more northern spread of the disease. In contrast, St. Louis encephalitis (SLE) arbovirus development and transmission are markedly enhanced by temperatures exceeding 25 °C. Rainfall and moisture patterns are also important, with most vectors (e.g., *Cx tarsalis*) benefitting from higher rainfall; but at least one (*Cx pipiens*) is enhanced by less rainfall, with outbreaks of its encephalitis syndrome being more common during high-temperature drought periods. Thus, effects of global warming and climate change on the incidence and spread of arbovirus-related encephalitis syndromes are difficult to predict. However, it generally appears that higher temperatures should enhance the abundance and wider U.S. geographic distribution of most of the competent mosquito vectors. All of this again assumes that higher temperatures and rainfall patterns will be such to allow adequate habitats for other hosts besides humans in the potential new range areas. Lastly, as noted before for the other infectious diseases discussed, the movement of populations into or out of the affected areas also will be important in determining any location-specific increased (or decreased) incidence of arbovirus-related encephalitises. Of special concern would be the introduction of any new arboviruses not now currently endemic in the United States (e.g., Japanese B encephalitis [VBE], not currently found in the United States but closely related to SLE in terms of involving *Culex* mosquitos and birds, with several *Culex* subspecies in the United States found to be effective vectors for the virus).

The above discussion of potential effects of global warming and climate change on the incidence and spread of infectious diseases is further complicated by considerations of possible impacts of expected sea-level rise in response to global warming. Some low-lying coastal areas now serving as excellent habitats for certain mosquitos, for example, might come to be inundated by seawater and no longer be available breeding areas. Or, increased storm surges or expansion of marshy areas reaching farther inland might contribute to creation of conditions in some areas more favourable to enhance mosquito breeding. Also of concern is the potential for disruption of sanitation systems. The spread of infectious diseases, besides the vector-borne types discussed above, could be increased because of flooding of coastal cities secondary to heavy precipitation events (e.g., hurricanes). Inundation of sewage treatment facilities and sewage lines might not only result in immediate spread of disease-containing fecal or other material, but damage to such sanitation system components could result in longer term disruption of waste-removal capabilities and the spread of disease.

Lastly, another concern with climate-induced heavy precipitation events or sea-level rise is the potential for flooding of inland or coastal waste disposal sites. This could result in increased spread of waterborne infectious diseases, depending on the specific materials present in such dumps and the extent of their dispersal caused by flooding. The flooding of dump sites containing hazardous chemical wastes represents yet another potential concern associated with sea-level rise. The spread of various toxic chemicals from such waste disposal sites could carry with it increased threats of many types of possible health effects, as well as potential environmental effects (natural vegetation and ecosystem damage, contamination of crop lands by toxic chemicals, etc.).

Difficulties in projecting region-specific climate change impacts are complicated further 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. Of much importance for this are varying roles played by atmospheric particles.

4.5.2.2 Airborne Particle Relationships to Global Warming and Climate Change

Atmospheric particles both scatter and absorb incoming solar radiation at visible light wavelengths. The scattering of solar radiation back to space leads to a decrease in transmission of visible radiation to the Earth's surface and, hence, to a decrease in the heating rate of the surface and the atmosphere. The absorption of either incoming solar radiation or outgoing terrestrial infrared radiation by atmospheric particles results in heating of the lower atmosphere. Interactions of atmospheric particles with electromagnetic radiation from the visible through the infrared spectral regions are responsible for their direct effects on climate, which are the result of the same physical processes responsible for visibility degradation. Visibility reduction is caused by particle scattering in all directions, whereas climate effects result mainly from scattering in the upward direction. The net effect of the above processes can be expressed as a radiative forcing, which is the change in the average net radiation at the top of the troposphere because of a change in solar (shortwave, or visible) or terrestrial (longwave, or infrared) radiation (Houghton et al., 1990). The radiative forcing drives the climate to respond, but because of uncertainties in a number of feedback mechanisms involving climate response, radiative forcing is used as a first-order estimate of the potential importance of various substances. Sulfate particles scatter solar radiation effectively and do not absorb at visible wavelengths, whereas they absorb weakly at infrared wavelengths (IPCC, 1995). Nitrate particles exhibit grossly similar properties. The effects of mineral dust particles are complex; they weakly absorb solar radiation but their overall effect on solar radiation depends on particle size and the reflectivity of the underlying surface. They absorb infrared radiation and thus contribute to greenhouse warming (Tegen et al., 1996). Organic carbon particles mainly reflect solar radiation, whereas elemental carbon and other black carbon particles (e.g., PAHs with H:C ratios of ≤ 0.3) are strong absorbers of solar radiation (IPCC, 1995). However, the optical properties of carbonaceous particles are modified if they become coated with water or sulfuric acid. Particles containing black carbon also can exert a direct effect after deposition onto surfaces that are more reflective (e.g., snow and ice). In this case, additional solar radiation is absorbed by the surface; conversely, more reflective particles deposited on a dark surface result in additional solar radiation being reflected back to space.

Anthropogenic (Twomey, 1974; Twomey, 1977) and biogenic (Charlson et al., 1987) sulfate particles also exert indirect effects on climate by serving as cloud condensation nuclei, which results in changes in the size distribution of cloud droplets by producing more particles with smaller sizes. The same mass of liquid water in smaller particles leads to an increase in amount of solar radiation that clouds reflect back to space because the total surface area of the cloud droplets is increased. This has been supported by satellite observations indicating that the effective radius of cloud droplets is smaller in the Northern Hemisphere than in the Southern Hemisphere (Han et al., 1994). Smaller cloud droplets also have a lower probability of precipitating and, thus, have a longer lifetime than larger ones. Although the effects of sulfate have been considered most widely, interactions with other aerosol components also may be important. Novakov and Penner (1993) have provided evidence that carbonaceous particles can modify the nucleation properties of sulfate particles.

The amount of solar radiation incident on the earth-atmosphere system, or the solar constant, is 1370 W m^{-2}, or 342.5 W m^{-2} on a globally averaged basis (calculated by dividing the solar constant by 4). The addition of sulfate and organic carbon as airborne PM results in enhanced scattering and net cooling, whereas the addition of particles containing elemental carbon results in absorption of solar and terrestrial radiation and net heating. The estimated raditive forcing because of the scattering of solar radiation back to space caused mainly by sulfate particles is −0.4 W m^{-2} (IPCC, 1995), with an uncertainty range of a factor of two. The uncertainty range reflects uncertainties in the emissions of SO_2, the amount of SO_2 that is oxidized to sulfate, the atmospheric lifetime of sulfate, and the optical properties of the sulfate particles. These values may be compared to the radiative forcing exerted by greenhouse gases of about + 2.4 W m^{-2}, with an uncertainty factor of 1.15 from the preindustrial era (ca. 1800) to 1994. Since the latter part of the 19th century, the mean surface temperature of the earth has increased from 0.3 to 0.6 °C according to the IPCC (1995) assessment. Estimates of the indirect effects of particles range from 0 to −1.5 W m^{-2} (IPCC, 1995). Because of a lack of quantitative knowledge, no central value could be given. Therefore, on a globally averaged basis, the direct and indirect effects of anthropogenic sulfate particles likely have offset partially the warming effects caused by increases in levels of greenhouse gases (Charlson et al., 1992).

Much of the work investigating the effects of particles on climate has focused on sulfate particles. However, particles containing elemental carbon (EC) from fossil fuel combustion and biomass burning or mineral dust may exert radiative forcing, with spatial distributions very different than for sulfate. Tegen et al. (1996) and Tegen and Lacis (1996) used a global scale three-dimensional model to evaluate the radiative forcing caused by mineral dust particles. Tegen and Lacis (1996) found that the sign and the magnitude of the radiative forcing depends on the height distribution of the dust and the effective radius of the particles. In particular, for a dust layer extending from 0 km to 3 km, positive radiative forcing at visible wavelengths is found for particle radii greater than 1.8 μm, whereas negative forcing is found for smaller particles. They calculated a global mean radiative forcing caused by mineral dust from all sources of 0.14 W m^{-2} and from mineral dust from lands disturbed by human activity of 0.09 W m^{-2}. This value represents a near cancellation between a much larger solar forcing of −0.25 W m^{-2} and a thermal forcing of 0.34 W m^{-2}. Uncertainty factors could not be estimated for these calculations because they were judged to be largely unknown. Haywood and Shine (1995) estimated a global mean radiative forcing of 0.1 W m^{-2}, with an uncertainty factor >3, caused by the absorption of solar radiation by EC released by fossil fuel combustion. The IPCC (1995) estimated a global mean radiative forcing of −0.1 W m^{-2} caused by particles produced by biomass burning, with an uncertainty factor of three. The global mean radiative forcing exerted by particles would then be −0.5 W m^{-2}, with an uncertainty of about a factor of 2.4. Figure 4-27 summarizes estimates of global mean radiative forcing exerted by greenhouse gases and various types of particles.

Deviations from the global mean values 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 4-27. 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.

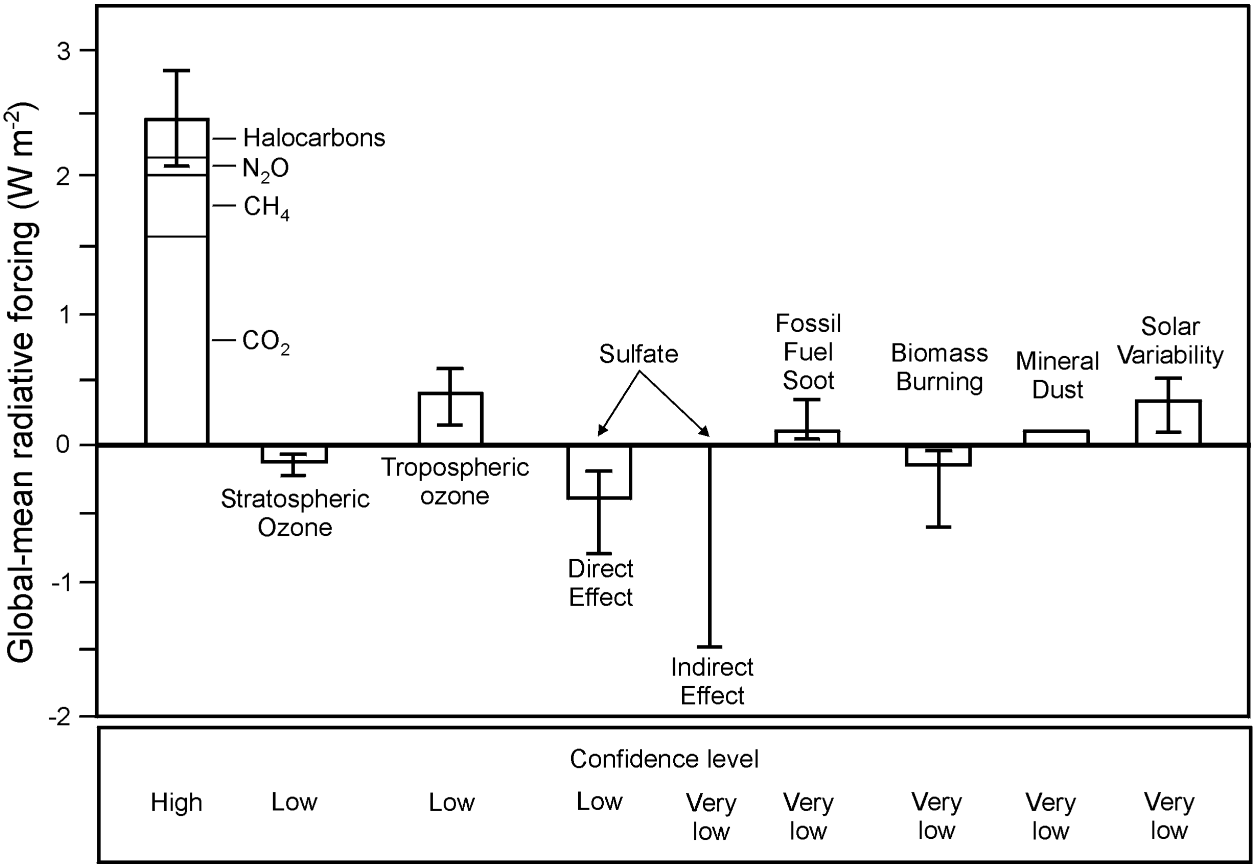

Figure 4-27. Estimated global mean radiative forcing exerted by gas and various particle phase species from 1850 to 1950.

Source: Adapted from IPCC (1995) and Tegen and Lacis (1996).

Observational evidence for the climatic effects of particles is sparse. 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.

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 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 in describing the effects of sulfate on the size distribution and number of droplets within a cloud. A complete assessment of the radiative effects of PM will require supercomputer calculations that incorporate the spatial and temporal behavior of particles of varying composition that have been emitted 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) caused by sulfate. However, uncertainties associated with the calculation of radiative effects of particles likely will remain much larger than those associated with well-mixed greenhouse gases.

This means that, although on a global scale atmospheric particles likely exert an overall net effect of slowing global warming, much uncertainty would apply to any modeling efforts aimed at projecting net effects on global warming processes, resulting climate change, and any consequent human health or environmental effects because of location-specific increases or decreases in anthropogenic emissions of atmospheric particles or their precursors. For example, any net impacts of regional sulfates in reducing global-climate-change-induced increases in local temperatures may well be offset partially by local surface level heating because of carbonaceous particles from diesel emissions or coal combustion energy generation being deposited on snow or ice covered surfaces or contributing to more rapid evaporation or rainout of water from overhead clouds.

4.6 SUMMARY

4.6.1 Particulate Matter Effects on Vegetation and Ecosystems

Human existence on this planet depends on ecosystems and the services and products they provide. Both ecosystem structure and function play an essential role in providing societal benefits. Society derives two types of benefits from the structural aspects of an ecosystem: (1) products with market value such as fish, minerals, forage, forest products, biomass fuels, natural fiber, and many pharmaceuticals, and the genetic resources of valuable species (e.g., plants for crops and timber and animals for domestication); and (2) the use and appreciation of ecosystem for recreation, aesthetic enjoyment, and study.

Ecosystem functions that maintain clean water, pure air, a green earth, and a balance of creatures, are functions that enable humans to survive. They are the dynamics of ecosystems. 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, climate, and the fixation of solar energy. Concern has risen in recent years concerning the integrity of ecosystems because there are few ecosystems on the Earth today that are not influenced by humans. For this reason, the deposition of PM and its impact on vegetation and ecosystems is of great importance.

The PM whose effects on vegetation and ecosystems are considered in this chapter 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 (measured as PM_{10}; $PM_{2.5}$, etc.) may, depending on the particular mix of deposited particles, lead to widely differing phytotoxic responses. This has not been characterized adequately.

Atmospheric deposition of particles to ecosystems takes place via both wet and dry processes through the three major routes indicated below.

(1) Precipitation scavenging, in which particles are deposited in rain and snow

(2) Fog, cloud water, and mist interception

(3) Dry deposition, a much slower, yet more continuous removal to surfaces

Deposition of heavy metal particles to ecosystems occurs by wet and dry processes. Dry deposition is considered more effective for coarse particles of natural origin and elements such as iron and manganese, whereas wet deposition generally is more effective for fine particles of atmospheric origin and elements such as cadmium, chromium, lead, nickel, and vanadium. The actual importance of wet versus dry deposition, however, is highly variable, depending on the type of ecosystem, location, and elevation.

Deposition of PM on above-ground plant parts can have either a physical and or chemical impact, or both. 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) be 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.

Chemical effects include excessive alkalinity or acidity. The effects of “inert” PM are mainly physical, whereas the effects of toxic particles are both chemical and physical. The effects of dust deposited on plant surfaces or on soil are more likely to be associated with their chemistry than with the mass of deposited particles and are usually of more importance than any physical effects. The majority of the easily identifiable direct and indirect effects, other than climate-change impacts, occur in severely polluted areas around heavily industrialized point sources such as limestone quarries; cement kilns; and iron; lead, and various smelting factories. Studies of the direct effects of chemical additions to foliage in particulate deposition have found little or no effects of PM on foliar processes; however, both conifers and deciduous species have shown significant effects on leaf surface structures after exposure to simulated acid rain or mist at pH 3.5. Many experimental studies indicate that epicuticular waxes (which function to prevent water loss from plant leaves) can be destroyed by acid rain in a few weeks. This function is particularly crucial in conifers because of the longevity of evergreen foliage.

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 indicator of metal stress. Because they are produced by plants as a response to sublethal concentrations of heavy metals, they can be used to indicate that heavy metals are involved in forest decline. Concentrations of the phytochelatins increased with altitude, as did forest decline, and they also increased across regions showing increased levels of forest injury.

Secondary organics formed in the atmosphere 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). The chemical substances listed under the above headings are not criteria pollutants controlled by NAAQS as cited under CAA Sections 108 and 109 (U.S. Code, 1991), but rather are controlled under CAA Sect.112, Hazardous Air Pollutants. Their possible effects in the environment on humans and ecosystems are discussed in many other government documents and publications. They are mentioned 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 impact 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 the 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 yields have been reported as being sensitive to the amount of sunlight received, and crop losses have been attributed to increased airborne particle levels in some areas of the world.

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 chlorofluorcarbons and other ozone-depleting substances has resulted in heightened concern regarding potentially serious increases in the amount of solar UV-B (SUVB) radiation reaching the Earth’s surface. Plant species vary enormously in their response to UV-B exposures, and large differences in response also occur among different genotypes within a species. In general, dicotyledonous plants are more sensitive than monocotyledons from similar environments.

In addition, plant responses may differ depending on stage of development. Because plants evolved under the selective pressure of ambient UV-B radiation in sunlight, they have developed adaptive mechanisms. Although inhibition of photosynthesis is a detrimental growth effect, flavonoid synthesis represents acclimation. Plants growing under full light have been shown to be protected against UV-B effects but not when growing under weak visible light. A common adaptation is alteration in leaf transmission properties, which results in attenuation of UV-B in the epidermis before it can reach the leaf interior.

Indirect effects of PM on plants are usually the most significant because they can alter nutrient cycling in ecosystems and inhibit plant uptake of nutrients and, therefore, have a great impact on ecosystem biodiversity. Indirect effects occur through the soil and result from the deposition of heavy metals, nitrates, sulfates, or acidic precipitation and their impact on the soil microbial community. The soil environment is one of the most dynamic sites of biological interaction in nature. Bacteria in the soil are essential components of the nitrogen and sulfur cycles that make these elements available for plant uptake. Fungi 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 and fungi in nutrient cycling and availability determine plant and ecosystem response.

Major impacts of PM on soil environments occur through deposition of nitrates and sulfates and the acidifying effect of the H^+ ion associated with these compounds in wet and dry deposition. Although the soils of most of North American forest ecosystems are nitrogen limited, there are some forests that exhibit severe symptoms of nitrogen saturation. They include the high-elevation, spruce-fir ecosystems in the Appalachian Mountains; the eastern hardwood watersheds at the Fernow Experimental Forest near Parsons, WV; the mixed conifer forest and chaparral watershed with high smog exposure in the Los Angeles Air Basin; the high-elevation alpine watersheds in the Colorado Front Range; and a deciduous forest in Ontario, Canada.

Nitrogen saturation results when additions to soil background nitrogen (nitrogen loading) exceed the capacity of plants and soil microorganisms to utilize and retain nitrogen. An ecosystem no longer functions as a sink under these circumstances. Possible ecosystem responses to nitrate saturation, as postulated by Aber and his coworkers, include (1) a permanent increase in foliar nitrogen and reduced foliar phosphorus and lignin because of the lower availability of carbon, phosphorus, and water; (2) reduced productivity in conifer stands caused by disruptions of physiological function; (3) decreased root biomass and increased nitrification and nitrate leaching; (4) reduced soil fertility, the results of 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. The appearance of nitrogen in soil solution is an early symptom of excess nitrogen. In the final stage, disruption of forest structure becomes visible.

Changes in nitrogen supply can have a considerable impact on an ecosystem's nutrient balance. Increases in soil nitrogen play a selective role. Plant succession patterns and biodiversity are affected significantly by chronic nitrogen additions in some 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. For example, 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. Excess nitrogen inputs to unmanaged heathlands in the Netherlands also have been found to result in nitrophilous grass species replacing slower growing heath species. Over the past several decades, the composition of plants in the forest herb layers had 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.

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). Together with excess nitrogen runoff 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.

Acidic deposition has played a major role in soil acidification in some areas of Sweden, elsewhere in Europe, and in eastern North America. Soil acidification and its effects result from deposition of nitrates, sulfates, and associated H^+ ion. A major concern is that soil acidity will lead to nutrient deficiency. Growth of tree species can be affected when high aluminum-to-nutrient ratios limit uptake of calcium and magnesium and create a nutrient deficiency. Calcium is essential in the formation of wood and the maintenance of cells (the primary plant tissues necessary for tree growth), and it must be dissolved in soil water to be taken up by plants. Acidic deposition can increase aluminum concentrations in soil water by lowering the pH in aluminum-rich soils through dissolution and ion-exchange processes. Aluminum in soil can then be taken up by roots more readily than calcium because of its greater affinity for negatively charged surfaces. Tree species can be adversely affected if altered Ca/Al ratios impair Ca or Mg uptake.

Overall, then, PM produced by human activities has the potential to cause the loss of ecosystem biodiversity in ways that reduces the ability of ecosystems to provide the services that society requires to sustain life. The major impacts of PM on ecosystems are the indirect effects that occur through the soil and affect plant growth, vigor, and reproduction. Mineral nutrient cycling can be altered by the deposition of heavy metals. The deposition of nitrogen and sulfur and the acidifying effects of the two in association with the H^+ ion in precipitation also alter biogeochemical cycling, cause soil acidification, alter the Ca/Al ratio, and impact the growth of vegetation and forest trees, in particular. Leaching of nitrates and other minerals through runoff can impact coastal and aquatic wetlands and, thus, influence their ability to produce the products and services necessary for human society.

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 distinquished 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), the light scattering coefficient, and fine PM 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}). Atmospheric particles are frequently divided into fine and coarse particles. 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 change in the optical properties of the atmosphere over the length of the sight path.

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. Haziness in the southeastern United States, caused by increased atmospheric sulfate, has increased by ca. 80% since the 1950s and is greatest in the summer months, followed by the spring and fall, and winter. Light scattering by nitrate aerosols is the major cause of visibility impairment in Southern California. Nitrates contribute about 40% to the total light extinction in Southern California and accounts for 10 to 20% of the total extinction in other U.S. areas.

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 Pacific Northwest, Oregon, Idaho, and Montana, accounting for 40 to 45% of the total extinction. Also, 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 U.S. areas.

Coarse mass and soil, primarily considered “natural extinction”, is responsible for some of the visibility impairment in northern California and Nevada, Oregon, southern Idaho, and western Wyoming. Dust transported from Southern California and the subtropics has been associated with regional haze in the Grand Canyon and other southwestern U.S. class I areas.

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 that protects against environmentally induced corrosion. The natural process of metal corrosion from exposure to natural environmental elements is enhanced by exposure to anthropogenic pollutants, in particular SO_2, rendering 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 life usefulness of the material soiled. 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 Particulate Matter on the Transmission of Solar Ultraviolet Radiation and Global Warming Processes

Extensive potential future impacts on human health and the environment are projected to occur because of increased transmission of solar ultraviolet radiation (UV-B) through the Earth's atmosphere, secondary to stratospheric ozone depletion resulting from anthropogenic emissions of chlorofluorcarbons (CFCs), halons, and certain other gases. However, the estimation of the likely future extent of detrimental effects caused by increased penetration of solar UV-B to the Earth's surface is complicated by atmospheric particle effects, which vary depending on size and composition of particles that can differ substantially over different geographic areas and from season to season over the same area. Also, atmospheric particles greatly complicate projections of future trends in global warming processes because of emissions of greenhouse gases; consequent increases in global mean temperature, and resulting changes in regional and local weather patterns; and mainly deleterious (but some beneficial) location-specific human health and environmental impacts.

The physical processes (i.e., scattering and absorption) responsible for airborne particle effects on transmission of solar ultraviolet and visible 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. 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. Depending on the amount of absorbing substances in the particles, photolysis rates either can be increased or decreased.

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 the global warming effects caused by the buildup of greenhouse gases because the onset of the Industrial Revolution, 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. This also would be the case for any projections of impacts of location-specific airborne PM alterations on potential human health or environmental effects associated with either increased atmospheric transmission of solar UV radiation or global warming secondary to accumulation of stratospheric ozone-deleting substances or “greenhouse gases.”

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APPENDIX 4A

Excerpted Key Points from the Executive Summary of the World Meteorological Organization 1998 Assessment of Stratospheric Ozone Depletion (World Meteorological Organization, 1999)

Among the provisions of the 1987 Montreal Protocol on Substances that Deplete the Ozone Layer was the requirement that the Parties to the Protocol base their future decisions on available scientific, environmental, technical, and economic information, as assessed by worldwide expert communities. Advances in the understanding of ozone science over this decade were assessed in 1988, 1989, 1991, and 1994. This information was input to the subsequent Amendments and Adjustments of the 1987 Protocol. The 1998 assessment summarized below is the fifth in that series.

Recent Major Scientific Findings and Observations

Since the Scientific Assessment of Ozone Depletion: 1994, significant advances have continued to be made in understanding of the impact of human activities on the ozone layer, the influence of changes in chemical composition on the radiative balance of the Earth's climate, and, indeed, the coupling of the ozone layer and the climate system. Numerous laboratory investigations, atmospheric observations, and theoretical and modeling studies have produced several key ozone- and climate-related findings that are discussed below.

- **The total combined abundance of ozone-depleting compounds in the lower atmosphere peaked in about 1994 and now is slowly declining. Total chlorine is declining, but total bromine is still increasing**. As forecast in the 1994 Assessment, the long period of increasing total chlorine abundances—primarily from the chlorofluorocarbons (CFCs), carbon tetrachloride (CCl_4), and methyl chloroform (CH_3CCl_3)—has ended. The peak total tropospheric chlorine abundance was 3.7 ± 0.1 parts per billion (ppb) between mid-1992 and mid-1994. The declining abundance of total chlorine results principally from reduced emissions of methyl chloroform. Chlorine from the major CFCs is still increasing slightly. The abundances of most of the halons continue to increase (for example, Halon-1211, almost 6% per year in 1996), but the rate has slowed in recent years. These halon increases likely are caused by emissions in the 1990s from the halon “bank,” largely in developed countries, and new production of halons in developing countries. The observed abundances of CFCs and chlorocarbons in the lower atmosphere are consistent with reported emissions.

- **The observed abundances of the substitutes for the CFCs are increasing**. Abundances of the hydrochlorofluorocarbons (HCFCs) and hydrofluorocarbons (HFCs) are increasing as a result of continuation of earlier uses and of their use as substitutes for the CFCs. In 1996, the HCFCs contributed about 5% to the tropospheric chlorine from the long-lived gases. This addition from the substitutes offsets some of the decline in tropospheric chlorine associated with methyl chloroform, but is still about 10 times less than that from the total tropospheric chlorine growth rate throughout the 1980s. The atmospheric abundances of HCFC-141b and HCFC-142b calculated from reported emissions data are factors of 1.3 and 2, respectively, smaller than observations. Observed and calculated abundances agree for HCFC-22 and HFC-134a.
- **The combined abundance of stratospheric chlorine and bromine is expected to peak before the year 2000.** The delay in this peak in the stratosphere compared with the lower atmosphere reflects the average time required for surface emissions to reach the lower stratosphere. The observations of key chlorine compounds in the stratosphere up through the present show the expected slower rate of increase and show that the peak had not occurred at the time of the most recent observations that were analyzed for this assessment.
- **The role of methyl bromide as an ozone-depleting compound is now considered to be less than was estimated in the 1994 Assessment, although significant uncertainties remain.** The current best estimate of the Ozone Depletion Potential (ODP) for methyl bromide (CH_3Br) is 0.4, compared with an ODP of 0.6 estimated previously. The change is caused primarily by both an increase in estimates of ocean removal processes and identification of an uptake by soils, with a smaller contribution from change in our estimate of the atmospheric removal rate. Recent research has shown that the science of atmospheric methyl bromide is complex and still not well understood. Current understanding of the sources and sinks of atmospheric methyl bromide is incomplete.

- **The rate of decline in stratospheric ozone at mid-latitudes has slowed; hence, the projections of ozone loss made in the 1994 assessment are larger than what has actually occurred.** Total column ozone decreased significantly at mid-latitudes (25 to 60°) between 1979 and 1991, with estimated linear downward trends of 4.0, 1.8, and 3.8% per decade, respectively, for northern mid-latitudes in winter/spring, northern mid-latitudes in summer/fall, and southern mid-latitudes year round. However, since 1991, the linear trend observed during the 1980s has not continued, rather, total column ozone has been almost constant at mid-latitudes in both hemispheres since the recovery from the 1991 Mt. Pinatubo eruption. The observed total column ozone losses from 1979 to the period 1994 to 1997 are about 5.4, 2.8, and 5.0%, respectively, for northern mid-latitudes in winter/spring, northern mid-latitudes in summer/fall, and southern mid-latitudes year round, rather than the values projected in the 1994 assessment assuming a linear trend: 7.6, 3.4, and 7.2%, respectively. Understanding of how changes in stratospheric chlorine/bromine and aerosol loading affect ozone suggests some of the reasons for the unsuitability of using a linear extrapolation of the pre-1991 ozone trend to the present.
- **The springtime Antarctic ozone hole continues unabated.** The extent of ozone depletion has remained essentially unchanged since the early 1990s. This behavior is expected given the near-complete destruction of ozone within the Antarctic lower stratosphere during springtime. The factors contributing to the continuing depletion are well understood.
- **The link between the long-term buildup of chlorine and the decline of ozone in the upper stratosphere has been firmly established.** Model predictions based on the observed buildup of stratospheric chlorine in the upper stratosphere indicate a depletion of ozone that is in good quantitative agreement with the altitude and latitude dependence of the measured ozone decline during the past several decades, which peaks at about 7% per decade near 40 km at mid-latitudes in both hemispheres.
- **The late-winter/spring ozone values in the Arctic were unusually low in six out of the last nine years, the six being years that are characterized by unusually cold and protracted stratospheric winters.** The possibility of such depletions was predicted in the 1989 assessment. Minimum Arctic vortex temperatures are near the threshold for large chlorine activation. Therefore, the year-to-year variability in temperature, which is driven by meteorology, leads to particularly large variability in ozone for current chlorine loading. As a

result, it is not possible to forecast the behavior of Arctic ozone for a particular year. Elevated stratospheric halogen abundances over the next decade or so imply that the Arctic will continue to be vulnerable to large ozone losses.

- **The understanding of the relation between increasing surface UV-B radiation and decreasing column ozone has been further strengthened by ground-based observations, and newly developed satellite methods show promise for establishing global trends in UV radiation.** The inverse dependence of surface UV radiation and the overhead amount of ozone, which was demonstrated in earlier assessments, has been further demonstrated and quantified by ground-based measurements under a wide range of atmospheric conditions. In addition, the influences of other variables, such as clouds, particles, and surface reflectivity, are better understood. These data have assisted the development of a satellite-based method to estimate global UV changes, taking into account the role of cloud cover. The satellite estimates for 1979 through 1992 indicate that the largest UV increases occur during spring at high latitudes in both hemispheres.
- **Stratospheric ozone losses have caused a cooling of the global lower stratosphere and global-average negative radiative forcing of the climate system.** The decadal temperature trends in the stratosphere have now been better quantified. Model simulations indicate that much of the observed downward trend in lower stratospheric temperatures (about 0.6 °C per decade from 1979 to 1994) is attributed to the ozone loss in the lower stratosphere. A lower stratosphere that is cooler results in less infrared radiation reaching the surface/troposphere system. Radiative calculations, using extrapolations based on the ozone trends reported in the 1994 assessment for reference, indicate that stratospheric ozone losses since 1980 may have offset about 30% of the positive forcing because of increases in the well-mixed greenhouse gases (i.e., carbon dioxide, methane, nitrous oxide, halocarbons) over the same time period. The climatic impact of the slowing of mid-latitude ozone trends and the enhanced ozone loss in the Arctic has not yet been assessed.
- **Based on past emissions of ozone-depleting substances and a projection of the maximum allowances under the Montreal Protocol into the future, the maximum ozone depletion is estimated to lie within the current decade or the next two decades, but its identification and the evidence for the recovery of the ozone layer lie still further ahead.** The falloff of total chlorine and bromine abundances in the stratosphere in the next century will be much

slower than the rate of increase observed in past decades, because of the slow rate at which natural processes remove these compounds from the stratosphere. The most vulnerable period for ozone depletion will be extended into the coming decades. However, extreme perturbations, such as natural events like volcanic eruptions, could enhance the loss from ozone-depleting chemicals. Detection of the beginning of the recovery of the ozone layer could be achievable early in the next century if decreasing chlorine and bromine abundances were the only factor. However, potential future increases or decreases in other gases important in ozone chemistry (such as nitrous oxide, methane, and water vapor) and climate change will influence the recovery of the ozone layer. When combined with the natural variability of the ozone layer, these factors imply that unambiguous detection of the beginning of the recovery of the ozone layer is expected to be well after the maximum stratospheric loading of ozone-depleting gases.

REFERENCE

World Meteorological Organization (WMO). (1999) Scientific assessment of ozone depletion: 1998. Geneva, Switzerland: World Meteorological Organization, Global Ozone and Monitoring Project; report no. 44.

APPENDIX 4B

Excerpted Key Points from the Executive Summary of the United Nations Environmental Programme 1998 Assessment of Environmental Effects of Ozone Depletion (United Nations Environmental Programme, 1998)

Decreased quantities of total-column ozone now are observed over large parts of the globe, permitting increased penetration of solar UV-B radiation (280 to 315 nm) to the Earth's surface. The present assessment deals with the possible consequences. The Atmospheric Science Panel predicts that the ozone layer will be in its most vulnerable state during the coming two decades. Some of the effects are expected to occur during most of the next century. Recent studies show that the effects of ozone depletion would have been dramatically worse without protective measures taken under the 1987 Montreal Protocol. The assessment is given in seven papers, summarized below:

(1) Changes in Ultraviolet Radiation

- **Stratospheric ozone levels are near their lowest points since measurements began, so current UV-B radiation levels are thought to be close to their maximum.** Total stratospheric content of ozone-depleting substances is expected to reach a maximum before the year 2000. All other things being equal, the current ozone losses and related UV-B increases should be close to their maximum. Increases in surface erythemal (sunburning) UV radiation relative to the values in the 1970s are estimated to be
    - about 7% at Northern Hemisphere mid-latitudes in winter/spring;
    - about 4% at Northern Hemisphere mid-latitudes in summer/fall;
    - about 6% at Southern Hemisphere mid-latitudes on a year-round basis;
    - about 130% in the Antarctic in the spring; and
    - about 22% in the Arctic in the spring.
- **The correlation between increases in surface UV-B radiation and decreases in overhead ozone has been demonstrated further and quantified by ground-based instruments under a wide range of conditions.** Improved measurements of UV-B radiation are now providing

better geographical and temporal coverage. Surface UV-B radiation levels are highly variable because of sun angle, cloud cover, and, also, because of local effects, including pollutants and surface reflections. With a few exceptions, the direct detection of UV-B trends at low- and mid-latitudes remains problematic because of this high natural variability, the relatively small ozone changes, and the practical difficulties of maintaining long-term stability in networks of UV-measuring instruments. Few reliable UV-B radiation measurements are available from pre-ozone-depletion days.

- **Satellite-based observations of atmospheric ozone and clouds are being used, together with models of atmospheric transmission, to provide global coverage and long-term estimates of surface UV-B radiation.** Estimates of long-term (1979 to 1992) trends in zonally averaged UV irradiances that include cloud effects are nearly identical to those for clear-sky estimates, providing evidence that clouds have not influenced the UV-B trends. However, the limitations of satellite-derived UV estimates should be recognized. To assess uncertainties inherent in this approach, additional validations involving comparisons with ground-based observations are required.
- **Direct comparisons of ground-based UV-B radiation measurements between a few mid-latitude sites in the Northern and Southern Hemispheres have shown larger differences than those estimated using satellite data.** Ground-based measurements show that summertime erythemal UV irradiances in the Southern Hemisphere exceed those at comparable latitudes of the Northern Hemisphere by up to 40%, whereas corresponding satellite-based estimates yield only 10 to 15% differences. Atmospheric pollution may be a factor in this discrepancy between ground-based measurements and satellite-derived estimates. UV-B measurements at more sites are required to determine whether the larger observed differences are globally representative.
- **High levels of UV-B radiation continue to be observed in Antarctica during the recurrent spring-time ozone hole.** For example, during ozone-hole episodes, measured biologically damaging radiation at Palmer Station, Antarctica (64 °S) has been found to approach and occasionally even exceed maximum summer values at San Diego, CA (32 °N).
- **Long-term predictions of future UV-B levels are difficult and uncertain. Nevertheless, current best estimates suggest that a slow recovery to pre-ozone-depletion levels may be expected during the next half-century.** Although the maximum ozone depletion, and hence

maximum UV-B increase, is likely to occur in the current decade, the ozone layer will continue to be in its most vulnerable state into the next century. The peak depletion and the recovery phase could be delayed by decades because of interactions with other long-term atmospheric changes (e.g., increasing concentrations of greenhouse gases). Other factors that could influence the recovery include nonratification or noncompliance with the Montreal Protocol and its Amendments and Adjustments and future volcanic eruptions. The recovery phase for surface UV-B irradiances probably will not be detectable until many years after the ozone minimum.

(2) Effects on Human and Animal Health

- **Recent estimates suggest that the increase in the risk of cataract and skin cancer because of ozone depletion would not have been controlled adequately by implementation of the Montreal Protocol (1987) alone, but can be achieved through implementation of its later provisions.** Risk assessments for the United States and northwestern Europe indicate large increases in cataracts and skin cancers under either the "no Protocol" or the early Montreal Protocol scenarios. Under scenarios based on later amendments (Copenhagen, 1992) and Montreal (1997), increases in cataracts and skin cancer attributable to ozone depletion return almost to zero by the end of the next century.
- **The increases in UV-B radiation associated with ozone depletion are likely to lead to increases in the incidence or severity of a variety of short- and long-term health effects, if current exposure practices are not modified by changes in behavior.**
- **Adverse effects on the eye will affect all populations irrespective of skin color.** Adverse impacts could include more cases of acute reactions such as "snowblindness", increases in cataract incidence or severity (and thus the incidence of cataract-associated blindness), and increases in the incidence (and mortality) from ocular melanoma and squamous cell carcinoma of the eye.
- **Effects on the immune system also will affect all populations but may be both adverse and beneficial.** Adverse effects include depressed resistance to certain tumors and infectious diseases, potential impairment of vaccination responses, and possibly increased severity of some autoimmune and allergic responses. Beneficial effects could include decreases in the severity of certain immunologic disease conditions, such as psoriasis and nickel allergy.

- **Effects on the skin could include increases in photoaging and skin cancer with risk increasing with fairness of skin.** Increases in UV-B are likely to accelerate the rate of photoaging, as well as increase the incidence (and associated mortality) of melanoma and nonmelanoma skin cancer, basal cell carcinoma, and squamous cell carcinoma.
- **Research is generating much new information being used to help reduce uncertainties associated with current risk estimates.** Evaluation of the impact of susceptibility genes is helping to identify highly susceptible populations so that their special risk can be assessed. Examination of the impacts of behavior changes, such as consuming diets that are high in antioxidants, avoiding sun exposure during the 4 h around solar noon, and wearing of covering apparel (e.g., hats, sunglasses), is beginning to identify important exposure patterns, as well as possible mitigation strategies.
- **Quantitative risk assessments for a variety of other effects, such as UV-B-induced immunosuppression of infectious diseases, are not yet possible.** New information continues to confirm the reasonableness of these concerns, but data that is adequate for quantitative risk assessment are not yet available.

(3) Effects on Terrestrial Ecosystems

- **Increased UV-B can be damaging for terrestrial organisms including plants and microbes, but all these organisms also have protective and repair processes.** The balance between damage and protection varies among species and even varieties of crop species; many species and varieties can accommodate increased UV-B. Tolerance of elevated UV-B by some species and crop varieties provides opportunities for genetic engineering and breeding to deal with potential crop-yield reductions because of elevated UV-B in agricultural systems.
- **Research in the past few years indicates that increased UV-B exerts effects more often through altered patterns of gene activity rather than damage.** These UV-B effects on regulation manifest themselves in many ways including changes in life-cycle timing, changes in plant form, and production of plant chemicals not directly involved in primary metabolism. These plant chemicals play a role in protecting plants from pathogens and insect attack and affect food quality for humans and grauine animals.
- **Terrestrial ecosystem responses to increased UV-B are evident primarily in interactions among species, rather than in the performance of individual species.** Much of the recent

experimentation indicates that increased UV-B affects the balance of competition among higher plants, the degree to which higher plants are consumed by insects, and susceptibility of plants to pathogens. These effects can be mediated, in large part, by changes in plant form and chemistry, but effects of UV-B on insects and microbes are also possible. The direction of these UV-B mediated interactions among species is often difficult to predict based only on single-organism responses to increased UV-B.

- **Effects of increased UV-B radiation can accumulate from year to year in long-lived perennial plants and from generation to generation in annual plants.** This effect has been shown in a few recent studies, but the generality of this accumulation among species is not presently known. If this phenomenon is widespread, this would amplify otherwise subtle responses to UV-B seen in a single growing season, for example, in forest trees.
- **Effects of increased UV-B must be taken into account together with other environmental factors including those associated with global change.** Responses of plants and other organisms to increased UV-B are modified by other environmental factors (e.g., CO, water stress, mineral nutrient availability, heavy metals, temperature). Many of these factors also are changing as the global climate is altered.

(4) Effects on Aquatic Ecosystems

- **Recent studies continue to demonstrate that solar UV-B and UV-A have adverse effects on the growth, photosynthesis, protein and pigment content, and reproduction of phytoplankton, thus affecting the food web.** These studies have determined biological weighting functions and exposure-response curves for phytoplankton and have developed new models for the estimation of UV-related photoinhibition. In spite of this increased understanding and enhanced ability to model aquatic impacts, considerable uncertainty remains with respect to quantifying effects of ozone-related UV-B increases at the ecosystem level.
- **Macroalgae and sea grasses show a pronounced sensitivity to solar UV-B.** They are important biomass producers in aquatic ecosystems. Most of these organisms are attached and so cannot avoid being exposed to solar radiation at their growth site. Effects have been found throughout the top 10 to 15 m of the water column.
- **Zooplankton communities, as well as other aquatic organisms including sea urchins, corals, and amphibians, are sensitive to UV-B.** There is evidence that, for some of these

populations, even current levels of solar UV-B radiation, acting in conjunction with other environmental stresses, may be a limiting factor, but quantitative evaluation of possible effects remains uncertain.

- **UV-B radiation is absorbed by and breaks down dissolved organic carbon (DOC) and particulate organic carbon (POC) and makes the products available for bacterial degradation and remineralization.** The degradation products are of importance in the cycling of carbon in aquatic ecosystems. Because UV-B breaks down DOC as it is absorbed, increase in UV-B can increase the penetration of both UV-B and UV-A radiation into the water column. As a consequence, the quantity of UV-B penetrating to a given depth both influences and is influenced by DOC. Warming and acidification result in faster degradation of these substances and, thus, enhance the penetration of UV radiation into the water column.
- **Polar marine ecosystems, where ozone-related UV-B increases are the greatest, are expected to be the oceanic ecosystems most influenced by ozone depletion.** Oceanic ecosystems are characterized by large spatial and temporal variabilities that make it difficult to select out UV-B-specific effects on single species or whole phytoplankton communities. Although estimates of reduction in both Arctic and Antarctic productivity are based on measurable short-term effects, there remain considerable uncertainties in estimating long-term consequences, including possible shifts in community structure. Reduced productivity of fish and other marine crops could have an economic impact, as well as affect natural predators; however, quantitative estimation of the possible effects of reduced production remain controversial.
- **Potential consequences of enhanced levels of exposure of aquatic ecosystems to UV-B radiation include reduced uptake capacity for atmospheric carbon dioxide (CO_2), resulting in the potential augmentation of global warming.** The oceans play a key role with respect to the budget of greenhouse gases. Marine phytoplankton are a major sink for atmospheric CO_2 and they have a decisive role in the development of future trends of CO_2 concentrations in the atmosphere. The relative importance of the net uptake of CO_2 by the biological pump and the possible role of increased UV-B in the ocean are still controversial.

(5) Effects on Biogeochemical Cycles

- **Effects of increased UV-B on emissions of CO_2 and carbon monoxide (CO) and on mineral nutrient cycling in the terrestrial biosphere have been confirmed by recent studies of a range of species and ecosystems.** The effects, both in magnitude and direction, of UV-B on trace gas emissions and mineral nutrient cycling are species specific and operate on a number of processes. These processes include changes in the chemical composition in living plant tissue; photodegradation (breakdown by light) of dead plant matter, including litter; release of CO from vegetation previously charred by fire; changes in the communities of microbial decomposers; and effects on nitrogen-fixing micro-organisms and plants. Long-term experiments are in place to examine UV-B effects on carbon capture and storage in biomass within natural terrestrial ecosystems.
- **Studies in natural aquatic ecosystems have indicated that organic matter is the primary regulator of UV-B penetration.** Enhanced UV-B can affect the balance between the biological processes that produce the organic matter and the chemical and microbial processes that degrade it. Changes in the balance have broad impacts on the effects of enhanced UV-B on biogeochemical cycles. These changes, which are reinforced by changes in climate and acidification, result from clarification of the water and changes in light quality.
- **Increased UV-B has positive and negative impacts on microbial activity in aquatic ecosystems that can affect carbon and mineral nutrient cycling, as well as the uptake and release of greenhouse and chemically reactive gases.** Photoinhibition of surface aquatic micro-organisms by UV- B can be offset partially by photodegradation of dissolved organic matter to produce substrates, such as organic acids and ammonium, that stimulate microbial activity.
- **Modeling and experimental approaches are being developed to predict and measure the interactions and feedbacks between climate change in UV-B-induced changes in marine and terrestrial biogeochemical cycles.** These interactions include alterations in the oxidative environment in the upper ocean and in the marine boundary layer and oceanic production and release of CO, volatile organic compounds (VOC), and reactive oxygen species (ROS, such as hydrogen peroxide and hydroxyl radicals). Climate-related changes in temperature and water supply in terrestrial ecosystems interact with UV-B radiation through biogeochemical processes operating on a wide range of time scales.

(6) Effects on Air Quality

- **Increased UV-B will increase the chemical activity in the lower atmosphere (the troposphere).** Troposphere ozone levels are sensitive to local concentrations of nitrogen oxides (NOx) and hydrocarbons. Model studies suggest that additional UV-B radiation reduces tropospheric ozone in clean environments (low NO_x) and increases tropospheric ozone in polluted areas (high NO_x).
- **Assuming other factors remain constant, additional UV-B will increase the rate at which primary pollutants are removed from the troposphere.** Increased UV-B is expected to increase the concentration of hydroxyl radicals (OH) and result in faster removal of pollutants. Increased concentrations of oxidants such as hydrogen peroxide and organic peroxides also are expected. The effects of UV-B increases on tropospheric ozone, OH, methane, CO, and possibly other tropospheric constituents, although not negligible, will be difficult to detect because the concentrations of these species also are influenced by many other variable factors (e.g., emissions).
- **No significant effects on humans or the environment have been identified from trifluoroacetic acid (TFA) produced by atmospheric degradation of HCFCs and HFCs.** Numerous studies have shown that TFA has, at most, moderate short-term toxicity. Insufficient information is available to assess potential chronic, developmental, or reproductive effects. The atmospheric degradation mechanisms of most substitutes for ozone-depleting substances are well established. HCFCs and HFCs are two important classes of substitutes. Atmospheric degradation of HCFC-123 (CF_3CHC1_2), HCFC-124 (CF_3CHFCI), and H FC-I34a (CF_3CH_2F) produces TFA. Reported measurements of TFA in rain, rivers, lakes, and oceans show it to be an ubiquitous component of the hydrosphere, present at levels much higher than can be explained by currently reported sources. The levels of TFA currently produced by the atmospheric degradation of HFCs and HCFCs are estimated to be orders of magnitude below those of concern and make only a minor contribution to the current environmental burden of TFA.

(7) Effects on Materials

- **Physical and mechanical properties of polymers are affected negatively by increased UV-B in sunlight.** Increased UV-B reduces the useful lifetimes of synthetic polymer products used outdoors and of biopolymer materials such as wood, paper, wool, and cotton. The reduction in service life of materials depends on the synergistic effect of increased UV-B and other factors, especially the temperature of the material during exposure to sunlight. Even under harsh UV exposure conditions, the higher temperatures largely determine the extent of increased UV-induced damage to photostabilized polyethylenes. However, accurate assessment of such damage to various materials is presently difficult to make because of limited availability of technical data, especially on the relationship between the dose of UV-B radiation and the resulting damage of the polymer or other material.

- **Conventional photostabilizers are likely to be able to mitigate the effects of increased UV levels in sunlight.** More effective photostabilizers for plastics have been commercialized in recent years. The use of these compounds allows plastic polymer products to be used in a wide range of different UV environments found worldwide. It is reasonable to expect existing photostabilizer technologies to be able to mitigate these effects of an increased UV-B on polymer materials. This, however, would increase the cost of the relevant polymer products, surface coatings, and treated biopolymer materials. However, the efficiencies of even the conventional photostabilizers under the unique exposure environments resulting from an increase in solar UV-B have not been well studied.

REFERENCE

United Nations Environment Programme (UNEP). (1998) Environmental effects of ozone depletion: 1998 assessment. J. Photochem. Photobiol. B 46: 1-4.

APPENDIX 4C

Excerpted Key Points from the Executive Summary of the Special Report of the International Panel on Climate Change Working Group II on the Regional Impacts of Climate Change: An Assessment of Vulnerability

Excerpts from Executive Summary materials from a Special Report of the IPCC Working Group II, The Regional Impacts of Climate Change: An Assessment of Vulnerability (IPCC, 1998) are incorporated below in this appendix to provide an overview of key points regarding the vulnerability of aquatic and terrestrial ecosystems, water resources, agriculture, and human habitability in North America to climate change.

Scope of the Assessment

The report was prepared at the request of the Conference of the Parties to the United Nations Framework Convention on Climate Change (UNFCCC) and its subsidiary bodies (specifically, the Subsidiary Body for Scientific and Technological Advice-SBSTA). The special report provides, on a regional basis, a review of state-of-the-art information on the vulnerability to potential changes in climate of ecological systems, socioeconomic sectors (agriculture, fisheries, water resources, and human settlements), and human health. The report reviews the sensitivity of these systems as well as options for adaptation. Though the report draws heavily on the sectoral impact assessments of the Second Assessment Report (SAR), it also draws on more recent peer-reviewed literature (*inter alia*, country studies programs).

Nature of the Issue

Human activities (primarily burning of fossil fuels and changes in land use and land cover) are increasing atmospheric concentrations of greenhouse gases, which alter radiative balances and tend to warm the atmosphere, and, in some regions, aerosols, which have an opposite effect on radiative balances and tend to cool the atmosphere. At present, in some locations primarily in the Northern Hemisphere, the cooling effects of aerosols can be large enough to more than offset the warming caused by greenhouse gases. Because aerosols do not remain in the atmosphere for long periods and global emissions of their precursors are not projected to increase substantially, aerosols will not offset the global long-term effects of greenhouse gases, which are long-lived. Aerosols can have important consequences for continental-scale patterns of climate change.

These changes in greenhouse gases and aerosols, taken together, are projected to lead to regional and global changes in temperature, precipitation, and other climate variables, resulting in global changes in soil moisture; an increase in global mean sea level; and prospects for more severe extreme high-temperature events, floods, and droughts in some places. Based on the range of sensitivities of climate to changes in the atmospheric concentrations of greenhouse gases (IPCC, 1996; WG I) and plausible changes in emissions of greenhouse gases and aerosols (lS92a-f, scenarios that assume no climate policies), climate models project that the mean annual global surface temperature will increase by 1 to 3.5 °C by 2100, that global mean sea level will rise by 15 to 95 cm, and that changes in the spatial and temporal patterns of precipitation will occur. The average rate of warming probably would be greater than any seen in the past 10,000 years, although the actual annual to decadal rate would include considerable natural variability, and regional changes could differ substantially from the global mean value. These long-term, large-scale, human-induced changes will interact with natural variability on time scales of days to decades (e.g., the El Niño-Southern Oscillation [ENSO] phenomenon) and, thus, influence social and economic well-being. Possible local climate effects caused by unexpected events such as a climate-change-induced change of flow pattern of marine water streams (e.g., the Gulf Stream) have not been considered, because such changes cannot be predicted with confidence at present.

Scientific studies show that human health, ecological systems, and socioeconomic sectors (e.g., hydrology and water resources, food and fiber production, coastal systems, human settlements), all of which are vital to sustainable development, are sensitive to changes in climate, including both the magnitude and rate of climate change, as well as to changes in climate variability. Whereas many regions are likely to experience adverse effects of climate change, some of which are potentially irreversible, some effects of climate change are likely to be beneficial. Climate change represents an important additional stress on those systems already affected by increasing resource demands, unsustainable management practices, and pollution, which in many cases may be equal to or greater than those of climate change. These stresses will interact in different ways across regions but can be expected to reduce the ability of some environmental systems to provide, on a sustained basis, key goods and services needed for successful economic and social development, including adequate food, clean air, and water; energy; safe shelter; low levels of disease; and employment opportunities. Climate change also will take place in the context of economic development, which may make some groups or countries less vulnerable to climate change, for example, by increasing the resources available for adaptation. Those that experience low rates of growth, rapid increases in population, and ecological degradation may become increasingly vulnerable to potential changes.

Approach of the Assessment

The report assesses the vulnerability of natural and social systems of major regions of the world to climate change. Vulnerability is defined as the extent to which a natural or social system is susceptible to sustaining damage from climate change. Vulnerability is a function of the sensitivity of a system to changes in climate (the degree to which a system will respond to a given change in climate, including both beneficial and harmful effects) and the ability to adapt the system to changes in climate (the degree to which adjustments in practices, processes, or structures can moderate or offset the potential for damage or take advantage of opportunities created because of a given change in climate). Under this framework, a highly vulnerable system would be one that is highly sensitive to modest changes in climate, where the sensitivity includes the potential for substantial harmful effects, and one for which the ability to adapt is severely constrained.

Because the available studies have not employed a common set of climate scenarios and methods, and because of uncertainties regarding the sensitivities and adaptability of natural and social systems, the assessment of regional vulnerabilities is necessarily qualitative. However, the report provides substantial and indispensable information on what currently is known about vulnerability to climate change.

In a number of instances, quantitative estimates of impacts of climate change are cited in the report. Such estimates are dependent on the specific assumptions employed regarding future changes in climate, as well as on the particular methods and models applied in the analyses. In interpreting these estimates, it is important to bear in mind that uncertainties regarding the character, magnitude, and rates of future climate change remain. These uncertainties impose limitations on the ability of scientists to project impacts of climate change, particularly at regional and smaller scales.

It is in part because of the uncertainties regarding how climate will change that the report takes the approach of assessing vulnerabilities rather than assessing quantitatively the expected impacts of climate change. The estimates are interpreted best as illustrative of the potential character and approximate magnitudes of impacts that may result from specific scenarios of climate change. They serve as indicators of sensitivities and possible vulnerabilities. Most commonly, the estimates are based on changes in equilibrium climate that have been simulated to result from an equivalent doubling of carbon dioxide (CO_2) in the atmosphere. Usually, the simulations have excluded the effects of aerosols. Increases in global mean temperatures corresponding to these scenarios mostly fall in the range of 2 to 5 °C. To provide a temporal context for these scenarios, the range of projected global mean warming by 2100 is 1 to 3.5 °C, accompanied by a mean sea-level rise of 15 to 95 cm, according to the IPCC Second Assessment Report. General circulation model (GCM) results are used in this analysis to justify the order of magnitude of the changes used in the sensitivity analyses. They are not predictions that climate will change by specific magnitudes in particular countries or regions. The amount of literature available for assessment varies in quantity and quality among the regions.

Overview of Regional Vulnerabilities to Global Climate Change

The report's assessment of regional vulnerability to climate change focuses on ecosystems, hydrology and water resources, food and fiber production, coastal systems, human settlements, human health, and other sectors or systems (including the climate system) important to 10 regions that encompass the Earth's land surface. Wide variation in the vulnerability of similar sectors or systems is to be expected across regions, as a consequence of regional differences in local environmental conditions; preexisting stresses to ecosystems; current resource-use patterns; and the framework of factors affecting decision making, including government policies, prices, preferences, and values. Nonetheless, some general observations, based on information contained in the IPCC Second Assessment Report (SAR) (IPCC, 1995) and synthesized from the regional analyses in the 1998 assessment, provide a global context for assessment of each region's vulnerability. The general types of vulnerabilities are discussed first below, followed by more specific discussion of projected likely regional vulnerabilities most directly applicable to the United States.

Ecosystems

Ecosystems are of fundamental importance to environmental function and to sustainability, and they provide many goods and services critical to individuals and societies. These goods and services include (1) providing food, fiber, fodder, shelter, medicines, and energy; (2) processing and storing carbon and nutrients; (3) assimilating wastes; (4) purifying water, regulating water runoff, and moderating floods; (5) building soils and reducing soil degradation; (6) providing opportunities for recreation and tourism; and (7) housing the Earth's entire reservoir of genetic and species diversity. In addition, natural ecosystems have cultural, religious, aesthetic, and intrinsic existence values. Changes in climate have the potential to affect the geographic location of ecological systems, the mix of species that they contain, and their ability to provide the wide range of benefits on which societies rely for their continued existence. Ecological systems are intrinsically dynamic and are constantly influenced by climate variability. The primary influence of anthropogenic climate change on ecosystems is expected to be through the rate and magnitude of change in climate means and extremes; climate change is expected to occur at a rapid rate relative to the speed at which ecosystems can adapt and reestablish themselves; and through the direct effects of increased atmospheric CO_2 concentrations, which may increase the productivity and efficiency of water use in some plant species. Secondary effects of climate change involve changes in soil characteristics and disturbance regimes (e.g., fires, pests, diseases), which would favor some species over others and thus change the species composition of ecosystems.

Based on model simulations of vegetation distribution, which use GCM-based climate scenarios, large shifts of vegetation boundaries into higher latitudes and elevations can be expected. The mix of species within a given vegetation class likely will change. Under equilibrium GCM climate scenarios, large regions show drought-induced declines in vegetation, even when the direct effects of CO_2 fertilization are included. By comparison, under transient climate scenarios, in which trace gases increase slowly over a period of years, the full effects of changes in temperature and precipitation lag the effects of a change in atmospheric composition by a number of decades; hence, the positive effects of CO_2, precede the full effects of changes in climate.

Climate change is projected to occur at a rapid rate relative to the speed at which forest species grow, reproduce, and reestablish themselves (past tree species' migration rates are believed to be on the order of 4 to 200 km per century). For mid-latitude regions, an average warming of 1 to 3.5 °C over the next 100 years would be equivalent to a poleward shift of the present geographic bands of similar temperatures (or "isotherms") by approximately 150 to 550 km, or an altitude shift of about a 150 to 550 m. Therefore, the species composition of forests is likely to change; in some regions, entire forest types may disappear, and new assemblages of species and, hence, new ecosystems may be established. As a consequence of possible changes in temperature and water availability under doubled equivalent-CO_2 equilibrium conditions, a substantial fraction (a global average of one-third, varying by region from one-seventh to two-thirds) of the existing forested area of the world likely would undergo major changes in broad vegetation types, with the greatest changes occurring in high latitudes and the least in the tropics. In tropical rangelands, major alterations in productivity and species composition would occur because of altered rainfall amount and seasonality and increased evapotranspiration, although a mean temperature increase alone would not lead to such changes.

Inland aquatic ecosystems will be influenced by climate change through altered water temperatures, flow regimes, water levels, and thawing of permafrost at high latitudes. In lakes and streams, warming would have the greatest biological effects at high latitudes, where biological productivity would increase and lead to expansion of cool-water species' ranges, and at the low-latitude boundaries of cold- and cool-water species ranges, where extinctions would be greatest. Increases in flow variability, particularly the frequency and duration of large floods and droughts, would tend to reduce water quality, biological productivity, and habitat in streams. The geographical distribution of wetlands is likely to shift with changes in temperature and precipitation, with uncertain implications for net greenhouse gas emissions from nontidal wetlands. Some coastal ecosystems (saltwater marshes, mangrove ecosystems, coastal wetlands, coral reefs, coral atolls, and river deltas) are particularly at risk from climate change and other stresses. Changes in these ecosystems would have major negative effects on freshwater supplies, fisheries, biodiversity, and tourism.

Adaptation options for ecosystems are limited, and their effectiveness is uncertain. Options include establishment of corridors to assist the "migration" of ecosystems, land-use management, plantings, and restoration of degraded areas. Because of the projected rapid rate of change relative to the rate at which species can reestablish themselves, the isolation and fragmentation of many ecosystems, the existence of multiple stresses (e.g., land-use change, pollution), and limited adaptation options, ecosystems (especially forested systems, montane systems, and coral reefs) are vulnerable to climate change.

Hydrology and Water Resources

Water availability is an essential component of welfare and productivity. Currently, 1.3 billion people do not have access to adequate supplies of safe water, and 2 billion people do not have access to adequate sanitation. Although these people are dispersed throughout the globe, reflecting subnational variations in water availability and quality, some 19 countries (primarily in the Middle East and northern and southern Africa) face such severe shortfalls that they are classified as either water-scarce or water-stressed; this number is expected to roughly double by 2025, in large part because of increases in demand resulting from economic and population growth. For example, most policy makers now recognize drought as a recurrent feature of Africa's climate. However, climate change will further exacerbate the frequency and magnitude of droughts in some places.

Changes in climate could exacerbate periodic and chronic shortfalls of water, particularly in arid and semi-arid areas of the world. Developing countries are highly vulnerable to climate change because many are located in arid and semi-arid regions, and most derive their water resources from single-point systems such as bore holes or isolated reservoirs. These systems, by their nature, are vulnerable because there is no redundancy in the system to provide resources, should the primary supply fail. Also, given the limited technical, financial, and management resources possessed by developing countries, adjusting to shortages or implementing adaptation measures will impose a heavy burden on their national economies. There is evidence that flooding is likely to become a larger problem in many temperate and humid regions, requiring adaptations not only to droughts and chronic water shortages but also to floods and associated damages, raising concerns about dam and levee failures.

The impacts of climate change will depend on the baseline condition of the water supply system and the ability of water resources managers to respond not only to climate change but also to population growth and changes in demands; technology; and economic, social, and legislative conditions.

Various approaches are available to reduce the potential vulnerability of water systems to climate change. Options include pricing systems, water efficiency initiatives, engineering and structural improvements to water supply infrastructure, agriculture policies, and urban planning and management. At the national/regional level, priorities include placing greater emphasis on integrated, cross-sectoral water resources management, using river basins as resource management units, and encouraging sound pricing and management practices. Given increasing demands, the prevalence and sensitivity of many simple water management systems to fluctuations in precipitation and runoff, and the considerable time and expense required to implement many adaptation measures, the water resources sector in many regions and countries is vulnerable to potential changes in climate.

Food and Fiber Production

Currently, 800 million people are malnourished; as the world's population increases and incomes in some countries rise, food consumption is expected to double over the next three to four decades. The most recent doubling in food production occurred over a 25-year period and was based on irrigation, chemical inputs, and high-yielding crop varieties. Whether the remarkable gains of the past 25 years will be repeated is uncertain. Problems associated with intensifying production on land already in use (e.g., chemical and biological runoff, waterlogging and salinization of soils, soil erosion and compaction) are becoming increasingly evident. Expanding the amount of land under cultivation (including reducing land deliberately taken out of production to reduce agricultural output) also is an option for increasing total crop production, but it could lead to increases in competition for land and pressure on natural ecosystems, increased agricultural emissions of greenhouse gases, a reduction in natural sinks of carbon, and expansion of agriculture to marginal lands, all of which could undermine the ability to sustainably support increased agricultural production.

Changes in climate will interact with stresses that result from actions to increase agricultural production, affecting crop yields and productivity in different ways, depending on the types of agricultural practices and systems in place. The main direct effects will be through changes in factors such as temperature, precipitation, length of growing season, and timing of extreme or critical threshold events relative to crop development, as well as through changes in atmospheric CO_2 concentration (which may have a beneficial effect on the growth of many crop types). Indirect effects will include potentially detrimental changes in diseases, pests, and weeds, the effects of which have not yet been quantified in most available studies. Evidence continues to support the findings of the IPCC SAR that “global agricultural production could be maintained relative to baseline production” for a growing population under 2×CO_2 equilibrium climate conditions. In addition, the regional findings of this special report lend support to concerns over the “potential serious consequences” of increased risk of hunger in some regions, particularly the tropics and subtropics. Generally, middle to high latitudes may experience increases in productivity, depending on crop type, growing season, changes in temperature regimes, and the seasonality of precipitation. In the tropics and subtropics, where some crops are near their maximum temperature tolerance and where dry-land, nonirrigated agriculture predominates, yields are likely to decrease. The livelihoods of subsistence farmers and pastoral peoples, who make up a large portion of rural populations in some regions, also could be affected negatively. In regions where there is a likelihood of decreased rainfall, agriculture could be significantly affected.

Fisheries and fish production are sensitive to changes in climate and currently are at risk from overfishing, diminishing nursery areas, and extensive inshore and coastal pollution. Globally, marine fisheries production is expected to remain about the same in response to changes in climate; high-latitude freshwater and aquaculture production is likely to increase, assuming that natural climate variability and the structure and strength of ocean currents remain about the same. The principal impacts will be felt at the national and local levels, as centers of production shift. The positive effects of climate change, such as longer growing seasons, lower natural winter mortality, and faster growth rates in higher latitudes, may be offset by negative factors such as changes in established reproductive patterns, migration routes, and ecosystem relationships.

Given the many forces bringing profound change to the agricultural sector, adaptation options that enhance resilience to current natural climate variability and potential changes in means and extremes and address other concerns (e.g., soil erosion, salinization) offer no- or low-regret options. For example, linking agricultural management to seasonal climate predictions can assist in incremental adaptation, particularly in regions where climate is strongly affected by ENSO conditions. The suitability of these options for different regions varies, in part because of differences in the financial and institutional ability of the private sector and governments in different regions to implement them. Adaptation options include changes in crops and crop varieties; development of new crop varieties; changes in planting schedules and tillage practices; introduction of new biotechnologies; and improved water-management and irrigation systems, which have high capital costs and are limited by availability of water resources. Other options, such as minimum- and reduced-tillage technologies, do not require such extensive capitalization but do require high levels of agricultural training and support.

In regions where agriculture is well adapted to current climate variability or where market and institutional factors are in place to redistribute agricultural surpluses to make up for shortfalls, vulnerability to changes in climate means and extremes generally is low. However, in regions where agriculture is unable to cope with existing extremes, where markets and institutions to facilitate redistribution of deficits and surpluses are not in place, or where adaptation resources are limited, the vulnerability of the agricultural sector to climate change should be considered high. Other factors also will influence the vulnerability of agricultural production in a particular country or region to climate change, including the extent to which current temperatures or precipitation patterns are close to or exceed tolerance limits for important crops, per capita income, the percentage of economic activity based on agricultural production, and the preexisting condition of the agricultural land base.

Coastal Systems

Coastal zones are characterized by a rich diversity of ecosystems and a great number of socioeconomic activities. Coastal human populations in many countries have been growing at double the national rate of population growth. Currently, it is estimated that about half of the global population lives in coastal zones, although there is large variation among countries. Changes in climate will affect coastal systems through sea-level rise and an increase in storm-surge hazards and possible changes in the frequency or intensity of extreme events.

Coasts in many countries currently face severe sea-level rise problems as a consequence of tectonically and anthropogenically induced subsidence. An estimated 46 million people per year currently are at risk of flooding from storm surges. Climate change will exacerbate these problems, leading to potential impacts on ecosystems and human coastal infrastructure. Large numbers of people also potentially are affected by sea-level rise, for example, tens of millions of people in Bangladesh would be displaced by a 1-m increase (the top of the range of IPCC Working Group I estimates for 2100) in the absence of adaptation measures. A growing number of extremely large cities are located in coastal areas, which means that large amounts of infrastructure may be affected. Although annual protection costs for many nations are relatively modest, about 0.1% of gross domestic product (GDP), the average annual costs to many small island states total several percent of GDP. For some island nations, the high cost of providing storm-surge protection would make it essentially infeasible, especially given the limited availability of capital for investment.

Beaches, dunes, estuaries, and coastal wetlands adapt naturally and dynamically to changes in prevailing winds and seas, as well as sea-level changes; in areas where infrastructure development is not extensive, planned retreat and accommodation to changes may be possible. It also may be possible to rebuild or relocate capital assets at the end of their design life. In other areas, however, accommodation and planned retreat are not viable options, and protection using hard structures (e.g., dikes, levees, floodwalls, barriers) and soft structures (e.g., beach nourishment, dune restoration, wetland creation) will be necessary. Factors that limit the implementation of these options include inadequate financial resources, limited institutional and technological capability, and shortages of trained personnel. In most regions, current coastal management and planning frameworks do not take account of the vulnerability of key systems to changes in climate and sea level or long lead times for implementation of many adaptation measures. Inappropriate policies encourage development in impact-prone areas. Given increasing population density in coastal zones; long lead times for implementation of many adaptation measures; and institutional, financial, and technological limitations (particularly in many developing countries), coastal systems should be considered vulnerable to changes in climate.

Human Health

In much of the world, life expectancy is increasing; in addition, infant and child mortality in most developing countries is droping. Against this positive backdrop, however, there appears to be a widespread increase in new and resurgent vectorborne and infectious diseases, such as dengue, malaria, hantavirus, and cholera. In addition, the percentage of the developing world’s population living in cities is expected to increase from 25% (in 1960) to more than 50% by 2020, with percentages in some regions far exceeding these averages. These changes will bring benefits only if accompanied by increased access to services such as sanitation and potable water supplies; they also can lead to serious urban environmental problems, including air pollution (e.g., particulates, surface ozone, lead), poor sanitation, and associated problems in water quality and potability, if access to services is not improved.

Climate change could affect human health through increases in heat-stress mortality, tropical vector-borne diseases, urban air pollution problems, and decreases in cold-related illnesses. Compared with the total burden of ill health, these problems are not likely to be large. In the aggregate, however, the direct and indirect impacts of climate change on human health do constitute a hazard to human population health, especially in developing countries in the tropics and subtropics; these impacts have considerable potential to cause significant loss of life, affect communities, and increase health-care costs and lost work days. Model projections (which entail necessary simplifying assumptions) indicate that the geographical zone of potential malaria transmission would expand in response to global mean temperature increases at the upper part of the IPCC-projected range (3 to 5 °C by 2100), increasing the affected proportion of the world's population from approximately 45% to approximately 60% by the latter half of the next century. Areas where malaria is currently endemic could experience intensified transmission (on the order of 50 to 80 million additional annual cases, relative to an estimated global background total of 500 million cases). Some increases in non-vector-borne infectious diseases, such as salmonellosis, cholera, and giardiasis, also could occur as a result of elevated temperatures and increased flooding. However, quantifying the projected health impacts is difficult because the extent of climate induced health disorders depends on other factors, such as migration, provision of clean urban environments, improved nutrition, increased availability of potable water, improvements in sanitation, the extent of disease vector-control measures, changes in resistance of vector organisms to insecticides, and more widespread availability of health care. Human health is vulnerable to changes in climate, particularly in urban areas, where access to space conditioning may be limited, as well as in areas where exposure to vector-borne and communicable diseases may increase and health-care delivery and basic services, such as sanitation, are poor.

Regional Vulnerability to Global Climate Change

Discussions about two geographic regions (North American and Polar regions) assessed in the report are included here because of their relevance to the continental United States and Alaska, respectively.

North American Region

This region consists of Canada and the United States south of the Arctic Circle. Within the region, vulnerability to and the impacts of climate change vary significantly from sector to sector and from subregion to subregion. This “texture” is important in understanding the potential effects of climate change on North America, as well as in formulating and implementing viable response strategies.

Ecosystems. Most ecosystems are moderately to highly sensitive to changes in climate. Effects are likely to include both beneficial and harmful changes. Potential impacts include northward shifts of forest and other vegetation types, which would affect biodiversity by altering habitats and would reduce the market and nonmarket goods and services they provide; declines in forest density and forested area in some subregions, but gains in others; more frequent and larger forest fires; expansion of arid land species into the great basin region; drying of prairie pothole wetlands that currently support over 50% of all waterfowl in North America; and changes in distribution of habitat for cold-, cool-, and warm-water fish. The ability to apply management practices to limit potential damages is likely to be low for ecosystems that are not already intensively managed.

Hydrology and Water Resources. Water quantity and quality are particularly sensitive to climate change. Potential impacts include increased runoff in winter and spring and decreased soil moisture and runoff in summer. The Great Plains and prairie regions are particularly vulnerable. Projected increases in the frequency of heavy rainfall events and severe flooding also could be accompanied by an increase in the length of dry periods between rainfall events and in the frequency or severity of droughts in parts of North America. Water quality could suffer and would decline where minimum river flows decline. Opportunities to adapt are extensive, but their costs and possible obstacles may be limiting.

Food and Fiber Production. The productivity of food and fiber resources of North America is moderately to highly sensitive to climate change. Most studies, however, have not fully considered the effects of potential changes in climate variability; water availability; stresses from pests, diseases, and fire; or interactions with other, existing stresses. Warmer climate scenarios (4 to 5 °C increases in North America) have yielded estimates of negative impacts in eastern, southeastern, and corn belt regions and positive effects in northern plains and western regions. More moderate warming produced estimates of predominately positive effects in some warm-season crops. Vulnerability of commercial forest production is uncertain, but is likely to be lower than less intensively managed systems because of changing technology and management options. The vulnerability of food and fiber production in North America is thought to be low at the continental scale, though subregional variation in losses or gains is likely. The ability to adapt may be limited by information gaps; institutional obstacles; high economic, social, and environmental costs; and the rate of climate change.

Coastal Systems. Sea level has been rising relative to the land along most of the coast of North America, and falling in a few areas, for thousands of years. During the next century, a 50-cm rise in sea level from climate change alone could inundate 8500 to 19,000 square kilometers of dry land, expand the 100-year flood plain by more than 23,000 square kilometers, and eliminate as much as 50% of North America's coastal wetlands. The projected changes in sea level because of climate change alone would underestimate the total change in sea level from all causes along the eastern seaboard and Gulf Coast of North America. In many areas, wetlands and estuarine beaches may be squeezed between advancing seas and dikes or seawalls built to protect human settlements. Several local governments are implementing land-use regulations to enable coastal ecosystems to migrate landward as sea level rises. Saltwater intrusion may threaten water supplies in several areas.

Human Settlements. Projected changes in climate could have positive and negative impacts on the operation and maintenance costs of North American land and water transportation. Such changes also could increase the risks to property and human health and life as a result of possible increased exposure to natural hazards (e.g., wildfires, landslides, extreme weather events) and result in increased demand for cooling and decreased demand for heating energy, with the overall net effect varying across geographic regions.

Human Health. Climate can have wide-ranging and potentially adverse effects on human health via direct pathways (e.g., thermal stress, extreme weather and climate events) and indirect pathways (e.g., disease vectors and infectious agents, environmental and occupational exposures to toxic substances, food production). In high-latitude regions, some human health impacts are expected because of dietary changes resulting from shifts in migratory patterns and abundance of native food sources.

Conclusions. Taken individually, any one of the impacts of climate change may be within the response capabilities of a subregion or sector. The fact that they are projected to occur simultaneously and in concert with changes in population, technology, economics, and other environmental and social changes, however, adds to the complexity of the impact assessment and the choice of appropriate responses. The characteristics of subregions and sectors of North America suggest that neither the impacts of climate change nor the response options will be uniform.

Many systems of North America are moderately to highly sensitive to climate change, and the range of estimated effects often includes the potential for substantial damages. The technological capability to adapt management of systems to lessen or avoid damaging effects exists in many instances. The ability to adapt may be diminished, however, by the attendant costs, lack of private incentives to protect publicly owned natural systems, imperfect information regarding future changes in climate and the available options for adaptation, and institutional barriers. The most vulnerable sectors and regions include long-lived natural forest ecosystems in the east and interior west, water resources in the southern plains, agriculture in the southeast and southern plains, human health in areas currently experiencing diminished urban air quality, northern ecosystems and habitats, estuarine beaches in developed areas, and low-latitude cool and cold-water fisheries. Other sectors and subregions may benefit from opportunities associated with warmer temperatures or, potentially, from CO_2 fertilization, including west coast coniferous forests; some western rangelands; reduced energy costs for heating in the northern latitudes; reduced 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.

Polar (Arctic and Antarctic) Regions

The polar regions include some very diverse landscapes, and the Arctic and the Antarctic are very different in character. The Arctic is defined here as the area within the Arctic Circle; the Antarctic here includes the area within the Antarctic Convergence, including the Antarctic continent, the Southern Ocean, and the sub-Antarctic islands. The Arctic can be described as a frozen ocean surrounded by land, and the Antarctic as a frozen continent surrounded by ocean. The projected warming in the polar regions is greater than for many other regions of the world. Where temperatures are close to freezing on average, global warming will reduce land ice and sea ice, the former contributing to sea-level rise. However, in the interiors of ice caps, increased temperature may not be sufficient to lead to melting of ice and snow, and will tend to have the effect of increasing snow accumulation.

Ecosystems. Major physical and ecological changes are expected in the Arctic. Frozen areas close to the freezing point will thaw and undergo substantial changes with warming. Substantial loss of sea ice is expected in the Arctic Ocean. As warming occurs, there will be considerable thawing of permafrost, leading to changes in drainage, increased slumping, and altered landscapes over large areas. Polar warming probably will increase biological production but may lead to different species composition on land and in the sea. On land, there will be a tendency for polar shifts in major biomes such as tundra and boreal forest and associated animals, with significant impacts on species such as bear and caribou. However, the Arctic Ocean geographically limits northward movement. Much smaller changes are likely for the Antarctic, but there may be species shifts. In the sea, marine ecosystems will move poleward. Animals dependent on ice may be disadvantaged in both polar areas.

Hydrology and Water Resources. Increasing temperature will thaw permafrost and melt more snow and ice. There will be more running and standing water. Drainage systems in the Arctic are likely to change at the local scale. River and lake ice will break up earlier and freeze later.

Food and Fiber Production. Agriculture is severely limited by the harsh climate. Many limitations will remain in the future, although some small northern extension of farming into the Arctic may be possible. In general, marine ecological productivity should rise. Warming should increase growth and development rates of nonmammals; ultraviolet-B (UV-B) radiation is still increasing, however, which may adversely affect primary productivity as well as fish productivity.

Coastal Systems. As warming occurs, the Arctic could experience a thinner and reduced ice cover. Coastal and river navigation will increase, with new opportunities for water transport, tourism, and trade. The Arctic Ocean could become a major global trade route. Reductions in ice will benefit offshore oil production. Increased erosion of Arctic shorelines is expected from a combination of rising sea level, permafrost thaw, and increased wave action as a result of increased open water. Further breakup of ice shelves in the Antarctic peninsula is likely. Elsewhere in Antarctica, little change is expected in coastlines and probably in its large ice shelves.

Human Settlements. Human communities in the Arctic will be substantially affected by the projected physical and ecological changes. The effects will be particularly important for indigenous peoples leading traditional lifestyles. There will be new opportunities for shipping, the oil industry, fishing, mining, tourism, and migration of people. Sea ice changes projected for the Arctic have major strategic implications for trade, especially between Asia and Europe.

Conclusions. The Antarctic peninsula and the Arctic are very vulnerable to projected climate change and its impacts. Although the number of people directly affected is relatively small, many native communities will face profound changes that impact on traditional lifestyles. Direct effects could include ecosystem shifts, sea and river-ice loss, and permafrost thaw. Indirect effects could include feedbacks to the climate system such as further releases of greenhouse gases, changes in ocean circulation drivers, and increased temperature and higher precipitation with loss of ice, which could affect climate and sea level globally. The interior of Antarctica is less vulnerable to climate change, because the temperature changes envisaged over the next century are likely to have little impact and very few people are involved. However, there are considerable uncertainties about the mass balance of the Antarctic ice sheets and the future behavior of the West Antarctic ice sheet (low probability of disintegration over the next century). Changes in either could affect sea level and Southern Hemisphere climates.

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APPENDIX 4D

Excerpted Materials from the U.S. Global Change Research Program Assessment Overview Report on Climate Change Impacts on the United States (U.S. Global Change Research Program, 2000) and Subsidiary Regional Assessment Reports

The subject Assessment Overview on Climate Change Impacts on the United States (USGCRP, 2000) was prepared by the USGCRP National Assessment Synthesis Team (NAST) and represents an important landmark for the U.S. national process of research analyses and dialog about coming changes in climate, their impacts, and possible adaptation measures that can be taken. NAST consists of a committee of experts drawn from governments, academia industry, and nongovernmental organizations (NGO’s). The subject overview is based on a much more extensive, detailed “foundation” report, written by NAST in coordination with independent regional and sector assessment teams. The subject assessment, required by a 1990 U.S. law, was conducted under the USGCRP in response to a request from the President’s Science Advisor. The materials presented below are excerpted from the September 2000 NSTC review draft of the assessment overview and, if necessary, later will be appropriately corrected to reflect the final versions of the report due out in fall 2000, after completion of all peer-review and clearance precesses. Selected material derived from one or another of the specific regional assessments also are presented in this appendix. The materials selected for presentation here are meant to provide an informative introduction to the latest available expert assessment of potential sector and regional-scale impacts of climate change in the United States and to illustrate the difficulties in projecting likely varying location-specific mixes of potential deleterious and beneficial effects of climate change.

The past record of 1000 years of global temperature and CO_2 emissions change, as depicted by the assessment overview, is shown in Figure 4D-1. As noted in the Figure 4D-1, there appears to be a relatively close correlation between marked parallel increases in anthropogenic carbon emissions starting roughly in the latter part of the 18th century, increasing atmospheric CO_2 concentrations, and notable increasing global average temperature trends.

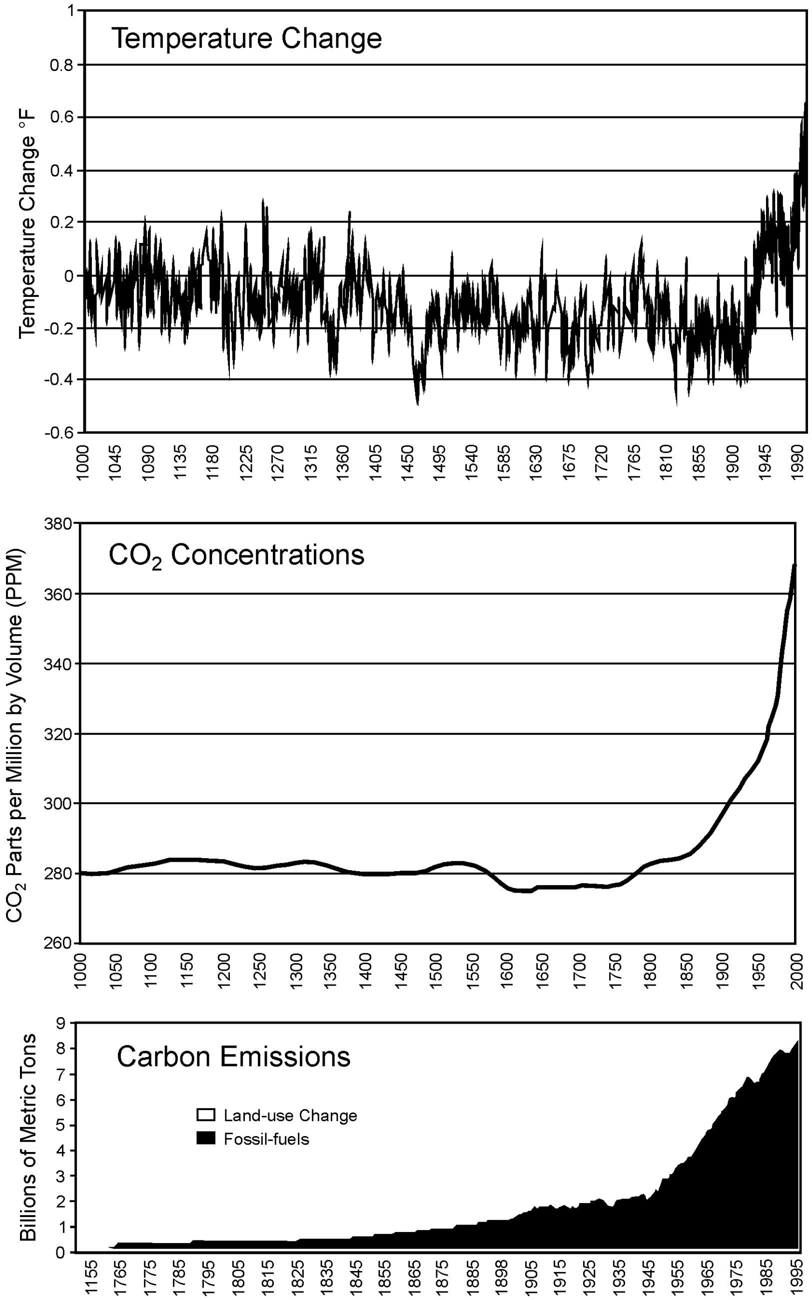


Figure 4D-1. Records of Northern Hemisphere surface temperatures, CO_2 concentrations, and carbon emissions show a close correlation. Temperature Change: reconstruction of annual-average Northern Hemisphere surface air temperatures derived from historical records, tree rings, and corals (blue), and air temperatures directly measured (purple). CO_2 Concentrations: record of global CO_2 concentration for the last 1000 years, derived from measurements of CO_2 concentration in air bubbles in the layered ice cores drilled in Antarctica (blue line) and from atmospheric measurements since 1957. Carbon Emissions: reconstruction of past emissions of CO_2 as a result of land clearing and fossil fuel combustion since about 1750 (in billions of metric tons of carbon per year.

The two primary models used to project future changes in global climate in the USGCRP assessment were developed at the Canadian Climate Centre and the Hadley Centre in the United Kingdom and have been peer-reviewed extensively by other scientists. Both incorporate similar assumptions about future emissions of carbon dioxide and other major greenhouse gases (both approximate the IPCC "business as usual" scenario with a 1% per year increase in greenhouse gases and growing sulfur emissions). These models were the best fit to a list of criteria developed for the U.S. National Assessment. Climate models developed at the National Center for Atmospheric Research (NCAR), NOAA's Geophysical Fluid Dynamics Laboratory (GFDL), NASA's Goddard Institute for Space Studies (GISS), and Max Planck Institute (MPI) in Germany also were used in various aspects of the assessment. Although the physical principles driving the models are similar, they differ in how they represent the effects of some important processes, with the two primary models yielding different views of 21st century climate. On average over the United States, the Hadley model projects a much wetter climate than does the Canadian model, although the Canadian model projects a greater increase in temperature than does the Hadley. Both projections are plausible, given current understanding. See Figure 4D-2 for plots of U.S. average temperature increases projected by the different models. In all climate models, increases in temperature for the United States are significantly higher than global average temperature increases (see Table 4D-1), because of the fact that all models project warming to be greatest at middle to high latitudes (partly because melting snow and ice make the surface less reflective of sunlight, allowing it to absorb more heat). Warming also will be greater over land than over the oceans because it takes longer for the oceans to warm.

Uncertainties about future climate stem from a wide variety of factors (e.g., questions about how to represent clouds and precipitation in climate models and uncertainties about how emissions of greenhouse gases will change). These uncertainties result in differences in climate model projections. Examining these differences aids in understanding the range of risk or opportunity associated with a plausible range of future climate changes. These differences in model projections also raise questions about how to interpret model results, especially at the regional level, where projections can differ significantly.

One of the most important world-wide consequences of the overall global warming increases projected for the 21st century is sea level rise, and it can be expected to impact Alaska, coastal areas of the continental United States, and U.S. Hawaiian and Carribean islands regions,

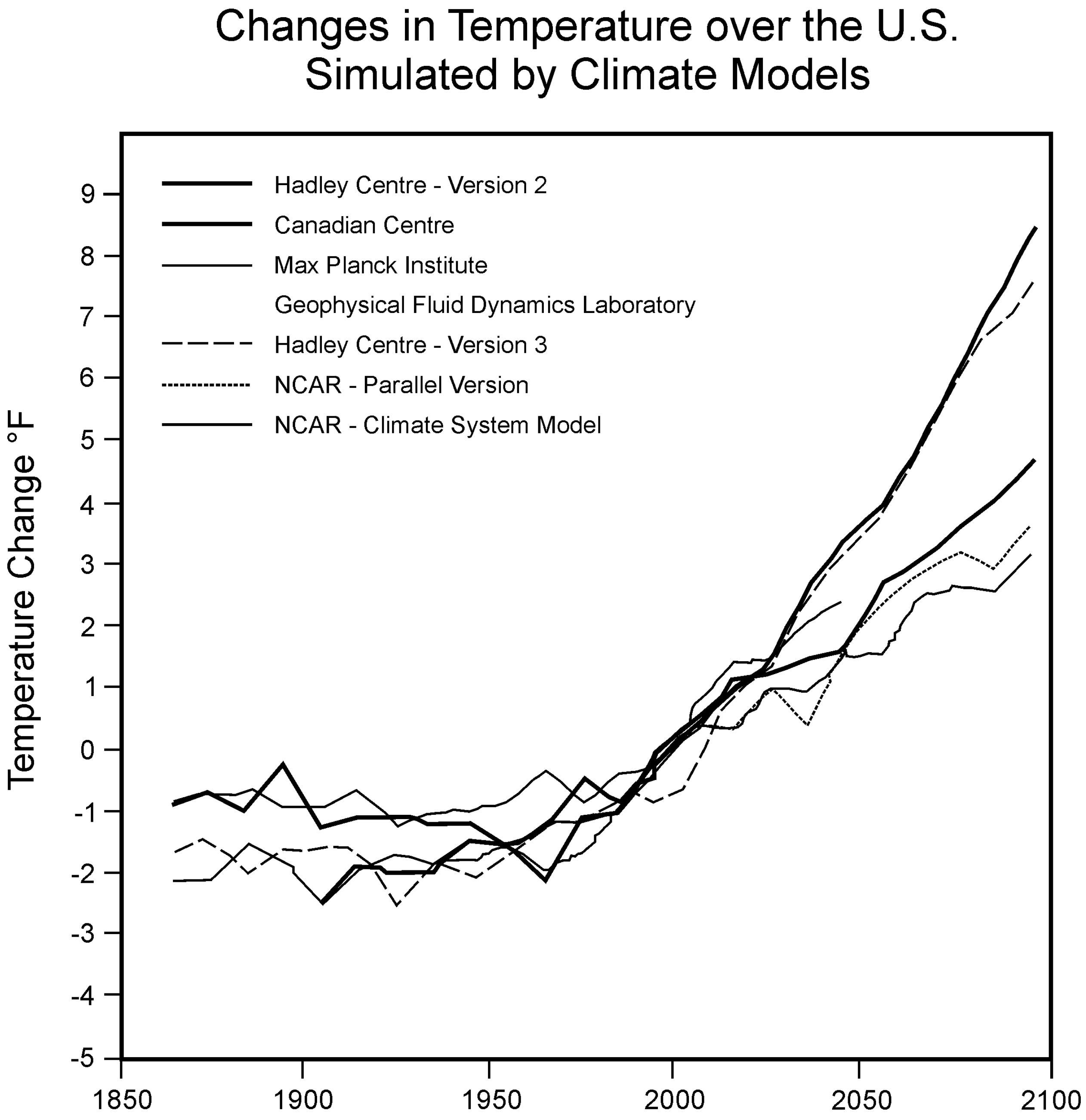


Figure 4D-2. **Simulation of decadal average changes in temperature from leading climate models on historic and projected changes in CO_2 and sulfate atmospheric concentrations. For the 21st century, the projected global temperature increase is 4.9 °F for the Hadley model and 7.4 °F for the Canadian model. The model with the smallest projected increase in global temperature is the NCAR Climate System Model at 3.6 °F. By comparison, the projected increase in temperature for the 21st century over the contiguous United States is Canadian, 9.4 °F, Hadley, 5.5 °F, and NCAR Climate System Model, 4.0 °F.**

TABLE 4D-1. RANGE OF PROJECTED WARMING IN THE 21ST CENTURY

	Global	United States
Hadley Model	+4.9 °F	+5.5 °F
Canadian Model	+7.4 °F	+9.4 °F
NCAR Climate System Model	+3.6 °F	+4.0 °F

as well. Figure 4D-3 illustrates sea level rise predicted by the Canadian and Hadley models used in the USGCRP assessment. The sea level rise projected by either model can be expected to pose threats, not only in terms of potential inundation of low lying portions of the Hawaiian and Carribean islands, but also in terms of shoreline erosion in portions of Alaska and the continental United States. Those continental United States areas most vulnerable to future sea level rise are those low lying areas already experiencing rapid erosion rates, as depicted in Figure 4D-4. Substantial impacts can be expected, including losses of coastal wetlands important for migratory birds and degradation of estuarine sound complexes providing shallow water fishery nurseries (most immediately because of salt water incursions resulting from sea level rise and other impacts resulting from more frequent and extensive algal-toxic blooms impacting coastal commercial fish and shell fish harvests secondary to increased nutrient out flows caused by extreme rain fall events [e.g., during hurricanes]).

The main climate models used all predict notable increases in the minimum and maximum annual average temperatures in the United States during the next 100 years. Projected changes in temperature minimum and maxima are likely more important than average temperatures, in that they influence such things as human comfort, heat and cold stress in plants and animals, maintenance of snow pack, and pest populations (low temperatures kill many pests and higher minimum temperatures may allow increased overwinter survival of pests). The largest increases in temperature are projected over much of the southern United States in summer, dramatically raising the heat index (a measure of discomfort based on temperature and humidity). Also, following an average 5 to 10% increase in average U.S. precipitation over the last century, the climate models project notable changes in precipitation during the 21st century. The Canadian

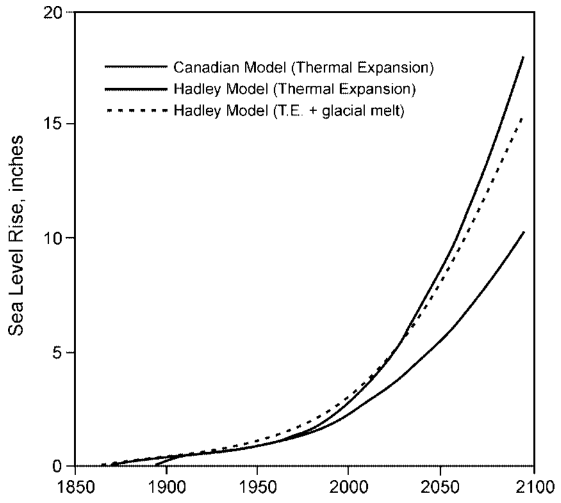


Figure 4D-3. **Historic and projected changes in sea level (in inches) based on the Canadian and Hadley model simulations. The Canadian model projection includes only the effects of thermal expansion of warming ocean waters. The Hadley projection includes both thermal expansion and the additional sea-level rise projected because of melting of land-based glaciers. Neither model includes consideration of possible sea-level changes because of polar ice melting or accumulation of snow on Greenland and Antarctica.**

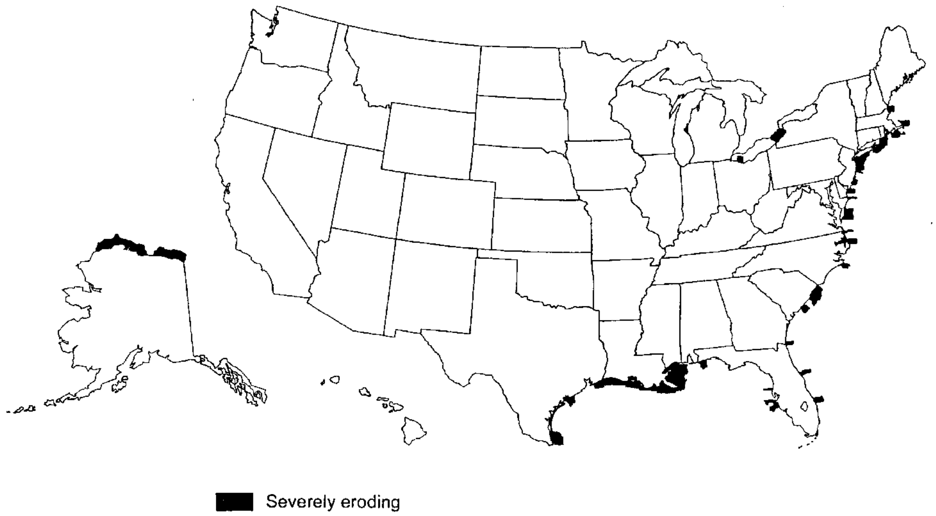


Figure 4D-4. **This map is a preliminary classification of annual shoreline erosion throughout the United States, in coarse detail and resolution. The areas most vulnerable to future sea-level change are those with low relief that are already experiencing rapid erosion rates, such as the Southeast and Gulf Coast.**

model predicts the largest percentage increases in precipitation in California and the Southwest; but east of the Rocky Mountains, the southern half of the United States is projected to have decreased precipitation (with especially large decreases in eastern Colorado, western Kansas, and in an arc stretching from Louisiana to Virginia). The Hadley model predicts largest percentage increases in southern California and the Southwest, along with lesser increases for the rest of the nation, except for small areas of the Northwest and the Gulf Coast. Both models also predict increases in frequency of heavy precipitation effects, largely because of shifts in storm activity and tracks. Soil moisture critical for both agriculture and natural ecosystems may, despite increased precipitation, actually undergo marked decreases in some areas, because of offsetting evaporation rates increased by higher temperatures during projected scenarios of likely increased periods of drought for some U.S. regions.

The predicted changes in temperature and precipitation are expected to result in varying impacts of climate change on ecosystems various U.S. regions. Such impacts will likely include the following.

- Changes in productivity and carbon storage capacity of ecosystems (decreases in some places and increases in others are very likely).
- Shifts in the distribution of major plant and animal species are likely.
- Some ecosystems, such as alpine meadows, are likely to disappear in some places because the new local climate will not support them or there are barriers to their movement.
- In many places, it is very likely that ecosystem services, such as air and water purification, landscape stabilization against erosion, and carbon storage capacity will be reduced. These losses likely will occur in the wake of episodic, large-scale disturbances that trigger species migrations or local extinctions.
- In some places, it is very likely that ecosystems services will be enhanced where climate-related stresses are reduced.

The USGCRP assessment provides extensive detailed evaluations of the above and other types of impacts projected to occur as consequences of changing weather patterns (and consequent shifts in temperature, precipitation, etc.). Such evaluations are summarized in the overview assessment in relation to several overall sectors (water resources, agriculture, forests, coastal areas and marine resources, and human health) and in relation to different regions of the United States.

The following concise statements highlight some of the more salient points emerging from the overall sector evaluations.

- **Water.** Rising temperatures and greater precipitation are likely to lead to more evaporation and greater swings between wet and dry conditions. Changes in the amount and timing of rain, snow, runoff, and soil moisture are very likely. Water management, including pricing and allocation, will very likely be important in determining many impacts.
- **Agriculture.** Overall productivity of American agriculture likely will remain high and is projected to increase throughout the 21st century, with northern regions faring better than southern ones. Though agriculture is highly dependent on climate, it is also highly adaptive Weather extremes, pests, and weeds likely will present challenges in a changing climate. Falling commodity prices and competitive pressures are likely to stress farmers and rural communities.
- **Forests.** Rising CO_2 concentrations and modest warming are likely to increase forest productively in many regions. With larger increases in temperature, increased drought is likely to reduce forest productivity in some regions, notably in the Southeast and Northwest. Climate change is likely to cause shifts in species ranges, as well as large changes in disturbances such as fire and pests.
- **Coastal Areas and Marine Resources.** Coastal wetlands and shorelines are vulnerable to sea-level rise and storm surges, especially when climate impacts are combined with the growing stressed of increasing human population and development. It is likely that coastal communities will be affected increasingly by extreme events. The negative impacts on natural ecosystems are very likely to increase.
- **Human Health.** Heat-related illnesses and deaths, air pollution, injuries and deaths from extreme weather events, and diseases carried by water, food, insects, ticks, and rodents, have all been raised as concerns for the United States in a warmer world. Modern public health efforts will be important in identifying and adapting to these potential impacts.

The USGCRP Assessment also evaluated sector impacts in relation to various U.S. regions, broken out as depicted in Figure 4D-5 derived from the overview assessment (USGCRP, 2000). That assessment highlighted the following important points in relation to expected major impacts in each of the regions evaluated.

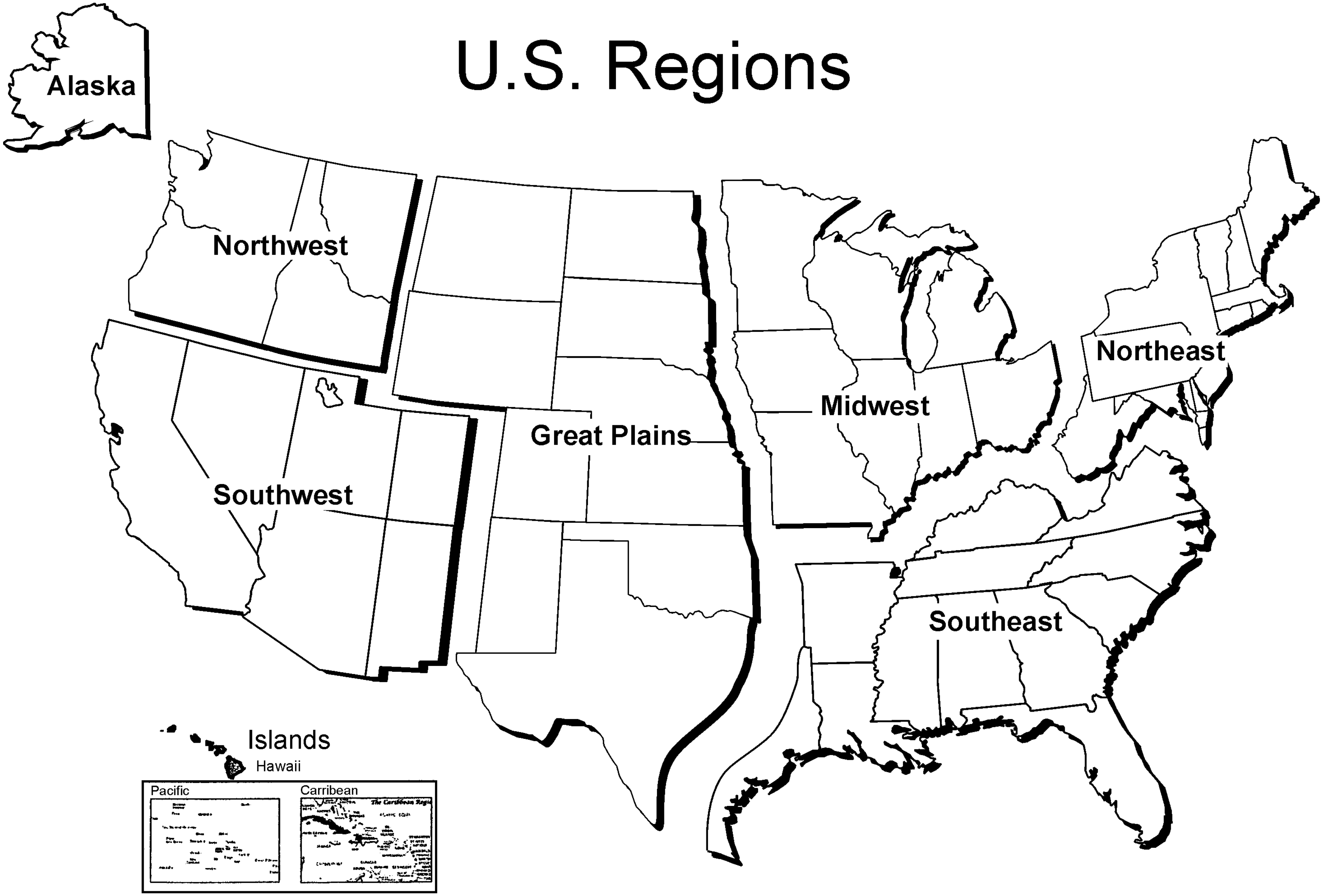


Figure 4D-5. Breakout of U.S. regions as evaluated by USGCRP, based on the overview assessment depiction.

- **Alaska.** Sharp winter and springtime temperature increases are very likely to cause continued thawing of permafrost, further disrupting forest ecosystems, roads, and buildings.
- **Northwest.** Increasing stream temperatures are very likely to further stress migrating fish, complicating restoration efforts.
- **Mountain West.** Higher winter temperatures are very likely to reduce snowpack and peak runoff and shift the peak to earlier in the spring, reducing summer runoff and complicating water management for flood control, fish runs, cities, and irrigation.
- **Southwest.** With an increase in precipitation, the desert ecosystems native to this region are likely to decline, whereas grasslands and shrublands likely are to expand.
- **Midwest/Great Plains.** Higher CO_2 concentrations are likely to offset the effects of rising temperatures on forests and agriculture for several decades, increasing productivity.
- **Southern Great Plains.** Prairie potholes, which provide important habitat for ducks and other migratory waterfowl, are likely to dry up in a warmer climate.
- **Great Lakes.** Lake levels are likely to decline, leading to reduced water supply and more costly transportation. Shoreline damage caused by high water levels is likely to decrease.
- **Northern and Mountain Regions.** It is very probable that warm weather recreational opportunities, such as hiking, will expand, whereas cold weather activities, such as skiing, will contract.
- **Northeast, Southeast, and Midwest.** Rising temperatures are very likely to increase the heat index dramatically in summer, with impacts to health and comfort. Warmer winters are likely to reduce cold-related stresses.
- **Appalachians.** Warmer and moister air very likely will lead to more intense rainfall events, increasing the potential for flash floods.
- **Southeast.** Under warmer wetter scenarios, the range of southern tree species is likely to expand. Under hotter and drier scenarios, it is likely that far southeastern forests will be displaced by grasslands and savannas.
- **Southeast Atlantic Coast.** It is very probable that rising sea levels and storm surge will threaten natural ecosystems and human coastal development and reduce buffering capacity against storm impacts.
- **Southeast Gulf Coast.** Inundation of coastal wetlands will very likely increase, threatening fertile areas for marine life, migrating birds, and waterfowl.

- **Islands.** More intense El Niño and La Niña events are possible and are likely to create extreme fluctuations in water resources for island citizens and the tourists who sustain local economies.

Other materials from the overview assessment summarize regional concerns with regard to different types of sector impacts. Tables 4D-2 and 4D-3 present two examples drawn from the overview assessment, denoting concerns or impacts regarding water resources and types of ecosystems, respectively, likely to be impacted in different U.S. regions.

TABLE 4D-2. TYPES OF WATER CONCERNS PROJECTED TO BE IMPORTANT FOR U.S. REGIONS CONSEQUENT TO FUTURE CLIMATE CHANGE[a]

Region	Floods	Droughts	Snowpack	Groundwater	Lake, River, and Reservoir Levels	Quality
Northeast	X	X	X	X		X
Southeast	X	X		X		X
Midwest	X	X	X	X	X	X
Great Plains	X	X	X	X	X	X
West	X	X	X	X	X	X
Northwest	X	X	X		X	
Alaska		X	X			
Islands	X	X		X		X

[a] This table identifies some of the key regional concerns about water. Many of these issues were raised and discussed by stakeholders during regional workshops and other Assessment meetings held between 1997 and 2000.

As seen in Table 4D-2, different types of water impacts are projected to be of important widespread concern across many different U.S. regions. It should be noted that some limited beneficial effects may occur in some regions (e.g., longer periods of open-water transportation on navigable rivers and sounds in and around Alaska).

The overview assessment notes that the information presented in Table 4D-3 represents only a partial list of potential impacts for major ecosystem types and that, although the impacts often are stated in terms of plant-community impacts, it is important to recognize that such plant-community changes also will have animal habitat effects and consequent impacts on both terrestrial and aquatic animal species. Both the plant and animal impacts can have further consequent impacts on human health and welfare, which also can be expected to vary considerably from region to region.

TABLE 4D-3. PROJECTED FUTURE CLIMATE-CHANGE-INDUCED IMPACTS ON TYPES OF ECOSYSTEMS OF CONCERN TO DIFFERENT U.S. REGIONS

Ecosystem Type	Impacts	U.S. Regions							
		NE	SE	MW	GP	WE	PNW	AK	IS
Forests	Changes in tree species composition and alteration of animal habitat	**X**	**X**	**X**		**X**	**X**	**X**	**X**
	Displacement of forests by woodlands and grasslands under a warmer climate in which soils are drier		**X**						
Grasslands	Displacement of grasslands by woodlands and forests under a wetter climate					**X**			
	Increase in success of nonnative invasive plant species				**X**	**X**	**X**		**X**
Tundra	Loss of alpine meadows as their species are displaced by lower elevation species	**X**				**X**	**X**	**X**	
	Loss of northern tundra as trees migrate poleward							**X**	
	Changes in plant community composition and alteration of animal habitat							**X**	
Semi-arid and Arid	Increase in woody species and loss of desert species under wetter climate					**X**			
Freshwater	Loss of prairie pot holes with more frequent drought conditions				**X**				
	Habitat changes in rivers and lakes as amount and timing of runoff changes and water temperatures rise	**X**	**X**	**X**	**X**	**X**	**X**		
Coastal and Marine	Loss of coastal wetlands as sea level rises and coastal development prevents landward migration	**X**	**X**			**X**	**X**		**X**
	Loss of barrier islands as sea-level rise prevents landward migration	**X**	**X**						
	Changes in quantity and quality of freshwater delivery to estuaries and bays alter plant and animal habitats	**X**	**X**			**X**	**X**	**X**	**X**
	Loss of coral reefs as water temperature increases		**X**					**X**	**X**
	Changes in ice location and duration alter marine mammal habitat							**X**	

The USGCRP (2000) assessment included extensive detailed evaluation of projected climate change impacts on the different U.S. regions depicted in Figure 4D-5. Overview reports on those detailed evaluations by various regional assessment teams are in various stages of preparation, with information pertaining to each being available via the internet at the following address: http://www.nacc.usgcrp.gov/regions/.

The wide variation in the types of projected impacts of climate change, both deleterious and some possible beneficial effects, can be readily illustrated by one example illustrated in Figure 4D-6. The figure depicts projected types of changes that may occur (with varying degrees of certainty indicated) as the consequence of climate change impacts on the Mid-Atlantic Region (MAR) of the United States, including both potentially negative and positive impacts.

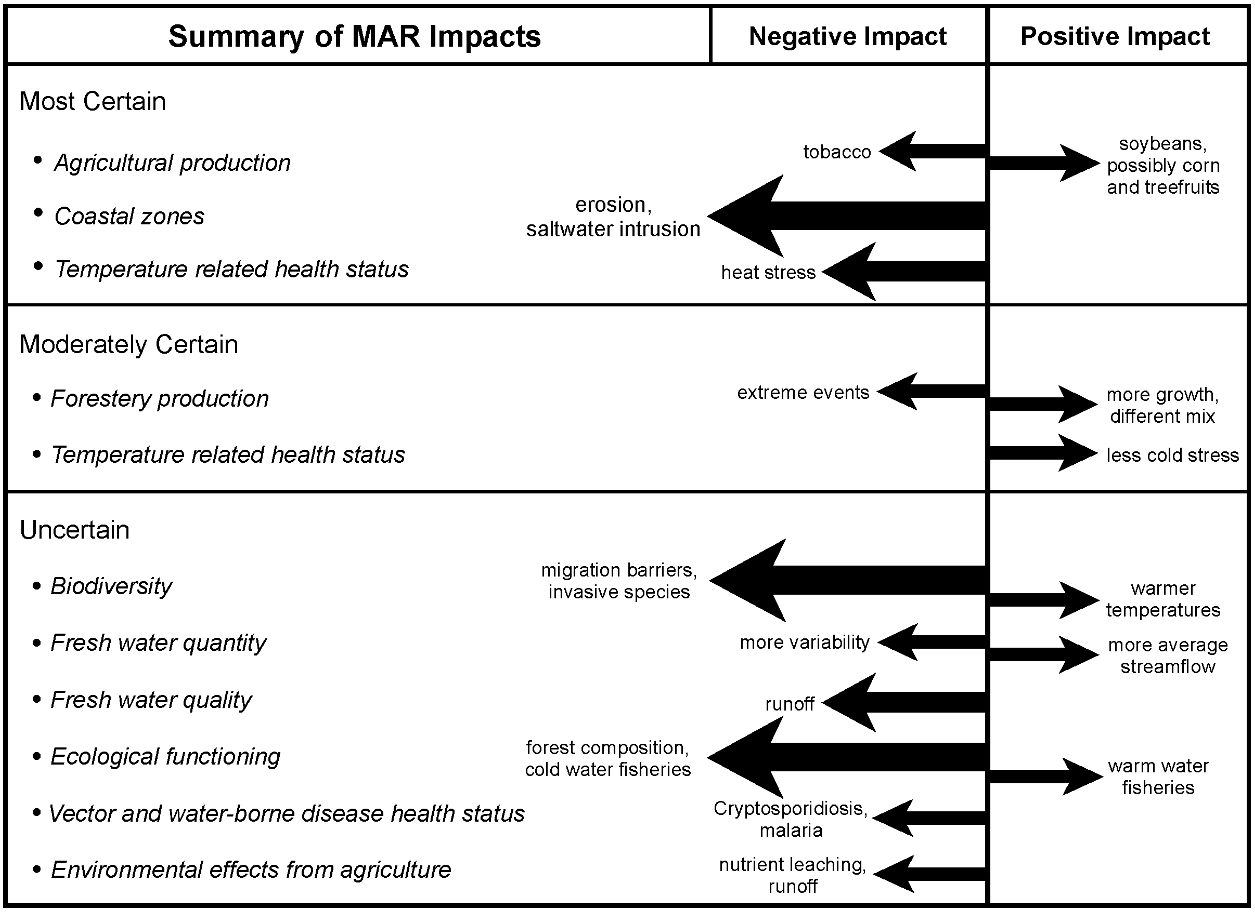


Figure 4D-6. Projected climate change impacts in the Mid-Atlantic Region (MAR) of the United States.

Source: Mid-Atlantic Regional Assessment Team (2000).

REFERENCES

Mid-Atlantic Regional Assessment (MARA) Team. (2000) Preparing for a changing climate: the potential consequences of climate variability and change (Mid-Atlantic overview). Washington, DC: U.S. Global Change Research Program (USGCRP).

U. S. Global Change Research Program (USGCRP, 2000) Climate Change Impacts on the United States: the Potential Consequences of Climate Variability and Change (Overview), Report of National Assessment Synthesis Team (NAST). NSTC Review Draft (September 2000).

APPENDIX 4E

Recent Model Projections of Excess Mortality Expected in U.S. Cities During Summer and Winter Seasons Because of Future Climate Change, Based on Kalkstein and Greene (1997)

TABLE 4E-1. MODELED PROJECTIONS OF DIRECT HUMAN HEALTH IMPACTS OF CLIMATE CHANGE: ESTIMATED TOTAL EXCESS MORTALITY IN U.S. URBAN AREAS FOR AN AVERAGE SUMMER SEASON, ASSUMING FULL ACCLIMATIZATION[a]

		Year 2020 Climate			Year 2050 Climate		
SMSA	Present climate	GFDL 89	UKMO	Max Planck	GFDL 89	UKMO	Max Planck
Anaheim	0	0	0	0	0	0	0
Atlanta	25	43	62	22	60	138	33
Baltimore	84	57	148	63	124	164	131
Birmingham	42	26	47	14	40	47	21
Boston	96	113	165	134	155	194	160
Buffalo	33	15	52	36	34	73	59
Chicago	191	243	538	421	359	583	550
Cincinnati	14	16	90	49	54	81	67
Cleveland	29	21	55	44	46	58	53
Columbus	33	24	83	51	51	90	78
Dallas	36	45	62	45	107	64	44
Denver	42	29	41	30	35	39	32
Detroit	110	84	240	164	130	271	256
Ft. Lauderdale	0	0	0	0	0	0	0
Greensboro	22	28	43	27	37	45	29
Hartford	38	21	42	32	38	50	41
Houston	7	7	16	7	15	17	6
Indianapolis	36	23	93	51	55	86	69
Jacksonville	0	0	0	0	0	0	0
Kansas City	49	79	173	93	121	156	105
Los Angeles	68	74	123	83	110	128	116
Louisville	17	0	2	0	0	1	1
Memphis	25	42	27	57	40	29	49
Miami	0	0	0	0	0	0	0
Minneapolis	59	55	185	148	123	215	186
Nassau	29	59	84	84	110	116	116
New Orleans	20	0	0	0	0	0	0
New York	307	363	753	498	460	999	727

TABLE 4E-1 (cont'd). MODELED PROJECTIONS OF DIRECT HUMAN HEALTH IMPACTS OF CLIMATE CHANGE: ESTIMATED TOTAL EXCESS MORTALITY IN U.S. URBAN AREAS FOR AN AVERAGE SUMMER SEASON, ASSUMING FULL ACCLIMATIZATION[a]

		Year 2020 Climate			Year 2050 Climate		
SMSA	Present climate	GFDL 89	UKMO	Max Planck	GFLD 89	UKMO	Max Planck
Newark	26	83	173	111	150	127	161
Philadelphia	129	99	362	191	246	477	323
Phoenix	0	0	0	0	0	0	0
Pittsburgh	39	32	66	64	61	83	95
Portland	9	13	22	11	23	31	14
Providence	47	39	80	52	73	96	74
Riverside	4	6	10	6	8	11	7
Salt Lake City	0	0	0	0	0	0	0
San Antonio	4	0	0	0	0	0	0
San Diego	0	0	0	0	0	0	0
San Francisco	28	24	23	23	18	24	23
San Jose	0	0	0	0	0	0	0
Seattle	5	1	0	2	0	0	1
St. Louis	79	149	173	158	212	155	189
Tampa	28	68	95	28	95	100	47
Washington, DC	0	0	0	0	0	0	0
Total	1,840	1,981	4,128	2,799	3,790	4,748	3,863

[a] Abbreviations: SMSA, standard metropolitan statistical area; GFDL, Geophysical Fluid Dynamics Laboratory Model; UKMO, United Kingdom Meteorological Office Model; Max Planck, Max Planck Institute Model. Values given are estimated excess deaths.

Source: Kalkstein and Green (1997).

TABLE 4E-2. MODELED PROJECTIONS OF DIRECT HUMAN HEALTH IMPACTS OF GLOBAL CLIMATE CHANGE: ESTIMATED TOTAL EXCESS MORTALITY IN U.S. URBAN AREAS FOR AN AVERAGE WINTER SEASON, ASSUMING FULL ACCLIMATIZATION[a]

		Year 2020 climate			Year 2050 climate		
SMSA	Present Climate	GFDL 89	UKMO	Max Planck	GFDL 89	UKMO	Max Planck
Anaheim	2	0	0	1	0	0	0
Atlanta	37	53	48	52	50	47	52
Baltimore	0	0	0	0	0	0	0
Birmingham	25	12	8	11	11	7	12
Boston	0	0	0	0	0	0	0
Buffalo	7	18	8	17	5	5	18
Chicago	2	4	3	4	4	2	5
Cincinnati	0	0	0	0	0	0	0
Cleveland	2	9	10	10	15	10	9
Columbus	12	1	2	1	3	2	1
Dallas	32	41	33	43	36	31	41
Denver	9	10	11	10	11	11	11
Detroit	34	15	20	15	18	25	14
Ft. Lauderdale	36	4	4	5	3	3	5
Greensboro	0	0	0	0	0	0	0
Hartford	0	0	0	0	0	0	0
Houston	24	33	29	35	29	27	33
Indianapolis	16	32	28	33	34	28	32
Jacksonville	0	0	0	0	0	0	0
Kansas City	12	51	36	46	42	35	46
Los Angeles	100	102	78	100	77	88	81
Louisville	16	12	17	12	19	15	12
Memphis	23	20	17	19	19	15	19
Miami	46	35	35	37	32	32	36
Minneapolis	0	0	0	0	0	0	0
Nassau	24	21	4	20	5	3	21

TABLE 4E-2 (cont'd). MODELED PROJECTIONS OF DIRECT HUMAN HEALTH IMPACTS OF GLOBAL CLIMATE CHANGE: ESTIMATED TOTAL EXCESS MORTALITY IN U.S. URBAN AREAS FOR AN AVERAGE WINTER SEASON, ASSUMING FULL ACCLIMATIZATION[a]

		Year 2020 climate			Year 2050 climate		
SMSA	Present Climate	GFDL 89	UKMO	Max Planck	GFDL 89	UKMO	Max Planck
New Orleans	52	56	51	54	51	47	54
New York	102	123	150	120	152	93	121
Newark	48	23	8	20	10	6	23
Philadelphia	85	80	14	73	36	9	82
Phoenix	26	25	26	25	26	27	26
Pittsburgh	19	20	29	21	24	31	21
Portland	17	15	12	15	12	10	13
Providence	27	21	34	33	35	36	21
Riverside	10	26	29	26	27	27	26
Salt Lake City	5	7	9	8	8	10	9
San Antonio	9	10	6	11	5	4	9
San Diego	17	26	16	24	16	18	16
San Francisco	85	39	30	42	30	21	26
San Jose	3	2	4	2	3	5	4
Seattle	13	40	45	37	46	47	43
St. Louis	50	61	68	60	53	61	61
Tampa	21	26	24	26	22	20	25
Washington, DC	19	31	38	30	20	35	31
Total	1,067	1,104	984	1,098	989	894	1,059

[a] Abbreviations: SMSA, standard metropolitan statistical area; GFDL, Geophysical Fluid Dynamics Laboratory Model; UKMO, United Kingdom Meteorological Office Model; Max Planck, Max Planck Institute Model. Values given are estimated excess deaths.

REFERENCE

Kalkstein, L. S.; Greene, J. S. (1997) An evaluation of climate/mortality relationships in large U.S. cities and the possible impacts of a climate change. Environ. Health Perspect. 105: 84-93.

5. HUMAN EXPOSURE TO PARTICULATE MATTER AND ITS CONSTITUENTS

5.1 INTRODUCTION

5.1.1 Purpose

Exposure is defined as the contact by an individual with a pollutant for a specific duration of time at a visible external boundary (modified from Duan 1982, 1991). For airborne particulate matter (PM), the breathing zone is considered the point of contact and the lung is the external boundary of concern. An individual's exposure is measured as the PM air concentration in his/her breathing zone over time. Understanding exposure is important, because it is individuals who experience adverse health effects associated with elevated PM concentrations in ambient air.

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 PM air concentrations. Thus, a major emphasis must be to develop an understanding of exposure to PM from ambient sources. However, personal exposure to total PM may result from exposure to PM from both ambient and nonambient sources. Therefore, it will be necessary to account for both in order to fully understand the relationship between PM and health effects. Personal exposure to PM from nonambient sources may be a confounder in community-based epidemiological studies in which ambient PM measures are correlated with community health parameters. 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.

The overall purpose of this chapter is to provide current exposure information that will aid in the understanding and interpretation of PM dosimetry, toxicology, and epidemiology studies assessed in later chapters. The specific objectives of this chapter, which are described below, 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 exposure to total PM and to PM from ambient and nonambient PM sources

(2) To provide a concise summary and review of recent data (since 1996) and findings from pertinent studies of personal exposure to total PM and to PM from ambient and nonambient sources

(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

(4) To evaluate the implications of using ambient PM concentrations as a surrogate for exposure in epidemiological 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 adverse health effects may be related to PM characteristics other than mass. PM from ambient and nonambient sources also may have differing physical and chemical characteristics and differing health effects. Ultimately, to understand and control health impacts caused by PM, it is important to quantify and understand exposure to those chemical constituents responsible for the 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, NRC Research Topic 1 recommends evaluating the relationship between outdoor measures versus actual human exposure 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 studies “should be designed to determine the extent to which members of the population contact these biologically important constituents and size fraction of concern in outdoor air, outdoor air that has penetrated indoors, and air pollutants generated indoors” (NRC, 1999). Thus, when biologically important constituents are identified, 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 chemical constituents will be required to more fully identify, understand, and control those sources of PM with adverse health effects and to accurately define the relationship between PM exposure and health outcomes.

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 (PM AQCD) (National Air Pollution Control Administration, 1969) did not discuss either *exposure* or *indoor concentrations.* The 1982 PM AQCD (U.S. Environmental Protection Agency, 1982) provided some discussion of indoor PM concentrations, reflecting an increase in microenvironmental and personal exposure studies. 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 concentrations and personal PM exposures of the residents were greater than ambient PM 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. Many of the studies cited showed poor correlations between personal exposure or indoor measurements of PM 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), for the first time, distinguished between ambient and nonambient PM exposure. This chapter builds on the work of the 1996 PM AQCD by further evaluating the ambient and nonambient components of PM, as well as reporting research that evaluates the relationship between ambient concentrations and total, ambient, and nonambient personal exposure.

5.2 STRUCTURE FOR THE CHAPTER

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 5.3 discusses the basic concepts of exposure, including definitions, methods for estimating exposure, and methods for estimating ambient components of exposure.
- Section 5.4 presents PM mass data, including a description of the key available studies, correlations of PM exposures with ambient concentrations, and factors that effect the correlations.
- Section 5.5 presents data on PM constituents, including a description of the key available studies, correlations with ambient concentrations, and factors that effect the correlations.
- Section 5.6 discusses the implications of using ambient PM concentrations in epidemiological studies of PM health effects.
- Section 5.7 summarizes key findings and limitations of the information.

5.3 BASIC CONCEPTS OF EXPOSURE

5.3.1 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 (μ**e**'s). 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 μ**e** and surrounding μ**e**'s (Mage, 1985). In general, people pass through a series of μ**e**'s, including outdoor, in-vehicle, and indoor μ**e**'s, as they go through time and space. Thus, total *daily* exposure for a single individual to PM can be expressed as the sum of various microenvironmental exposures that the person occupies in the day (modified from National Research Council, 1991).

In a given μ**e**, particles may originate from a wide variety of sources. For example, in an indoor μ**e**, PM may be generated by (1) indoor activities, (2) outdoor PM entering the indoor μ**e**, (3) the chemical interaction of outdoor air pollutants and indoor air or indoor sources, (4) transport from another indoor μ**e**, or (5) personal activities. All of these disparate sources have to be accounted for in a total human PM exposure assessment.

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 will be used throughout this section and will provide the terminology for evaluating personal exposure to total PM and PM from ambient and nonambient sources.

5.3.2 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 and perform their daily activities. *Indirect approaches* use available information on concentrations of chemicals in microenvironments, along with information about the time individuals spend in those microenvironments and personal PM generating activities. The indirect approach then uses models and data on microenvironmental air concentrations and time spent in microenvironments to estimate personal exposure. This section describes the methods to directly measure personal exposures and microenvironmental concentrations, as well

TABLE 5-1. CLASSES OF PARTICULATE MATTER EXPOSURE AND CONCENTRATION DEFINITIONS

Term	Notation	Definition
		General Definitions
Concentration	C	Air concentration of PM in a given microenvironment, expressed in $\mu g/m^3$
Personal Exposure	E	Contact at visible external boundaries of an individual with a pollutant for a specific duration of time; quantified by the amount of PM available in concentration units ($\mu g/m^3$) at the oral/nasal contact boundary for a specified time period (Δt). General term for any exposure variable.
Microenvironment	$\mu\mathbf{e}$	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 $\mu\mathbf{e}$ and surrounding $\mu\mathbf{e}$s
		Concentration Variables
Ambient PM	C_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.
Ambient-Outdoor PM	C_{ao}	Ambient PM in an outdoor microenvironment
Indoor PM	C_i	All PM found indoors
Ambient-Indoor PM	C_{ai}	Ambient PM that has infiltrated indoors (i.e., has penetrated indoors and remains suspended)
Indoor-Generated PM	C_{ig}	PM generated or formed indoors
		Exposure Variables
Personal Exposure to Indoor-Generated PM	E_{ig}	Sum of personal exposure resulting from indoor-generated PM
Personal Exposure to Ambient-Generated PM	E_{ag}	Sum of personal exposure caused by ambient-outdoor and ambient indoor PM (does not include resuspended ambient PM previously deposited indoors)
Personal Exposure to Personal-Activity PM	E_{pact}	Small-scale PM-generating activities that primarily influence exposure of the person performing the activity itself
Personal Exposure to Nonambient PM	E_{nonag}	Sum of personal exposure to indoor-generated and personal activity PM $E_{nonag} = E_{ig} + E_{pact}$
Personal Exposure to Total PM	E_t	Sum of all personal exposures to ambient and nonambient PM $E_t = E_{ig} + E_{pact} + E_{ag} = E_{nonag} + E_{ag}$

as the models used to estimate exposure. Several approaches to estimate personal exposure to ambient PM also are described.

5.3.2.1 Direct Measurement Methods

5.3.2.1.1 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 impacted by exhaled breath). The inlet to a PEM normally is placed at the outer limit of the breathing zone to avoid a negative sampling bias resulting from dilution of the collected air by exhaled breath depleted of PM. However, such placement does not allow for the sampling of *directly* inhaled cigarette smoke or inhaled air that passes through a dust mask. PEMs for PM use measurement techniques similar to those used for ambient PM. The PEM is a 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 and, 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.

Other methods used for ambient PM also have been adapted for use as a personal exposure monitor. For example, a personal nephelometer that measures particle number within a specific particle size range using light scattering has been used in personal exposure studies to obtain real-time measurements of PM.

5.3.2.1.2 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 also have also been used (Climet, LASX, SMPS, APS). Measurement techniques are discussed in Chapter 2.

5 3.2.2 Indirect Methods (Modeling Methods)

5.3.2.2.1 Personal Exposure Models

Exposure modeling for $PM_{2.5}$ mass 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. In addition, the time-varying dose profile of an exposed individual can be modeled only by using the time-series approach (McCurdy, 1997, 2000). We define the *personal exposure* of an individual to a chemical in air to be (NRC, 1991)

$$E = \int_{t=t_1}^{t=t_2} C(t)\, dt,$$

where

E is the personal exposure during the time period from t_1 to t_2, and

C(t) is the concentration near the nose and mouth not impacted by exhaled air, at time t.

In general, personal exposure models combine microenvironmental concentration data with human activity pattern data to estimate personal exposures. Time-averaged models also 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:

$$E = \sum_j E_j = \frac{1}{T}\left(\sum_j \overline{C}_j t_j \right), \tag{5-1}$$

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*, $\overline{C}_j$, weighted by the time spent in microenvironment *j*, t_j. T is the sum of t_j over all *j*. 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 exposure formulation 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).

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 below in Section 5.3.2.2.2.

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. Population cohorts with diverse characteristics can be constructed from the activity data in CHAD and used for exposure analysis and modeling (McCurdy, 2000). Table 5-2 is a summary listing 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 study, (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). GIS-based approaches to estimate health risks of environmental concentrations also have been developed (e.g., Beyea and Hatch, 1999; Jensen, 1999). A recent summary 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) used site-specific coefficient of haze (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 microenvironments when sufficient data was 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 will help 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 NERL. A first-generation population exposure model for PM, called the Stochastic Human Exposure and Dose Simulation (SHEDS-PM) model, recently has been

TABLE 5-2. ACTIVITY PATTERN STUDIES INCLUDED IN THE CONSOLIDATED HUMAN ACTIVITY DATABASE

Study Name	Calendar Time Period of the Study	Age[1]	Days[2]	Diary		Rate[5]	Documentation or Reference	Notes
				Type[3]	Time[4]			
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. (1989) Wiley et al. (1991b)	
CARB: Children	Apr 1989-Feb 1990	0 - 11	1,200	Retrospective	24h Standard	No	Wiley et al. (1991a)	
Cincinnati (EPRI)	Mar-Apr and Aug 1985	0 - 86	2,614	Diary	24h; nominal 7 p.m.-7 a.m.	Yes	Johnson (1989)	3 consecutive days; 186 P-D removed[7]
Denver (EPA)	Nov 1982-Feb 1983	18 - 70	805	Diary	24h; nominal 7 p.m.-7 a.m.	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 p.m.-7 a.m.	No	Akland et al. (1985) Hartwell et al. (1984)	Part of a CO PEM[6] study; 6 P-D removed[7]

Notes: [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		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
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.

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). This model is yet to be evaluated and is discussed for information purposes only because results from the case study have been only recently reported in a journal article submitted for peer review (Burke et al., 2001).

5.3.2.2.2 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 and the generation of particles from indoor sources:

$$V \, dC_i / dt = \nu P C_a - \nu C_i - kVC_i + Q_i, \tag{5-2}$$

where V = volume of the well-mixed indoor air (cubic meters),
C_i = concentration of indoor PM;
ν = volumetric air exchange rate between indoors and outdoors (cubic meters per hour);
P = penetration ratio, the fraction of ambient (outdoor) PM that is not removed from ambient air during its entry into the indoor volume;
C_a = concentration of PM in the ambient air (micrograms per cubic meter);
k = removal rate (per hour); and
Q_i = indoor sources of particles (micrograms per hour).

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 and ν.

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).

5.3.2.3 Methods of Estimating Personal Exposure to Ambient Particulate Matter

In keeping with the various components of PM exposure described above in Section 5.3.1, 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

$$\begin{aligned} E_t &= E_{ag} + E_{ig} + E_{pact} \\ E_t &= E_{ag} + E_{nonag}, \end{aligned} \tag{5-3}$$

where E_t is the total personal exposure to ambient and nonambient PM, E_{ag} is personal exposure to ambient PM (the sum of ambient PM while outdoors and ambient PM that has infiltrated indoors, while indoors), E_{ig} is personal exposure to indoor-generated PM, E_{pact} is personal exposure to PM from personal activity, and E_{nonag} is personal exposure to nonambient PM. 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.

5.3.2.3.1 Mass Balance Approach

Ambient-Indoor Concentrations of Particulate Matter

The mass balance model described above (Equation 5-2) 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, and assuming that all variables remain constant (Ott et al., 2000; Dockery and Spengler, 1981; Koutrakis et al., 1992). By substituting $dC_{ai} + dC_{ig}$ for dC_i in equation 5-2 and assuming dC_{ai} and $dC_{ig} = 0$, ambient-indoor PM (C_{ai}) and indoor-generated PM (C_{ig}), at equilibrium, are given by

$$C_{ai} = (C/_{ao}\, P\, a) \Big/ (a + k) \qquad (5\text{-}4)$$

$$C_{ig} = \left(Q_i / V\right) \Big/ (a + k)\,, \qquad (5\text{-}5)$$

where $a = \nu/V$, the number of air exchanges per hour. Equations 5-4 and 5-5 assume equilibrium conditions and, therefore, are valid only when the parameters k, a, C_{ao}, and Q_i are not changing rapidly and when the Cs are averaged over several hours. Under certain conditions (e.g., air-conditioned homes, homes with HVAC or air cleaners that cycle on and off, ambient pollutants with rapidly varying concentrations), nonequilibrium versions of the mass balance model (Ott et al., 2000; Freijer and Bloeman, 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 5-4 may be rearranged further to give C_{ai}/C_{ao}, the equilibrium fraction of ambient PM that is found indoors, defined as the infiltration factor (F_{INF}) (Dockery and Spengler, 1981).

$$F_{INF} = \frac{C_{ai}}{C_{ao}} = \frac{P\,a}{a + k} \tag{5-6}$$

The penetration ratio (P) and the decay rate (*k*) can be estimated using a variety techniques. A discussion of these variables and estimation techniques is given in Section 5.4.3.2.2. Because both P and *k* are a function of particle aerodynamic diameter, F_{INF} also will be a function of particle aerodynamic diameter.

Personal Exposure to Ambient-Generated Particulate Matter

Personal exposure to ambient-generated PM (E_{ag}) may be estimated using ambient-indoor PM concentration (C_{ai}) from the mass balance model, ambient outdoor PM concentrations (C_{ao}) and information on the time an individual spent in the various microenvironments. Mathematically, this may be expressed as

$$\begin{aligned} E_{ag} &= yC_{ao} + (1 - y)C_{ai} \\ &= yC_{ao} + \ (1 - y)C_{ao}\left[\frac{Pa}{(a + k)}\right], \end{aligned} \tag{5-7}$$

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 generated PM (E_{ag}) as the product of the ambient PM concentration (C_{ao} or C_a) 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 5-7 can be rearranged to obtain an expression for α:

$$\alpha = \frac{E_{ag}}{C_{ao}} = y + (1 - y)\left[\frac{P\,a}{a + k}\right]. \tag{5-8}$$

Substituting equation 5-6 in equation 5-8 gives a relationship for α in terms of the infiltration factor F_{INF} and the fraction of time spent in the various microenvironments:

$$\alpha = y + (1 - y)\ F_{INF}. \qquad (5\text{-}9)$$

Thus, personal exposures to ambient PM (E_{ag}) may be calculated from measurable quantities:

$$E_{ag} = \alpha\ C_{ao}. \qquad (5\text{-}10)$$

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).

The use of a mass balance model to separate personal exposure into two components because of exposure to ambient and nonambient concentrations is not novel. This approach, based on Equation 5-3 as given in Duan (1982) and called superposition of component concentrations, has been applied using multiple microenvironments 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-generated 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).

5.3.2.3.2 Tracer Species as Surrogates of Ambient-Generated Particulate Matter

The ratio of personal exposure to ambient concentration for a PM component that has no indoor sources may be used as a measure of the ratio of personal exposure to ambient PM to the ambient concentration of PM for PM of similar aerodynamic diameter (Wilson et al., 2000). Sulfate, in particular, often is used as a marker of outdoor air in indoor microenvironments

(Jones et al., 2000). It is found primarily in the $PM_{2.5}$ fraction of the aerosol (Cohen et al., 2000). Özkaynak et al. (1996a, b) and Janssen et al. (1999a) report, in the PTEAM and Netherlands studies respectively, that XRF analyses of indoor PM and the immediate outdoor PM show that sulfur is the only element reported with virtually identical mass concentrations in both indoor and outdoor air. Therefore, where there are no indoor sources of fine-mode sulfates, one may deduce that the ambient-to-personal relationship found for sulfates probably would be the same as that for unspeciated particulate matter of the same aerodynamic size range. This assumption has not been validated, however, and ambient PM with different physical or chemical characteristics may not behave similarly to sulfate.

Particulate 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. They also arise from the direct emissions of sulfur-containing particles from nonanthropogenic sources (e.g., volcanic activity, wind-blown soil). 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. 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 are also a source of sulfates. Studies that have used sulfate as a surrogate for ambient PM are discussed in Section 5.4.3.1 (i.e., Oglesby et al., 2000a; Sarnat et al., 2000; Ebelt, 2000).

5.3.2.3.3 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 epidemiologic 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).

5.4 SUMMARY OF PARTICULATE MATTER MASS DATA

5.4.1 Types of Particulate Matter Measurement Studies

A variety of field measurement studies have been conducted to quantify personal exposure to PM mass, measure microenvironmental concentrations of PM, and evaluate the relationship between personal exposure to PM and PM air concentrations measured at ambient sites.
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 into 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 (also referred to as a "convenience" samples) may not have same the characteristics that would lead to exposure as the general population. Thus, results of purposeful studies apply only to the subjects sampled on the days that they were sampled. In a purposeful study, statistically valid inferences cannot be made to any other population or period of time. Although such studies may report significant differences, confidence intervals, and *p* values, they have no inferential validity (Lessler and Kalsbeek,1992). However, most purposeful studies of PM personal exposure can provide data to develop relationships on important exposure factors and 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, (2) daily-average, and (3) pooled. These are discussed in Section 5.4.3.1.1.

5.4.2 Available Data

5.4.2.1 Personal Exposure Data

Table 5-4 gives an overview of the personal exposure studies that have been conducted and are reviewed in this section. This includes studies that have been reported since the 1996 AQCD.

TABLE 5-4. SUMMARY OF RECENT PERSONAL EXPOSURE STUDIES

Study Design	Study Location and Population	No. of Subjects	Study Period	Age	Days per Subject	PM Exposure[a] Metrics	PM Size Measured[b]	Co-Pollutant Metrics	Reference
Probability Studies									
Pooled	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. (2000a) Jantunen et al. (1998)
Pooled	Toronto, Canada	732	9/ 1995 - 8/1996	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)
Purposeful Studies									
Longitudinal	Wageningen, Netherlands, school children	13	1995	10-12	6	P, A, School	$PM_{2.5}$, PM_{10}		Janssen et al. (1999b)
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	7-8/1998	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)
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)

TABLE 5-4 (cont'd). SUMMARY OF RECENT PERSONAL EXPOSURE STUDIES (since 1996)

Study Design	Study Location and Population	No. of Subjects	Study Period	Age	Days per Subject	PM Exposure[a] Metrics	PM Size Measured[b]	Co-Pollutant Metrics	Reference
Purposeful Studies (cont'd)									
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	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_{2-10},$PM_{>10}$		Tamura et al. (1996b)
Pooled	Milan, Italy, office workers	100	Spring/summer and winter		1	P, Home, Office, Commuting	PM_{10}	NO_2, CO, VOCs	Carrer et al. (1998)

[a] All based on gravimetric measurements.
[b] P = personal, I = indoors, O = outdoors, A = ambient.

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 to answer the important questions related to exposure are limited. Few are based on probability sampling designs that allow study results to be inferred to the general population. Unfortunately, none of these probability studies uses a longitudinal study design. This limits our ability to provide population estimates 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. Many of these studies did not include ambient site measurements to allow comparisons with the exposure data, and approximately half of these studies monitored $PM_{2.5}$.

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 Particle Total Exposure Assessment Methodology (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) exposure study (Jantunen et al., 1998, 2000; Oglesby, et al., 2000); and a study of a small, highly polluted, area in Mexico City (Santos-Burgoa et al., 1998). Only preliminary results have been reported for the EXPOLIS study. 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 elderly with preexisting respiratory and heart diseases (hypertension, chronic obstructive pulmonary disease, and congestive heart disease). This is in keeping with air pollution analyses 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 Jassen et al. (1997, 1998a,b, 1999a,b) on purposefully selected samples of adults (50 to 70 years old) and children (10 to 12 years old). Several additional studies have focused on nonsmoking elderly populations in Amsterdam and Helsinki (Janssen et al., 2000), Tokyo (Tamura et al., 1996a), Baltimore (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. Only preliminary data are currently available, and results are not reported in this document.

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.

5.4.2.2 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. Studies that 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 effect 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 SMPS, 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). These studies have been able to assess penetration efficiency for ambient particles and microenvironments indoors 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 nephelometers that measure PM using light-scattering techniques. Recent PM exposure studies have used personal nephelometers (1 min avg time) to measure PM continuously (Howard-Reed et al., 2000; Quintana et al., 2000) 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). Several studies also have examined PM exposure in vehicles using both continuous and filter-based techniques.

5.4.2.3 Interpretation of 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 analyses are directed towards understanding the personal cloud, the variability in total PM exposure, and the personal exposure-to-ambient concentration relationships for PM. Results are highlighted here and given in more detail in Section 5.4.3. 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

TABLE 5-5. SUMMARY OF RECENT MICROENVIRONMENTAL MEASUREMENT STUDIES

Reference	Study Description	Instrument(s)	Size Fraction	Summary of Measurements	Notes/Findings
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 TEOM	0.02-10	Continuous PM distributions and size distributions obtained for indoor and outdoor air	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)	2.5	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		2.5	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)	Epidemiological study of maternal and infant health effects associated with indoor air pollution
			10	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, 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 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.
Rea et al. (2001) Baltimore, MD Fresno, CA	15 participants	Nephelometer (personal MIE) PEM	0.1-10 2.5 and 10	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%)	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.

TABLE 5-5 (cont'd). SUMMARY OF RECENT MICROENVIRONMENTAL MEASUREMENT STUDIES

Reference	Study Description	Instrument(s)	Size Fraction	Summary of Measurements	Notes/Findings
Residential Indoor: Nonsmoking Homes (cont'd)					
Quintana et al. (2000) San Diego, CA	Asthmatic children indoor and outdoor 9 homes	Nephelometer (personal MIE) Harvard impactors TEOM	0.1-10 2.5 and 10	Indoor and outdoor measurements collected using passive, active, and active heated nephelometers for comparison to PM mass measurements.	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
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)	2.5	1-h personal exposures measured simultaneously. Personal and ambient concentrations were compared.	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).
Lioy et al. (1999) NA	10 vacuum cleaners		0.3-0.5	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.
Residential Indoor: Other Home Types					
Brauer et al. (1996) Mexico	22 rural Mexican homes (smoking and nonsmoking)	Inertial impactor Nephelometer (Radiance)	10 2.5	Indoor $PM_{2.5}$: 132-555 $\mu g/m^3$ PM_{10}: 282-768 $\mu g/m^3$. Outdoor $PM_{2.5}$: 37 $\mu g/m^3$ PM_{10}: 68 $\mu g/m^3$; 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 $\mu g/m^3$ 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	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.
Nonresidential Microenvironments					
Bohadana et al. (2000)	Manufacturing plant, woodworkers		Not given	443 personal time-weighted average occupations samples of airborne dust	

TABLE 5-5 (cont’d). SUMMARY OF RECENT MICROENVIRONMENTAL MEASUREMENT STUDIES

Reference	Study Description	Instrument(s)	Size Fraction	Summary of Measurements	Notes/Findings
Nonresidential Microenvironments (cont’d)					
Donham et al. (2000) San Francisco, CA	34 poultry workers	NIOSH Method 0600 monitors probed respirators	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	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		4	Average respirable fraction: 4.5 mg/m^3	
Teschke et al. (1999)	Wood production wood finishing wood construction workers		≈50	1,632 observations from 1979-1997. Arithmetic mean exposure: 7.93 mg/m^3 Geometric mean exposure: 1.86 mg/m^3	
Baek et al. (1997) Korea	Indoor and outdoor smoking restaurants		3.5	Indoor concentrations: 33-475 μg/m^3 Outdoor concentrations: 12-172 μg/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	3.5	Smoking permitted: indoor 26.3-182 μg/m^3; outdoor <5-67 μg/m^3 Smoking prohibited: indoor 4-82 μg/m^3; outdoor 2-67 μg/m^3	I/O nonsmoking: 2.2. I/O smoking: 3.4
Houseman et al. (in press) Boston, MA	Indoor and outdoor restaurants, stores	TSI DUSTRAK	10	Indoor restaurants: 14-278 μg/m^3 Outdoor restaurants: 7-281 μg/m^3 Indoor stores: 12-206 μg/m^3 Outdoor stores: 7-281 μg/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 ‘t Mannetje (1998) Vancouver, BC	indoor restaurants, various smoking policies		2.5 10	Nonsmoking: PM$_{2.5}$ 7-65 μg/m^3; PM$_{10}$ <10-74 μg/m^3 Restricted smoking (>40% nonsmoking) PM$_{2.5}$ 11-163 μg/m^3 ; PM$_{10}$ 24-89 μg/m^3 Unrestricted smoking: PM$_{2.5}$ 47-253 μg/m^3 ; PM$_{10}$ 51-268 μg/m^3	
Lee and Chang (1999) Hong Kong	indoor and outdoor 5 classrooms		10	Indoor PM$_{10}$: 30-470 μg/m^3 Outdoor PM$_{10}$: 20-617 μg/m^3	

TABLE 5-5 (cont'd). SUMMARY OF RECENT MICROENVIRONMENTAL MEASUREMENT STUDIES

Reference	Study Description	Instrument(s)	Size Fraction	Summary of Measurements	Notes/Findings
Traffic-Related Microenvironments					
Praml and Schierl (2000) Munich, Germany	Trams and buses, rural and urban	Continuous millipore polycarbonate filter	10	n = 201 4-h trips, mean concentration 155 μg/m^3 range: 13-686 μg/m^3 I/O: 2.8	Tram > circular bus route > radial bus route Day > night
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
Monn et al. (1997) Switzerland	Spatial scale from a city street	Harvard **μe** monitor	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 μg/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		2.5 10	Air exchange rates measured at various ventilation settings and speeds. Monitoring vehicle followed a diesel bus or truck.	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
Roorda-Knape et al. (1998) van Vliet et al. (1997) Netherlands	Gradient in distance from roadway	Harvard impactor	2.5 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. (in press) Boston, MA	Indoor and outdoor vehicles buses, subways	TSI DUSTRAK	PM_{10}	Vehicle concentrations ranged from 33-170 μg/m^3. Outdoor vehicle concentrations ranged from 40-144 μg/m^3. Bus concentrations: 17-268 μg/m^3; outdoor 10-203 μg/m^3 Subway: 28-174 μg/m^3; outdoor 8-203 μg/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		2.5 10	$PM_{2.5}$ background: 21-35 μg/m^3; roadway 23-43 μg/m^3 PM_{10} background:13-32 and 29-62 μg/m^3; roadway 16-56 and 30-75 μg/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 μg/m^3.

TABLE 5-6. PAPERS INTERPRETING 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; $PM_{2.5}$ ≈ 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, higher correlations of personal exposure with ambient concentrations were not observed.
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 epidemiological 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.
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 the average person is exposed to.	On average, a person is exposed to >75% of ambient $PM_{2.5}$ and >64% of ambient PM_{10} measured by the community monitor.

concentrations, compared to healthy elderly, children, and the general population. The analysis by Wallace (2000a) and three subsequent longitudinal studies (Williams 2000a,b,c; Ebelt et al., 2000; Sarnat et al., 2000) support hypothesis 1 but not hypothesis 2. Özkaynak and Spengler (1996) show that at least 50% of personal PM_{10} exposure for the general population is because of ambient particles that significantly contribute to inhaled particles. Wilson and Suh (1997) conclude 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) give 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 on average a person is exposed to >75% of ambient $PM_{2.5}$ and >64% of ambient PM_{10}. Mage et al. (1999) use 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.

5.4.3 Factors Influencing and Key Findings on Particulate Matter Exposures

5.4.3.1 Correlations of Personal/Microenvironmental Particulate Matter with Ambient Particulate Matter

The relationship between measured personal PM exposure and PM concentrations measured at ambient sites has been of interest to exposure analysts. Many of the studies, summarized above in Table 5-4, have analyzed this relationship using measurements of personal PM exposures and ambient PM concentrations. The statistical correlation between these measurements for the various personal exposure studies is discussed in this section.

5.4.3.1.1 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 and daily ambient PM concentration for each individual subject. The longitudinal correlation coefficient, r, may differ for each subject, and 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 different subjects are studied on subsequent days (sometimes called a "cross-sectional" study design). The different subject/different day data are combined, pooled, 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. This type of correlation is sometimes called cross-sectional, but will be called pooled in this chapter because only a limited number of participants are monitored on any given day. *Daily-average correlations* are calculated using the average exposure across subjects for each day. Daily-average correlations describe the relationship between daily community-averaged personal PM exposure and daily ambient PM concentration. This type of correlation could be called cross-sectional, but given that the pooled correlation also is referred to as cross-sectional, the term daily average is used here.

Studies that have reported longitudinal correlations also typically have reported pooled correlations. However, pooling of the data for the correlation has been handled differently across the various studies. 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). In other studies, daily averages across subjects were calculated and the correlation determined from the daily averages (Williams et al., 2000b). A third approach also was used in other studies to simulate a cross-sectional study design (Janssen et al., 1997, 1998a, 1999c). In this approach, a random-sampling procedure was used to select a random day from each subject's measurements to use for the correlation. This procedure was repeated many times, and statistics such as the mean and standard deviation of the pooled correlation coefficient were reported.

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 much higher than the correlations obtained from a pooled data set. Wallace (2000a) reviewed a number of longitudinal studies found that the median longitudinal correlation coefficient was much higher than the pooled correlation coefficient for the same data (see Tables 1 and 2 Wallace, 2000a). Williams et al. (2000a,b) and Evans et al. (2000) reported higher correlation coefficients for daily-average correlations compared to longitudinal correlations.

5.4.3.1.2 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, where available. The correlation coefficient (r) between total personal PM exposures and 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.

5.4.3.1.3 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.

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	106	18.2 ± 14.6			11.4 ± 4.1	Median L	0.48 (-0.68-0.83)	n = 16 COPD subjects		
		Range		2- 91			4 - 29	P	0.15			
Evans et al. (2000) – Fresno, CA												
$PM_{2.5}$	24 h	$\bar{x}$	24	13.3	9.7	20.5	21.7	P	0.41^4	Fresno-1 study	P_{p-i}	0.81^4
		Range		1 - 24	4 - 17	4 - 52	6 - 37				P_{p-o}	0.80^4
$PM_{2.5}$	24 h	$\bar{x}$	12	11.1	8.0	10.1	8.6	P	0.84^4	Fresno-2 study	P_{p-i}	0.95^4
		Range		7 - 16	4 - 12	5 - 20	4 - 16				P_{p-o}	0.80^4
Janssen et al. (1997) – Netherlands												
PM_{10}	24 h	$\bar{x}$ ± SD	301	105.2 ± 28.7			38.5 ± 5.6	Median L	0.63 (0.1-0.9)	n = 45 school children		
		Range		57 - 195			25 - 56	Median L	0.63	With nonsmoking parents		
								Median L	0.59	With smoking parents		
								Mean P	0.28 (0.12)^5	All		
								Mean P	0.45 (0.16)^5	With nonsmoking parents		
								Mean P	0.20 (0.19)^5	With smoking parents		
Janssen et al. (1998a) – Netherlands												
PM_{10}	24 h	$\bar{x}$ ± SD	262	61.7 ± 18.3	35.0 ± 9.4		41.5 ± 4.3	Median L	0.50 (-0.41-0.92)	n = 37 adults	Med. L_{p-i}	0.72 (-0.10-0.98)
		Range		38 - 113	19 - 65		32 - 50	Median P	0.50 (0.07-0.83)^5	No ETS exposure	Med. L_{i-a}	0.73 (-0.88-0.95)
								Median P	0.34 (-0.09-0.67)^5	All		
Janssen et al. (1999c) – Netherlands												
$PM_{2.5}$	24 h	$\bar{x}$ ± SD	77	28.3 ± 11.3			17.1 ± 2.8	Median L	0.86 (-0.11-0.99)	n = 13 school children		
		Range		19 - 60			14 - 22	Median P	0.41 (-0.28-0.93)^5			
$PM_{2.5}$	24 h	$\bar{x}$ ± SD	55	24.4 ± 4.9			17.1 ± 2.6	Median L	0.92	With nonsmoking parents		
		Range		19 - 33			15 - 22	Median P	0.82^5			
$PM_{2.5}$	24 h	$\bar{x}$ ± SD	22	37.0 ± 17.4			17.1 ± 3.7			With smoking parents		
		Range		21 - 60			14 - 21					

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	$\bar{x}$ ± SD Range	338	24.3 ± 25.7 9 - 134	28.6 ± 41.8 9 - 239		20.6 ± 4.0 13 - 31	Median L Median L	0.79 (-0.41-0.98) 0.85	n = 36 elderly w/CV disease No ETS exposures	Med. L$_{p-i}$ Med. L$_{i-a}$	0.91 (-0.28-1.0) 0.84(-0.00-0.98)
Janssen et al. (2000) – Finland												
PM$_{2.5}$	24 h	$\bar{x}$ ± SD Range	336	10.8 ± 4.4 4 - 33	11.0 ± 4.0 3 - 27		12.6 ± 2.0 10 - 18	Median L	0.76 (-0.12-0.97)	n = 46 elderly w/CV disease	Med. L$_{p-i}$ Med. L$_{i-a}$	0.89 (0.14-1.0) 0.70 (-0.15-0.94)
Linn et al. (1999) – Los Angeles												
PM$_{2.5}$	24 h	$\bar{x}$ ± SD Range	60	23.8 ± 15.1 4 - 65	23.5 ± 15.3 4 - 92	24.8 ± 14.5 4 - 63		P	0.26[6]		P$_{i-a}$ P$_{o-a}$	0.26[6] 0.47[6]
PM$_{10}$	24 h	$\bar{x}$ ± SD Range	59	34.8 ± 14.8 5 - 85	32.6 ± 15.6 9 - 105	39.8 ± 18.3 7 - 97	33 ± 15 9 - ??	P	0.22[6]		P$_{i-a}$ P$_{o-a}$	0.32[6] 0.66[6]
Rojas-Bracho et al. (2000) – Boston												
PM$_{2.5}$	12 h	$\bar{x}$ ± SD Range	224	21.6 ± 13.6 1 - 128	17.5±14.1 2 - 73	14.2 ± 11.2 1 - 57		Median L	0.61 (0.10-0.93)[6]	n = 17 adults	Med. L$_{p-i}$ Med. L$_{i-o}$	0.87[6] 0.74[6]
PM$_{10}$	12 h	$\bar{x}$ ± SD Range	225	37.2 ± 22.8 9 - 211	31.9 ± 25.2 2 - 329	22.2 ± 18.7 3 - 76		Median L	0.35 (0.0-0.72)[6]		Med. L$_{p-i}$ Med. L$_{i-o}$	0.71[6] 0.50[6]
PM$_{10-2.5}$	12 h	$\bar{x}$ ± SD Range	222	15.6 ± 14.6 -11 - 103	14.5 ± 9.2 -3 - 255	8.1 ± 6.8 -2 - 64		Median L	0.30 (0.0-0.97)[6]		Med. L$_{p-i}$ Med. L$_{i-o}$	0.42[6] 0.20[6]
Sarnat et al. (2000) – Baltimore												
PM$_{2.5}$	24 h	$\bar{x}$ ± SD $\bar{x}$ ± SD	37 36	26.7 ± 13.7 18.5 ± 11.2			25.2 ± 11.5 5.6 ± 49.0	Median L Median L P P P P	0.76 (-0.21-0.95)[7] 0.25 (-0.38-0.81)[7] 0.89[8] 0.75[8] 0.50[8] 0.44[8]	n = 15 adults; summer n = 15 adults; winter High ventilation; summer Med. ventilation; summer Low ventilation; summer WINTER		
PM$_{10}$	24 h	$\bar{x}$ ± SD $\bar{x}$ ± SD	37 36	33.9 ± 11.7 28.0 ± 16.5			34.0 ± 12.8 7.5 ± 73.2	Median L Median L	0.64 (0.08-0.86)[7] 0.53 (-0.79-0.89)[7]	SUMMER WINTER		
PM$_{10-2.5}$	24 h	$\bar{x}$ ± SD $\bar{x}$ ± SD	37 36	7.2 ± 4.0 9.6 ± 7.9			8.4 ± 2.3 -1.3 ± 24.2	Median L Median L	0.11 (-0.60-0.64)[7] 0.32 (-0.48-0.68)[7]	SUMMER WINTER		

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)
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	$\bar{x}$	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	$\bar{x}$	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	$\bar{x}$	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]
Pooled Studies												
Bahadori (1998) – Nashville												
PM$_{2.5}$	12 h	$\bar{x}$ ± SD	30	21.7 ± 10.5	15.5 ± 6.6	23.4 ± 6.8		P	0.09	n = 10 COPD subjects;	P$_{p-i}$	0.72
		Range		10 - 67	5 - 40	3 - 61				daytime	P$_{i-o}$	0.31
PM$_{10}$	12 h	$\bar{x}$ ± SD	30	33.0 ± 16.9	21.6 ± 10.7	32.5 ± 8.1		P	-0.08	n = 10 COPD subjects;	P$_{p-i}$	0.43
		Range		5 - 88	9 - 77	7 - 76				daytime	P$_{i-o}$	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,	P$_{p-i}$	0.79
										outdoor lower than personal	P$_{i-o}$	0.33
PM$_{10}$	3 d	$\bar{x}$	141	67.9	29.8	24.3				No correlations reported		
Oglesby et al. (2000a) – EXPOLIS Basel												
PM$_{2.5}$	48 h	$\bar{x}$ ± SD	44	23.7 ± 17.1		19.0 ± 11.7		P	0.07	All		
			20	17.5 ± 13.0		17.7 ± 7.1		P	0.21	No ETS exposure		

TABLE 5-7 (cont.). PERSONAL MONITORING STUDIES FOR PM: MEASURED CONCENTRATIONS AND CORRELATION COEFFICIENTS

		Measured Concentration Levels ($\mu g/m^3$)						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)
Santos-Burgoa et al. (1998) – Mexico City												
PM_{10}	24 h	$\bar{x}$ ± SD	66	97 ± 44	99 ± 50			P	0.26		$P_{p\text{-}i}$ $P_{i\text{-}a}$	0.47 0.23
Tamura et al. (1996b) – Osaka												
PM_2	48 h							P	0.74			
PM_{10}	48 h							P	0.67			

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
$\bar{x}$ = 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; $r = \sqrt{(R^2)}$.
6. Spearman rank correlations.
7. Calculated, $r = \sqrt{(R^2)}$, from R^2 from a mixed model regression.

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, 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)

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 (SD) and 99 ± 50 $\mu g\ ^{-3}$, respectively, with an $\mathbf{r}_{\text{Personal/Ambient}} = 0.26$ ($p = 0.099$). Other correlations of interest were $\mathbf{r}_{\text{Personal/Indoor}} = 0.47$ ($p = 0.002$) and $\mathbf{r}_{\text{Indoor/Ambient}} = 0.23$ ($p = 0.158$). 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, with a few subjects, mostly smokers, being 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 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. However, when a panel contains subjects with homes of very different ventilation characteristics or covers more than one season, variations in α can be high across subjects.

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 and Helsinki, Finland, in the winter and spring of 1998 and 1999. In the Amsterdam study, with 338 to 417 observations, the mean 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 outdoors. In the Helsinki study, the mean $PM_{2.5}$ concentrations were 10.8 μg/m^3 for personal, 11.0 μg/m^3 for indoor air, and 12.6 μg/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, excluding homes with ETS. The correlation for indoors versus outdoors was 0.70 for all homes.

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; less than 5 h day^{-1}, on average, was 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.

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 were 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 were 0.26 and 0.22 for $PM_{2.5.}$ and PM_{10}, respectively. Day-to-day changes in $PM_{2.5}$ and PM_{10} measured outside the homes tracked concurrent PM_{10} measurements at the nearest ambient monitoring location, with R^2 values of 0.22 and 0.44, respectively. Day to day changes in PM mass measured indoors also tracked outdoors at the homes with R^2 values of 0.27 and 0.19 for PM_{10} and $PM_{2.5,}$ respectively.

Personal, indoor, and outdoor $PM_{2.5,}$ $PM_{10,}$ and $PM_{2.5\text{-}10}$ 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.

Bahadori et al. (2001) report a pilot study of the PM exposure of 10 nonrandomly chosen chronic obstructive pulmonary disease (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 a.m. to 8 p.m.) 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}.

5.4.3.1.4 A Correlation Between a Daily-Average Exposure and Ambient Concentrations

A recent biostatistical analysis (Zeger et al., 2000) suggests that the community mean exposure is the appropriate parameter for analyzing exposure error in community time-series epidemiology. Ott et al. (2000) suggest that the correlation of the community mean exposure with ambient concentrations will approach 1.0 for a large community and demonstrated this using data from the PTEAM study. Mage et al. (1999) calculated the daily-average exposure for three earlier studies with sufficient data and found that the coefficients for the correlation of daily averages with the ambient concentrations were high ($R^2 \approx 0.9$). Two new studies have obtained sufficient data to calculate a daily-average correlation.

The 1997 Baltimore pilot study was followed up in July and August 1998 by a more extensive study in which identical samplers were used for personal, indoor, and outdoor measurements. The participants, aged 72 to 93 (mean 81) years, included healthy members, as well as subjects with COPD and cardiovascular disease. The participants lived in an 18-story retirement facility that provided a self-contained living environment. There was a central HVAC system for common areas but each apartment had an individually controlled HVAC system. The subjects had limited exposures to indoor-generated sources of PM because of their low frequency/duration of activities like cooking, cleaning, or interacting with tobacco smokers (Williams et al., 2000a,b). As a result, the daily-average correlation coefficient was very high ($r = 0.89$) between personal exposure and ambient concentrations of $PM_{2.5}$. Median longitudinal correlations were also high ($r = 0.81$; range = 0.38 to 0.98).

Evans et al. (2000) report two panel studies in Fresno, CA, with daily-average correlation coefficients of 0.41 and 0.84.

5.4.3.1.5 Correlations Using Sulfate as a Surrogate for 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 exposure and ambient concentrations of $PM_{2.5}$ (Ebelt et al., 2000). However, the correlation between personal exposure and ambient concentrations of SO_4^{2-} was much higher. The results for $PM_{2.5}$ and sulfate are compared in Figure 5-1. Ebelt et al. (2000) conclude the following.

> We found SO_4^{2-} to be a good measure of exposure to accumulation mode PM of ambient origin. Personal and ambient measures of SO_4^{2-} were highly correlated over time, unlike the moderate correlation found for $PM_{2.5}$. The individual correlations demonstrated that ambient SO_4^{2-} was a consistently strong predictor across all individuals and all levels of exposure, whereas for $PM_{2.5}$ correlations varied by individual and were dependent upon the level of personal exposure. Although indoor sources likely contribute to personal exposures of $PM_{2.5}$, accounting for such variables did not lead to models with the same predictive power as found for SO_4^{2-}.

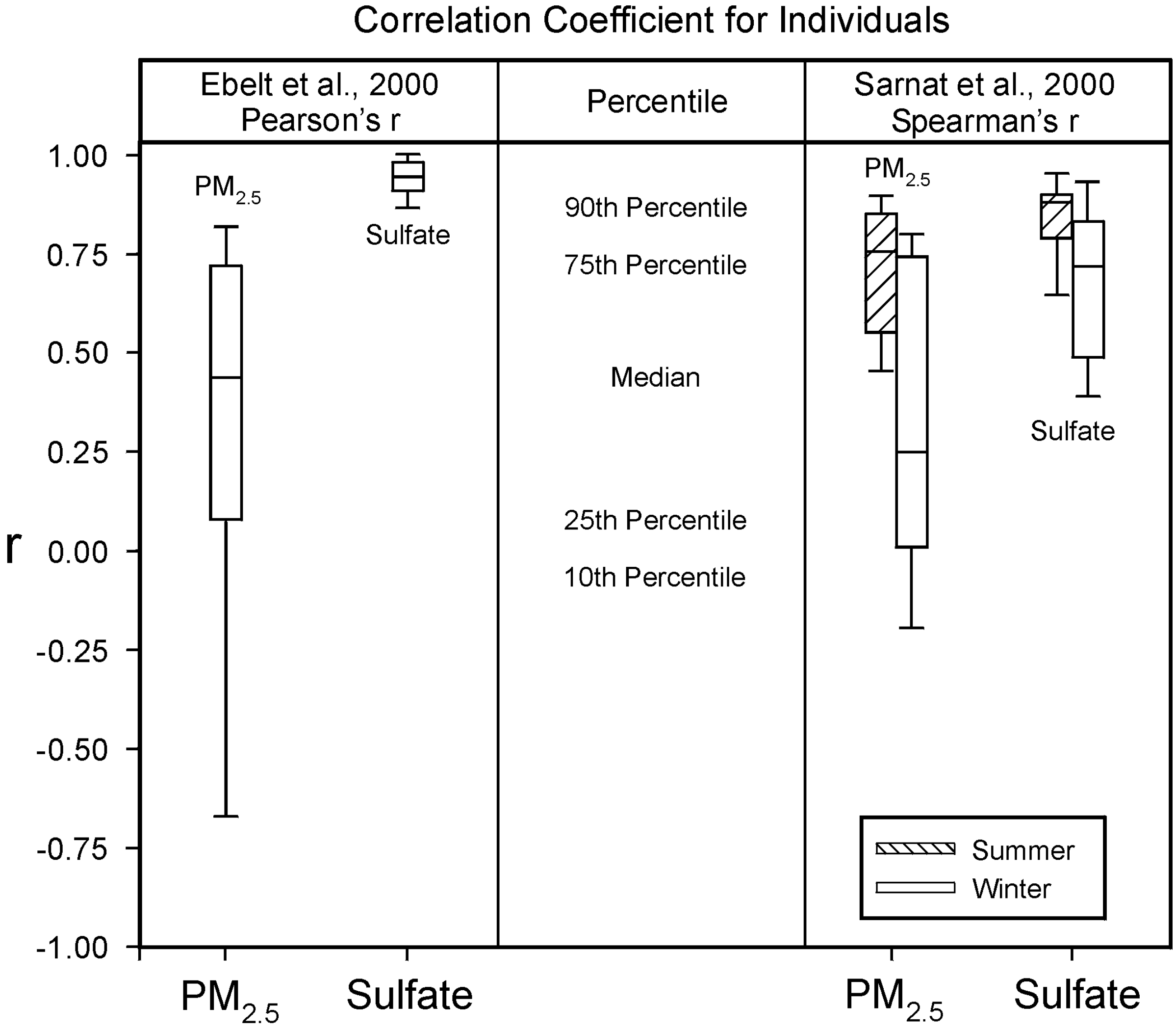


Figure 5-1. Comparison of correlation coefficients for longitudinal analysis of personal exposure versus ambient concentrations for individual subjects for $PM_{2.5}$ and sulfate.

Similarly, we found that accounting for spatial variability in ambient levels did not improve the relationship between ambient concentrations and measured personal exposures. Overall, we have shown that a personal measure of exposure to outdoor source PM is highly related to variation in ambient levels of PM.

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-}. The ranges of correlations are shown in Figure 5-1 along with similar data from Ebelt et al. (2000).

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 for personal exposure on ambient concentration for total $PM_{2.5}$ and for sulfate for each of the three ventilation conditions. Personal exposure to sulfate may be taken as a surrogate for personal exposure to ambient accumulation-mode PM in the absence of indoor sulfate sources. Figure 5-2 shows a comparison of the regressions and indicates how the use of a sulfate tracer as a surrogate for PM of ambient origin improves the correlation coefficient. The improvement is especially pronounced for the lowest ventilation conditions. For the lowest ventilation condition, R^2 improves from 0.25 to 0.72.

The Ebelt et al. (2000) and Sarnat et al. (2000) studies did not use their sulfate data to develop relationships between personal exposure to ambient PM and ambient PM concentrations for individual subjects, as suggested by Wilson et al. (2000). However, 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. However, the variation in ventilation status (and thus in the attenuation coefficient α) still would cause variations between ambient concentrations of PM and personal exposure to ambient PM, especially if the study continued long enough to extend through more than one season.

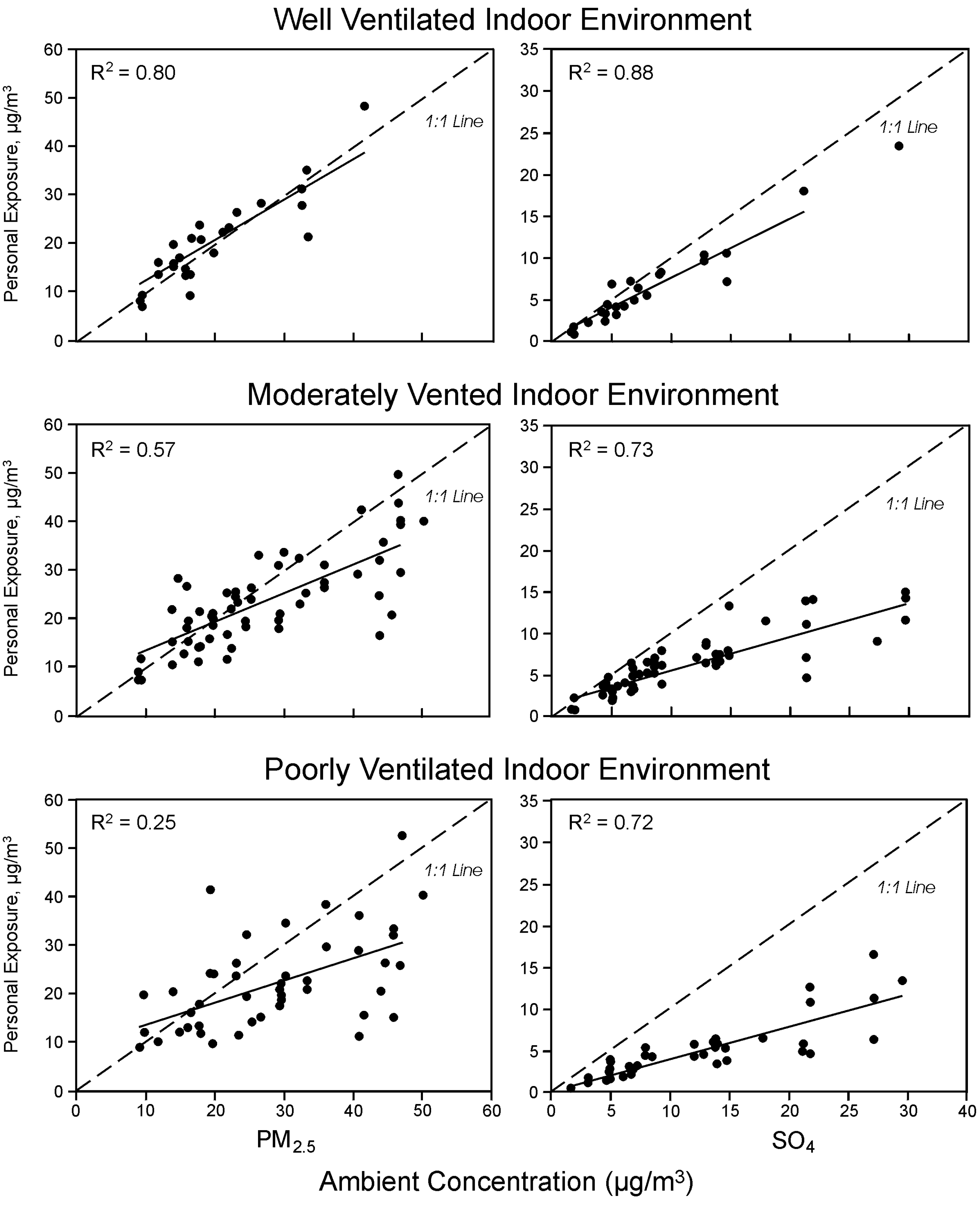


Figure 5-2. Personal exposure versus ambient concentrations for $PM_{2.5}$ and sulfate. (Slope estimated from mixed models).

Source: Sarnat et al. (2000).

5.4.3.1.6 Correlations Between Personal Exposure to Ambient and Nonambient Particulate Matter

The utility of treating personal exposure to ambient PM, E_{ag}, and personal exposure to nonambient PM, E_{nonag} , as separate and distinct components of total personal exposure to PM, E_t, was pointed out by Wilson and Suh (1997). The PTEAM study measured, in addition to indoor, outdoor, and personal PM, the air exchange rate for each home and collected information on the time spent in various indoor and outdoor μ**e**. This information is available for 147, 12-h daytime periods. With this information, it is possible to estimate the daytime E_{ag} and E_{nonag} as described in Section 5.3.2.3.1. 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 (E_t, E_{ag}, and E_{nonag}) are shown in Figure 5-3. The correlation coefficient for the pooled data set improves from r = 0.377 for E_t versus C_a (Figure 5-3a) to r = 0.856 for E_{ag} versus C_a (Figure 5-3b) because of the removal of the E_{nonag} , which, as shown in Figure 5-3c, is highly variable and independent of C_a. The correlation between E_{ag} and C_a is less than 1 because of the day-to-day variation in α_{it}. The regression analysis with E_t total PM gives $\overline{\alpha} = 0.711$ and $\overline{N} = 81.6\ \mu g/m^3$. The regression analysis with E_{ag} gives $\overline{\alpha} = 0.625$. The regression with E_{nonag} gives $\overline{N} = 79.2\ \mu g/m^3$. The finite intercept in the regression with E_{ag} must be attributed to bias or error in some of the measurements. No studies, other than PTEAM, have provided the quantity of data on E_t , C_a , C_i, and *a* required to conduct an analysis comparable to that shown in Figure 5-3.

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, recently have been attributed to statistical rather than physical causes. Ott et al. (2000), using their Random Component Superposition (RCS) model, solely attribute this to the averaging process. Because personal exposures also include contributions from ambient concentrations, the correlation between personal exposure and ambient concentrations increases as the number of subjects measured daily increases. Based on theory, Ott et al. (2000) predict expected correlations above 0.9 if 25 subjects had been studied during the PTEAM study and above 0.70 in the New Jersey study reported by Lioy et al. (1990).

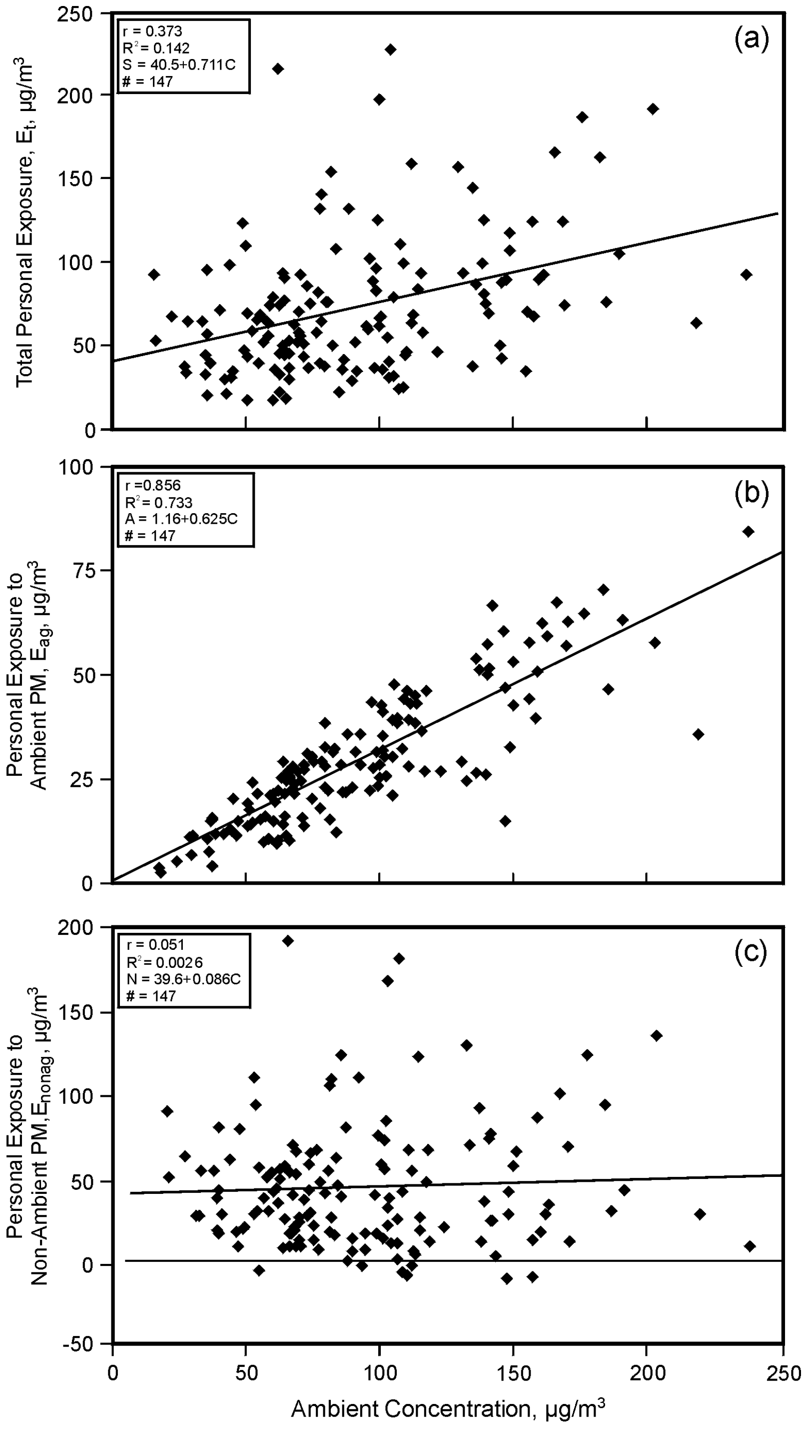


Figure 5-3. Regression analyses of aspects of daytime personal exposure to PM_{10} estimated using data from the PTEAM study. (a) Total personal exposure to PM, E_t, regressed on ambient concentration, C_a. (b) Personal exposure to ambient PM, E_{ag} regressed on C_a. (c) Personal exposure to nonambient PM, E_{nonag} regressed on C_a.

Source: Data taken from Clayton et al. (1993).

The RCS model introduced by Ott et al.(2000) presents a modeling framework to determine the contribution of ambient PM_{10} and indoor-generated PM_{10} on 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 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.

5.4.3.2 Factors That Affect Correlations

A number of factors will affect the relationship between personal exposure and PM measured at ambient-site community monitors. Spatial variability in outdoor microenvironments and penetration into indoor microenvironments will influence the relationship for ambient-generated PM, air-exchange rates and decay rates in indoor microenvironments will influence the relationship for both ambient-generated and total PM, whereas personal activities will influence the relationship for total PM but not ambient-generated PM. Information on these effects is presented in detail in the following section.

5.4.3.2.1 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 μ**e** near where people live, work, and play, obviously affects the 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. A few outdoor-to-outdoor monitoring studies also are included to highlight relationships among important μ**e** 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.

Oglesby et al. (2000), in a paper on the EXPOLIS-EAS study, conclude that very little spatial variability exists in Basel, Switzerland, between PM levels measured at fixed site monitors and the participant's outdoor μ**e**. 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) conclude that a single monitor may be used to adequately describe the ambient gradient 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 mo 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 changes 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; an urban and a semi-urban site separated by 1.6 km, and 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 μg m^{-3}.

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 $PM_{2.5-10}$, 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 health effects in the Utah Valley were associated with stagnation and thermal inversions trapping anthropogenically derived PM_{10}, whereas, no increases in 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 ($PM_{2.5\text{-}10} = PM_{10}\text{-}PM_{2.5}$), then the expected variance in the coarse fraction is the sum of 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 the fine mass collected using the same lower 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. 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 spatially more uniformly 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."

5.4.3.2.2 Physical Factors Affecting Indoor Microenvironmental Particulate Matter Concentrations

Several physical factors affect ambient particle concentrations in the indoor μ**e**, including air exchange, penetration, and particle deposition. Combined, these factors are critical variables that describe ambient particle dynamics in the indoor μ**e** and, to a large degree, significantly affect an individual's personal exposure to ambient-generated particles while indoors. The relationship between ambient outdoor particles and ambient particles that have infiltrated indoors is given by

$$C_{ai} / C_{ao} = Pa / (a + k), \tag{5-10}$$

where C_{ai} and C_{ao} are the concentration of ambient indoor and outdoor particles, respectively; *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 5-4 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 5-4). 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 analyses 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).

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 μ**e** 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., 2000a). This resulted in higher and more variable air-exchange rates in summer than during any other season (Figure 5-5). 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 μ**e**. Particle data

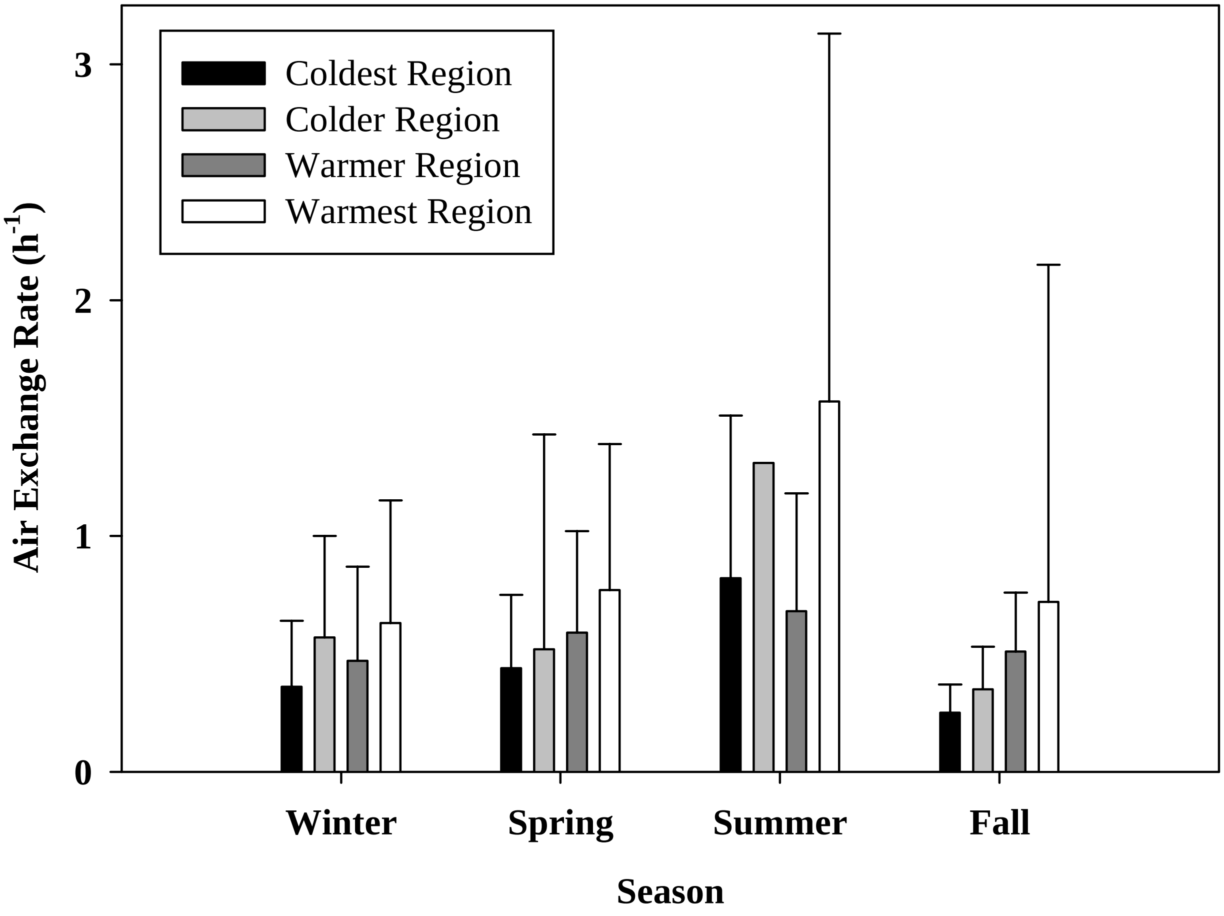


Figure 5-4. Air-exchange rates measured in homes throughout the United States. Climatic regions are based on heating-degree days: Coldest region ≥ 7000, Colder region = 5500 to 6999, Warmer region = 2500 to 4999, and Warmest region ≤ 2500 heating-degree days.

Based on data from Murray and Burmaster (1995).

collected during this study (Figure 5-6) shows the indoor/outdoor concentration ratios by particle size. Data show that for these nine homes in Boston, the fraction of ambient particles penetrating indoors is higher during summer when air exchange rates were higher than fall (Long et al., 2000b).

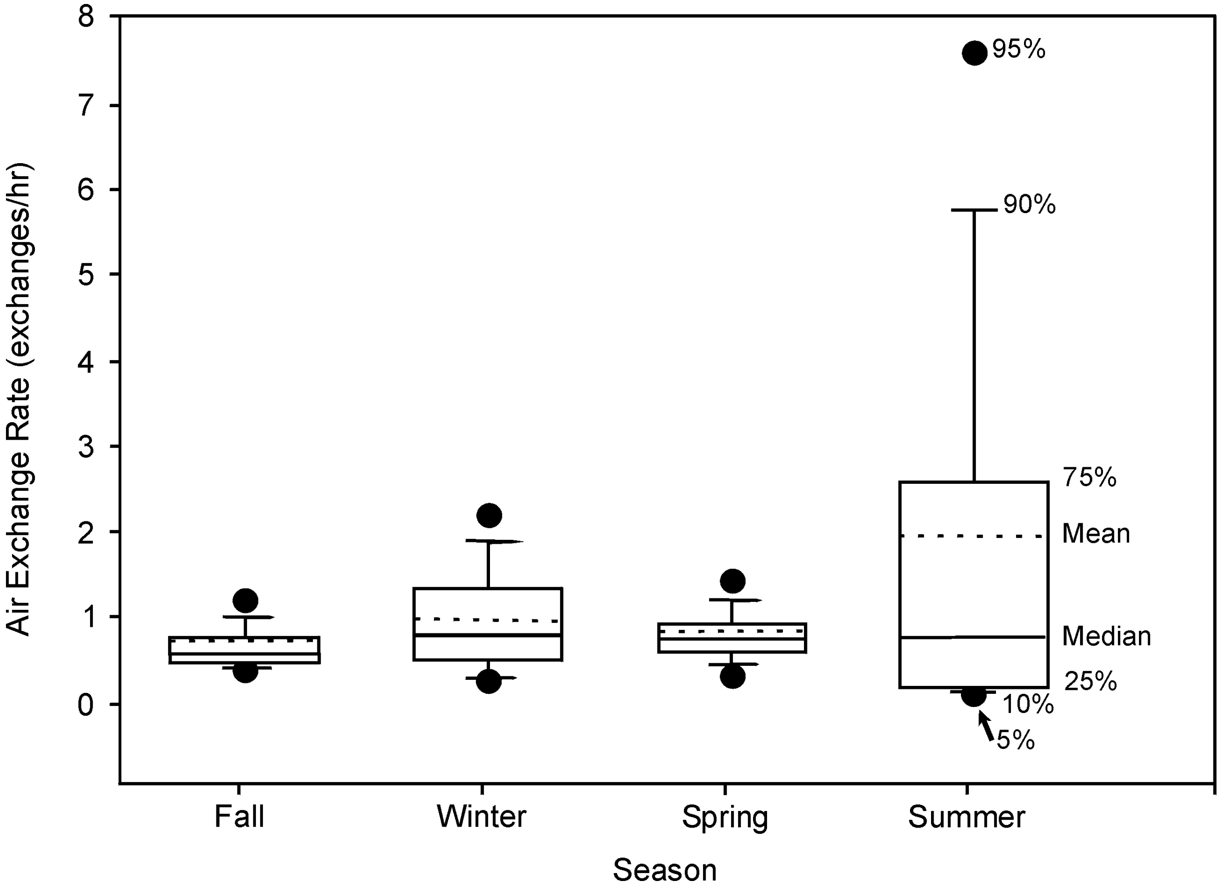


Figure 5-5. Box plots of hourly air-exchange rates stratified by season in Boston, MA, during 1998.

Source: Long et al. (2000a).

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 μ**e** because

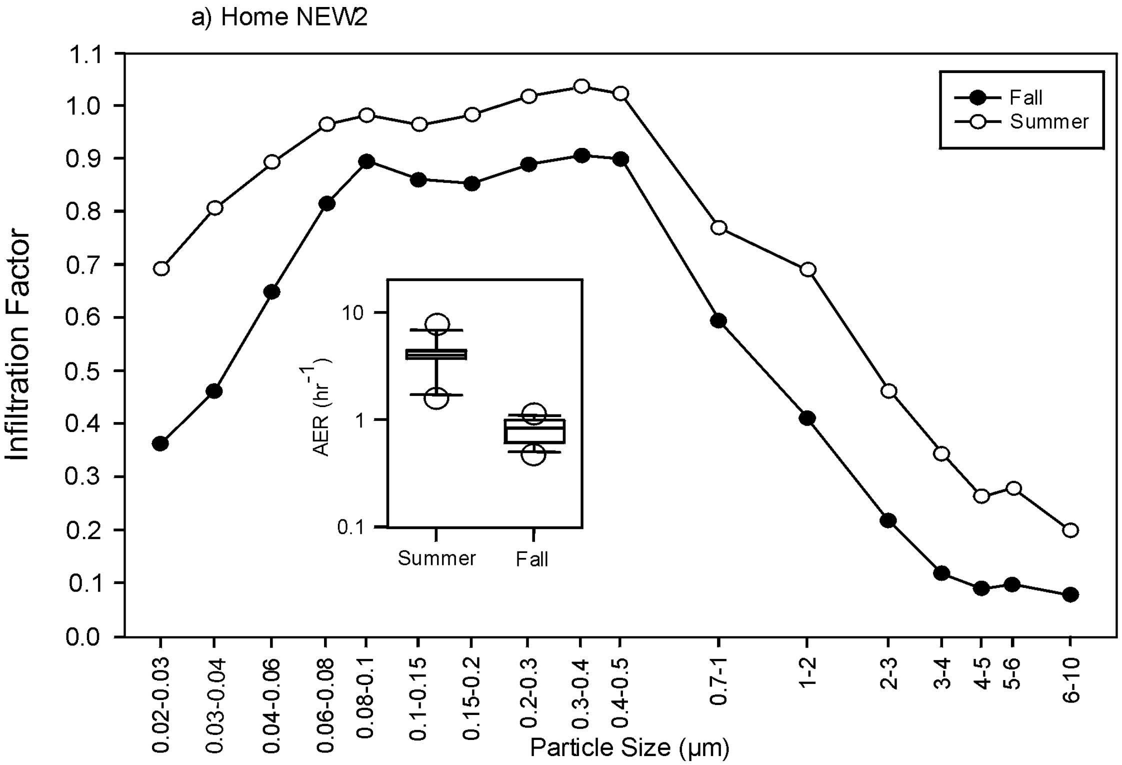


Figure 5-6. Geometric mean infiltration factor (indoor/outdoor ratio) for hourly nighttime, nonsource data for two seasons. Box plots of air exchange rates are shown as inserts for each plot. (Boston, 1998)

Source: Long et al. (2000b).

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.

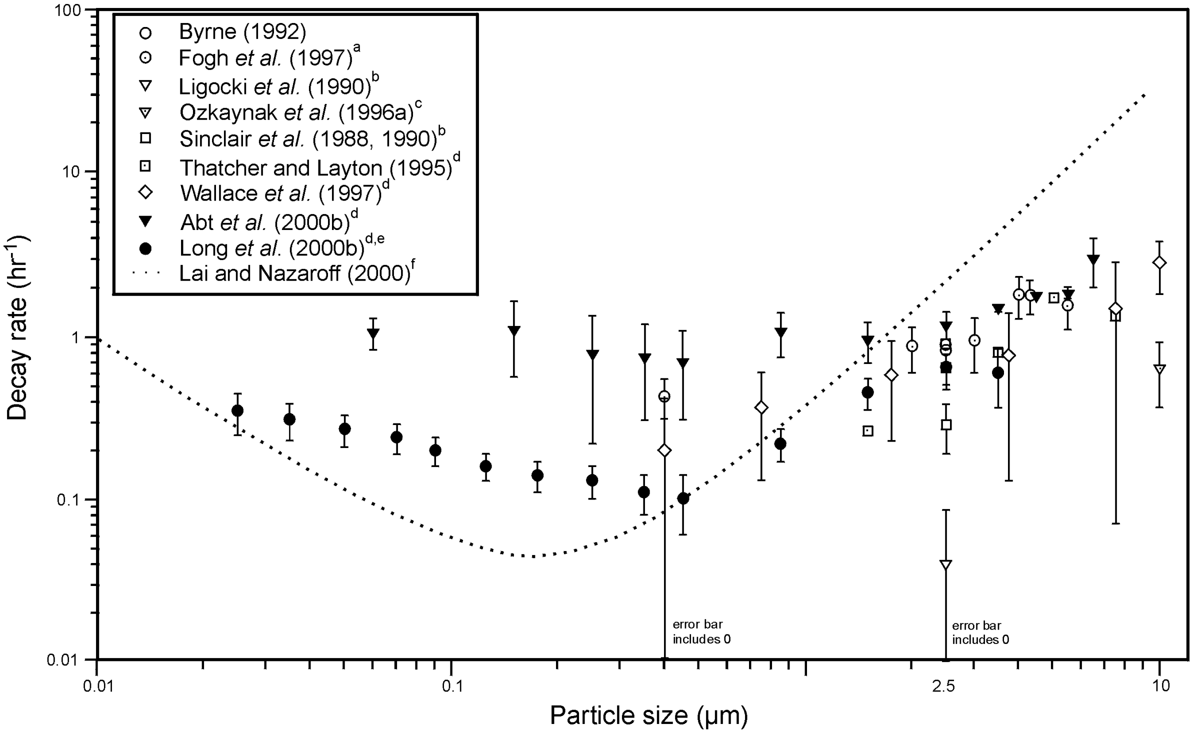
Particle penetration efficiency into the indoor μ**e** depends on particle size and air exchange rates. Penetration varies with particle size because of the size-dependent deposition of particles caused by impaction, interception, and diffusion of particles onto surfaces as they traverse through cracks 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 5-10).

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., 2000b; Abt et al., 2000b). These studies each demonstrated that the indoor/outdoor concentration ratios (C_{ao}/C in Equation 5-11) 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. (2000b) used a physical-statistical model, based on Equation 5-10, to estimate *k* and P during nonsource nighttime periods. The results for *k* reported by Long et al. (2000b) and Abt et al. (2000b) are compared with other studies in Figure 5-7. Although not shown in Figure 5-7, 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. (2000b) show that penetration was highest for accumulation-mode particles and decreased substantially for coarse-mode particles (Figure 5-8). The results for P reported by Vette et al. (2001) show similar trends, but are lower than those reported by Long et al. (2000b). This likely is because of lower air-exchange rates in the Fresno, CA, residence ($a \approx 0.5\ h^{-1}$; Vette et al., 2001) than the Boston, MA, residences ($a > 1\ h^{-1}$; Long et al., 2000b). 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.

Compositional Differences Between Indoor-Generated and Ambient-Generated 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



[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 represent $PM_{2.5}$

[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 theorectically 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 5-7. Comparison of deposition rates from this study with literature values (adapted from Abt et al., 2000b). Error bars represent standard deviations for same-study estimates.

Source: Long et al. (2000b).

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

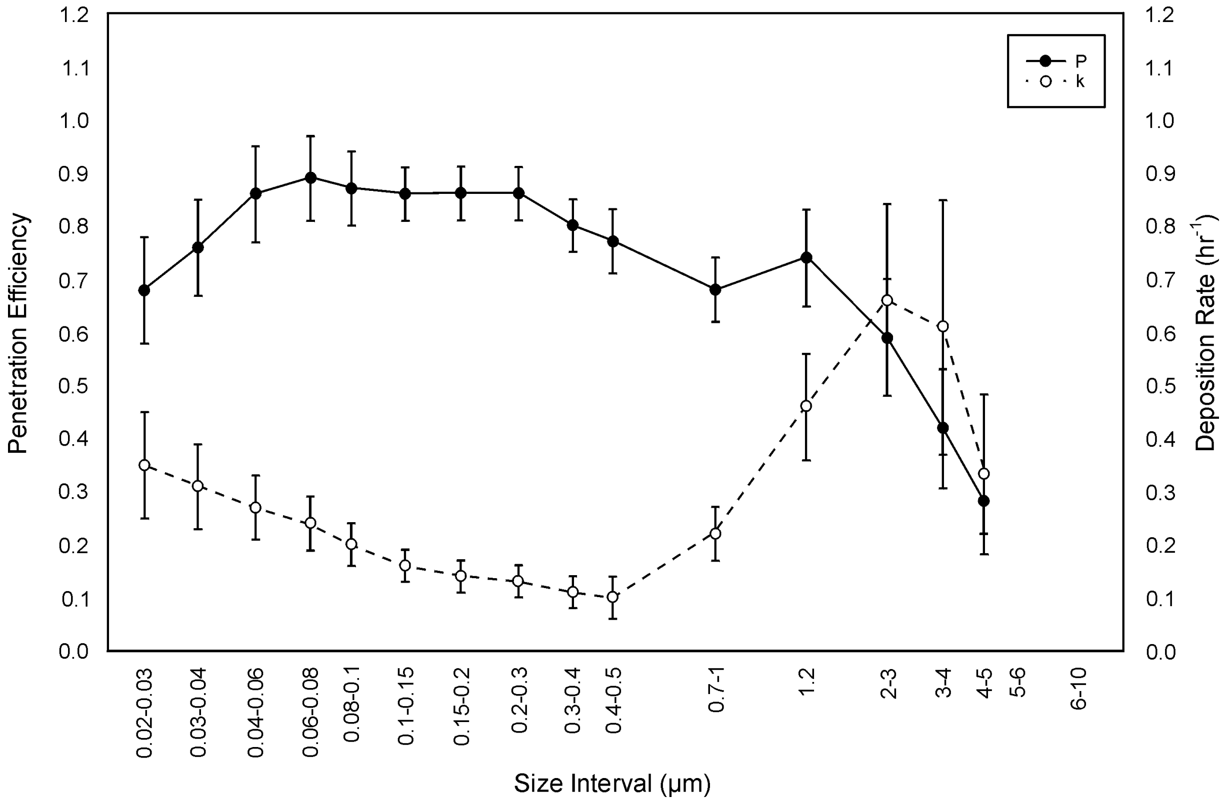


Figure 5-8. Penetration efficiencies and deposition rates from models of nightly average data. Error bars represent standard errors. (Boston, 1998, winter and summer)

Source: Long et al. (2000b).

> 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 have 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 μe are responsible for secondary particle formation and modification of existing particles. 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 BASE study (Hadwen et al., 1997). Long et al. (2000a) found that when PineSol (primary ingredient is α-pinene) was used indoors, indoor $PM_{2.5}$ mass concentrations increased by 3 to 32 μg 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 μg 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 findings (e.g., Jang and Kamens, 1999; Wainman et al., 2000).

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.), which 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 μ**e** also may be resuspended after deposition to indoor surfaces. Typically, resuspension of particles from any source involves coarse-mode particles (>1 μm); particles of smaller diameter are not resuspended efficiently. On the other hand, cooking produces both fine- and coarse-mode particles, whereas combustion sources typically produce fine-mode 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 impact 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. (2000a) 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. Table 5-8 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, whereas fine- and accumulation-mode particles were not affected by resuspension. Figure 5-9 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 5-9 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 (fine- and accumulation-mode particles) remain fairly constant during both day and night.

5.4.3.2.3 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 sources (E_{ag}), indoor sources (E_{ig}), and personal activities (E_{pact}). E_{ag} and E_{ig} are determined by the microenvironments in which an individual spends time; whereas E_{pact} is determined by the personal activities that he/she conducts while in those microenvironments.

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

TABLE 5-8. 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 μg/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. (2000a).

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

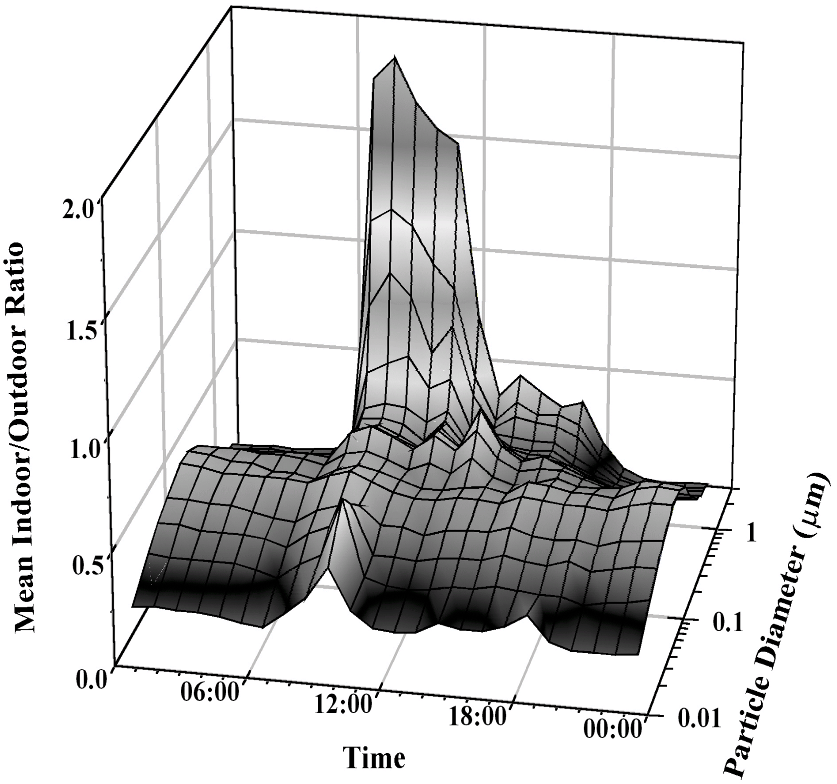


Figure 5-9. Mean hourly indoor/outdoor particle concentration ratio from an unoccupied residence in Fresno, CA, during spring 1999.

Source: Vette et al. (2001).

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 over 22,000 person-days of 24-h activity known as the Consolidated Human Activity Database, or CHAD (Glen et al., 1997). The information in CHAD will be 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 less 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 impact correlations between PM exposure and ambient site measurements for both total PM and PM of ambient origin.

5.4.3.3 Impact 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 outcome, 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 to ambient PM of similar aerodynamic size or directly as exposure surrogates in epidemiologic analyses. The 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 epidemiological studies (discussed more fully in Chapter 6) have evaluated the relationship 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. Özkaynak and Thurston (1987) evaluated the relationship between particulate matter 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 particulate matter 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.

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.

Laden et al. (2000) applied specific rotation factor analysis to particulate matter composition (XRF) data from six eastern cities (Ferris et al., 1979). Fine particulate matter 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, identify indoor and outdoor source categories and 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 not only the various source factors but also apportioning them among the different monitor locations (personal, indoor, and outdoor), was able to quantify an estimate of 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 starting a vehicle inside of an attached garage, accounted for another 10% of PM mass. The authors caution that these 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 was associated with indoor soil dispersed throughout the house, and one was associated 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 use explicitly 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-generated 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 heavy metal tracers; and, also, gas-phase pollutants) would be useful as demonstrated in the use of EC/OC and gas-phase pollutants by Mar et al. (2000).

5.4.3.4 Correlations of Particulate Matter with Other Pollutants

Several epidemiological 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 were determined, as well as that to $PM_{2.5}$ and $PM_{2.5\text{-}10}$ for a cohort 15 elderly subjects in Baltimore, MD. Sarnat et al. (2000) conclude that the potential for confounding of $PM_{2.5}$ by O_3, NO_2, or PM $_{2.5\text{-}10}$ appears to be limited, because, despite significant correlations observed among ambient pollutant concentrations, the correlations among personal exposures were low. Spearman correlations for 14 subjects in summer and 14 subjects in winter are given in Table 5-9 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. It should be noted that measured personal exposures to O_3, NO_2, and SO_2 were below their respective LOD for 70% of the samples.

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 and the correlations are given for each microenvironment in Table 5-10: 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

TABLE 5-9. 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).

TABLE 5-10. 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).

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 correlated significantly to $PM_{2.5}$ in the winter.

Carrer et al. (1998) present data on the correlations among personal and microenvironmental PM_{10} exposures and concentrations and selected environmental chemicals that were monitored simultaneously (using a method that was 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). Surprisingly, because most of the chemical substances are associated with motor vehicular emissions, there was no significant correlation between “commuting PM_{10}” and any of the substances (Carrer et al., 1998).

5.5. SUMMARY OF PARTICULATE MATTER CONSTITUENT DATA

5.5.1 Introduction

Atmospheric PM contains a number of chemical constituents that may be of significance with respect to the 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 polycyclic aromatic hydrocarbons (PAHs) in ambient, personal, and microenvironmental PM samples. But, 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).

5.5.2 Monitoring Studies That Address Particulate Matter Constituents

A limited number of studies have measured the constituents of PM in personal or microenvironmental samples. Relevant studies published in recent years 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 aerosol acidity, sulfate, ammonia, and nitrate concentrations. Also, a number of studies have measured PAHs, both indoors and outdoors. Other than the PAHs, there is little data on organic constituents of PM.

TABLE 5-11. 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.

TABLE 5-12. 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. (1993b,c)	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. (1993a)	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.

5.5.3 Key Findings

5.5.3.1 Correlations of Personal and Indoor Concentrations with Ambient Concentrations of Particulate Matter Constituents

The elemental composition of PM 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, with sulfur being the only exception.

The PTEAM data also showed good agreement between the concentrations of the elements measured outdoors at 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 in personal samples (median particle exposure of 101 μg/m^3), 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. But the outdoor concentrations measured at the participant's 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 participant's 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 5-11 and 5-12. Key findings from these studies include those shown below.

- 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. But, 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). But 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 5-13.

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.

TABLE 5-13. 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).

Similar results for ammonia were reported by Waldman and Liang (1993). They reported that levels of ammonia in institutional settings that they monitored 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 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 5-10.

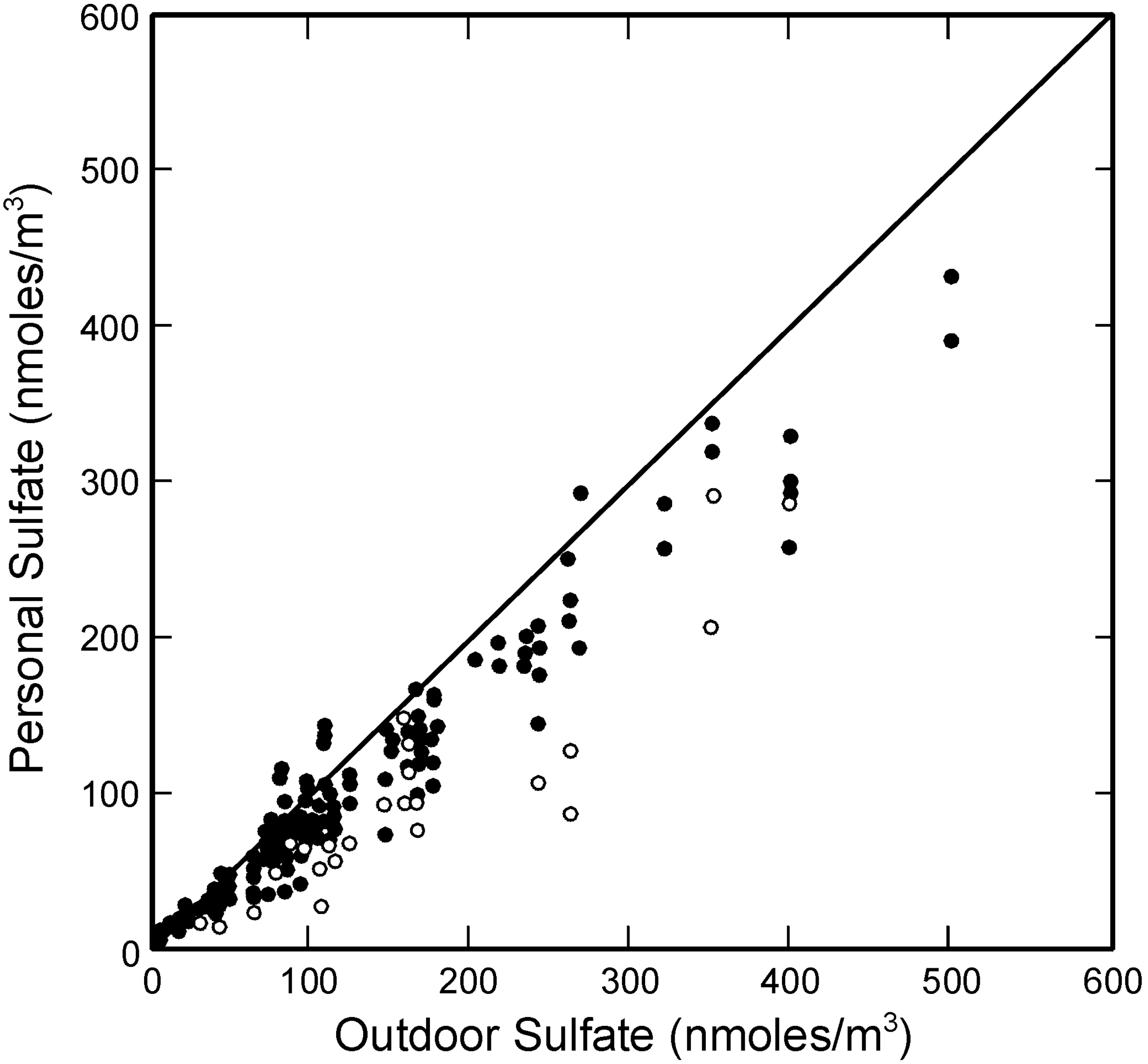


Figure 5-10. Personal versus outdoor $SO_4^=$ in State College, PA. Open circles represent children living in air conditioned homes; the solid line is the 1:1 line.

Source: Suh et al. (1993b).

Indoor/outdoor relationships were measured 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_{ao}, given by the slope of the regression lines (Table 5-14), 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 the data indicate that indoor $PM_{2.5}$ mass may not always be a good indicator of exposure to ambient combustion material caused by the influence of indoor sources of particles. However, ambient sulfate, SO_2, nitrate, soot, and total particulate number displayed strong correlations with indoor exposure. Ambient $PM_{2.5}$ mass was not a good indicator of indoor $PM_{2.5}$ mass exposure.

TABLE 5-14. STATISTICAL CORRELATION OF OUTDOOR (x) VERSUS INDOOR (y) CONCENTRATION FOR MEASURED SPECIES (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	Intercept	r^2	Average Outdoors
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).

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 ($n = 40$, $r = 0.85$). Oglesby et al. (2000) concluded that

> "for regional air pollution, fixed-site fine particle levels are valid exposure surrogates. For source-specific exposures, however, fixed-site data are probably not the optimal measure. Still, in air pollution epidemiology, ambient $PM_{2.5}$ levels may be more appropriate exposure estimates than total personal $PM_{2.5}$ exposure, since the latter reflects a mixture of indoor and outdoor sources."

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 are summarized below.

- 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 (Sheldon et al., 1993b,c) were similar to the 125-home study. The higher-ring, particle-bound PAH's 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 μg/m^3). Higher indoor levels were seen in smoker's homes compared with nonsmoker's 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 outdoor—especially motor vehicular traffic—and indoor sources contributed to indoor PAH concentrations.

5.5.4 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 and removal mechanisms, indoor air chemistry, and indoor sources. 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 impact substantially the correlation between indoor and ambient concentrations (Özkaynak et al., 1996b). Penetration factors for PM will impact 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. These factors must be fully evaluated when attempting to correlate ambient, personal, and indoor PM concentrations.

5.5.5 Limitations of Available Data

The previous discussion demonstrates that there is very 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. Although there is some data on acid aerosols, the comparisons between the personal and indoor data generally have been with outdoor measurements at the participant's 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 to relate personal or indoor concentrations with outdoor or ambient site concentrations of SVOCs, which 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.

5.6. IMPLICATIONS OF USING AMBIENT PARTICULATE MATTER CONCENTRATIONS IN EPIDEMIOLOGIC STUDIES OF PARTICULATE MATTER HEALTH EFFECTS

In this section, the exposure issues that relate to the interpretation of the findings from epidemiologic studies of PM health effects are examined. This section examines the errors that may be associated with using ambient PM concentrations in epidemiologic 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 epidemiology studies is presented.

5.6.1 Potential Sources of Error Resulting from Using Ambient Particulate Matter Concentrations in Epidemiologic Analyses

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 epidemiologic 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 epidemiologic 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, $SO_4^=$, IP_{15}, RSP, COH, KM, etc. A critical question often raised in the interpretation of results from acute or chronic epidemiologic community-based studies of PM is whether the use of ambient stationary site PM concentration data influences or biases the findings from these studies. Because the health outcomes are measured on individuals, the epidemiologists might prefer to use personal exposure measurements (total, ambient, or nonambient) instead of surrogates, such as ambient PM concentration measurements collected at one or more ambient monitoring sites in the community. Use of ambient concentrations could lead to misclassification of individual exposures and to errors in the epidemiologic 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 will be classified incorrectly if only ambient monitoring data are used to estimate individual level exposures to PM. Thus, bias or loss of precision in the epidemiologic analysis may result from improper assessment of exposures using data routinely collected by the neighborhood monitoring stations.

Because individuals are exposed to particles in a multitude of indoor and outdoor microenvironments during the course of a day, concern over 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 and outdoor-generated PM (cf. Wallace, 2000b; Brown and Paxton, 1998; Ebelt et al., 2000). Consequently, numerous findings reported in the epidemiologic 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, has 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 epidemiology 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-generated PM and exposures caused by nonambient PM) with ambient or outdoor PM concentrations, for each of the three types of exposure study design. In addition, several factors influencing 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,
- 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 epidemiologic study.

To facilitate the discussion of these topics, a brief review of concepts pertinent to exposure analysis issues in epidemiology is presented.

5.6.2 Associations Between Personal Exposures and Ambient Particulate Matter Concentrations

As defined earlier 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 (E_t) that occur in these indoor and outdoor microenvironments can be classified as those resulting from PM of outdoor origin (E_{ag}) and those primarily generated by indoor sources and personal activities (E_{nonag} = E_{ig}+E_{pact}). 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 the previous Sections 5.4.3.1.2 and 5.4.3.1.3, some of the recent studies conducted primarily in the United States, involving children, elderly, and subjects with COPD were reviewed, and they indicated that both intra- and interindividual 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.

Clearly, for cohort studies in which individual daily health response are obtained, individual longitudinal PM personal exposure data (including ambient-generated and nonambient components) provide the appropriate indicators. In this case, health responses of each individual can be associated with the total personal exposure, the ambient-generated exposure, or the nonambient exposure of each individual. Also, 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. Average personal exposures of these special subgroups to ambient-generated PM are correlated well with ambient PM concentrations regardless of individual variation in the absence of major microenvironmental sources.

There seem to be clear differences in the relationships of ambient (E_{ag}) and nonambient (E_{nonag}) exposure with ambient concentration (C_a). Various researchers have shown that E_{nonag} is independent of C_a, but that E_{ag} is a function of C_a. Wilson et al. (2000) explains the difference based on different temporal patterns that effect 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."

Ott et al. (2000) also discuss the reasons for assuming that E_{nonag} is independent of E_{ag} and C_a. They show that the nonambient component of total personal exposure is uncorrelated with the outdoor concentration data. Ott et al. (2000) show the $\overline{E}_{nonag}$ is similar for three population-based exposure studies, including 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), as well as a nonprobability-based study, conducted in Phillipsburg (Lioy et al., 1990). Based on these three studies, they conclude that $\overline{E}_{nonag}$ and the distribution of$(E_{nonag})_{it}$ 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 $\overline{E}_{nonag}$ can be treated as relatively constant from city to city. If $(E_{nonag})_t$ were constant, this would imply that it would have a zero correlation with $(C_a)_t$. However, this hypothesis of constant $(E_{nonag})_{it}$ has not been established fully because only a few studies have obtained the data needed to estimate $(E_{nonag})_{it}$. Although $\overline{E}_{nonag}$ is independent of C_a , it may not be independent of α. Sarnat et al. (2000) show that $\overline{E}_{nonag}$ goes up as the ventilation rate (and α) goes down. Lachenmeyer and Hidy (2000) also show, by comparing winter and summer regression equations, that as the slope (α) goes down, the intercept $(\overline{E}_{nonag})$ goes up.

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 E_{ig} and C_a have r near zero ($R^2 = 0.005$). Wilson et al. (2000) have shown the C_{ai} and C_{ig} also have r near zero ($R^2 = 0.03$). Figure 5-11 shows the relationship of estimated $(E_{nonag})_{it}$ and E_{nonag} with C_a (calculated by EPA from PTEAM and THEES data).

Based on these results it is reasonable to assume that ordinarily E_{nonag} has no relationship with C_a. Therefore, in linear nonthreshold models of PM health effects, E_{nonag} is not expected to contribute to the relative risk determined in a regression of health responses on C_a. Furthermore, in time-series analysis of pooled or daily heath data, it is expected that E_{ag} rather than E_t will have the stronger association with C_a.

5.6.3 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, mostly the elderly. 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 do crustal material. The chemical composition of even these broad categories of source classes may have distinct composition and 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

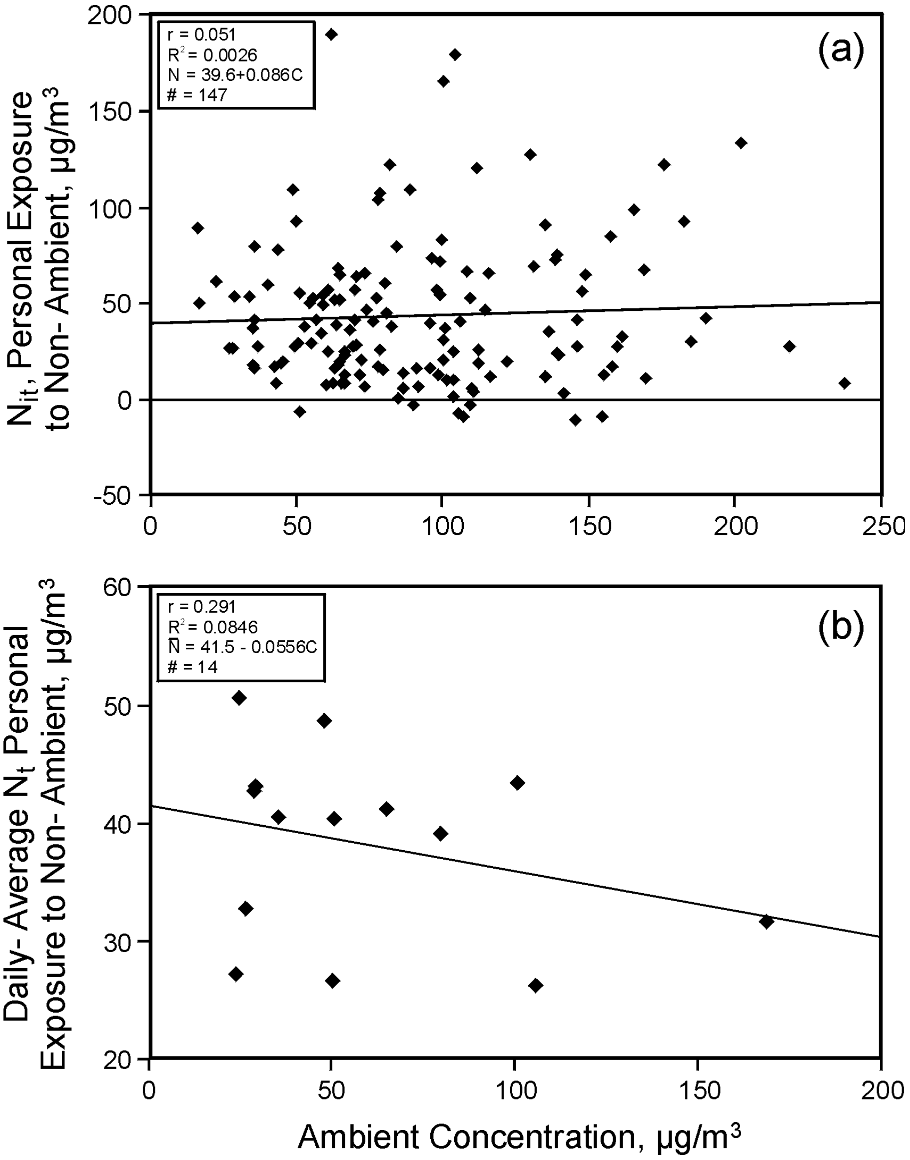


Figure 5-11. Plots of nonambient exposure to PM_{10}, (a) daytime individual values from PTEAM data and (b) daily-average values from THEES data.

Source: Data taken from (a) Clayton et al. (1993) and (b) Lioy et al. (1990).

toxic composition (Isukapalli et al. 2000). Thus, if indoor-generated and outdoor-generated PM were responsible for different types of health effects, or had significantly different toxicities on a per unit mass basis, it would be then be important that E_{ag} and E_{nonag} should be separated and treated as different species, 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. The relationships of toxicity to the chemical and physical properties of PM are discussed in Chapter 7.

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. Nonhome 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 effecting 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, it is impossible to ascertain at this point the magnitude and severity of these more complex exposure missclassification problems in the interpretation of results from PM epidemiology.

5.6.4 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 μ**e** 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 epidemiologic studies of PM. This topic is further discussed below in Section 5.6.5. However, as discussed earlier, the same assumption is not necessarily true for different components of PM, 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, and 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.

5.6.5 Analysis of Exposure Measurement Error Issues in Particulate Matter Epidemiology

The effects of exposure misclassification on relative risk estimates of disease using classical 2×2 contingency design (i.e., exposed/nonexposed versus diseased/nondiseased) have been studied extensively in the epidemiologic 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 (e.g., log-linear regression, Poissson, logit) models typically used in recent PM epidemiology has been more complicated. Recently, researchers 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). Some analysis in the context of cross-sectional epidemiology have also been conducted (e.g. Navidi et al., 1999).

The appropriateness of using ambient PM concentration as an exposure metric in the context of epidemiologic analysis of health effects associated with exposure to PM recently has been examined by a number of investigators (cf. Zeger et al., 2000; Dominici et al., 2000; Navidi et al., 1999; Özkaynak and Spengler, 1996). In the following section, the error analysis model framework developed in Zeger et al. (2000) will be discussed in the context of time-series epidemiology. After which, issues and implications of exposure errors to findings from long-term/chronic or cross-sectional epidemiology will be discussed briefly.

5.6.5.1 Analysis of Exposure Measurement Errors in Time-Series Studies

Zeger et al. (2000) provide a useful framework for analyzing exposure error in community time-series epidemiology. This framework, coupled with results from recent exposure studies, makes it possible to clarify some important questions regarding relationships among the three aspects of personal exposure (1) total personal, (2) personal caused by ambient PM, and (3) personal resulting from nonambient PM and ambient concentration. Consider the regression of a health response (i.e., mortality rate on day t, Y_t, against the ambient concentration of PM on day t, C_t). In analyzing pollution-level data on mortality and air pollution, log-linear regressions of the form:

$$\mathrm{Y}_{\mathrm{t}} = \exp\left[s(t) + C_t\beta_c + u_t\beta_u\right] \tag{5-11}$$

are fit, where Y_i is the expected mortality rate; *s(t)* is an arbitrary but smooth function of time, introduced to control for the confounding of longer trends and seasonality; C_t, is the average of multiple monitor measurements of ambient pollution measurement for day t; and u_t are other possible confounders such as temperature and dew point on the same or previous day. Each coefficient, β, in Equation 5-11 gives the expected change in the health response, Y, because of a unit change in its corresponding variable.

However, instead of Equation 5-11, Zeger et al. (2000) suggest that the analyst would like to know the corresponding relationship for personal exposure rather than ambient concentration,

$$\mathrm{Y}_{\mathrm{t}} = \exp[s(t) + E_t\beta_E + u_t\beta_u]. \tag{5-12}$$

Zeger et al. (2000) do not differentiate among the three aspects of personal or community exposure. To understand the error in β caused by using ambient concentrations instead of personal exposure in the regression analysis, it is necessary to examine the relationship between β_c, based on a unit change in the ambient concentration, C, and β_E, based on a unit change in one of the three aspects of personal exposure, E. In considering the consequences for β_c, as an estimate of β_E, of having a measure of ambient pollution C_t, rather than actual personal exposure E_{it}, it is convenient to express the desired pollution measurement, E_{it}, as C_t plus three error terms:

$$E_{it} = C_t + (E_{it} - \overline{E}_t) + (\overline{E}_t - C_t^*) + (C_t^* - C_t). \tag{5-13}$$

Here $\overline{E}_t$ represents the daily, community-average personal exposure. The first term, $(E_{it} - \overline{E}_t)$, is the error resulting from having only aggregated or community-averaged exposure rather than individual-level exposure data. The second term, $(E_t - C_t^*)$, is the difference between the average personal exposure and the true ambient pollutant level, and the third term, $(C^*_t - C_t)$, represents the difference between the true and the measured ambient concentration.

In the evaluation of these error terms, two types of measurement error often are considered in the context of epidemiology. The classical error model assumes that measurement error, $(C_t - E_t)$, depends on ambient measurements [simply referred to as C_t here instead of $(C_a)_t$]. The Berkson error model assumes that the measurement error is dependent on the true value or the personal exposure (E_t). The regression coefficient (β_C), estimated from the health effects model in the Berkson error case, gives an unbiased estimate of β_E. In the classical error case, β_C is a biased estimate of β_E, and the degree of bias depends on the correlation between the measurement error and C_t. The measurement error analysis of Zeger et al. (2000) includes three components: (1) an individual's deviation from the risk-weighted average personal exposure; (2) the difference between the average personal exposure and the true ambient level; and (3) the difference between the measured and the true ambient levels, which include the spatial variation of outdoor PM and instrument sampling error. Zeger et al. (2000) conclude that the first and third components are of the Berkson type and, therefore, are likely to have smaller effects on the relative risk estimates for PM. However, the second component can be a source of substantial bias if, for example, there are short-term associations of the contributions of indoor sources with ambient concentrations. However, recent analysis of PTEAM data (Mage et al., 2000) and theoretical considerations (Ott et al., 2000) indicate that it is unlikely that nonambient exposures will be correlated with the ambient concentration. Therefore, this type of bias is unlikely. However, if the community average exposure to ambient PM is less than the ambient concentration, the risk regression coefficient, β_C, will be biased low. According to Carrol (1995), $\beta_C = \alpha \beta_E$, where β_C is the percentage increase in risk because of a unit increase in ambient concentration, and β_E is the estimated percentage increase in risk because of a unit increase in the community-average personal exposure to ambient PM. Both Zeger et al. (2000) and Dominici et al. (2000) examine the nature of error with this second component. Both of these analyses conclude that the error introduced because of measured differences between the average personal exposure and ambient levels can bias the regression coefficients. In both cases they find the β_C is close to $\alpha \beta_E$.

This framework analysis demonstrates the importance of the daily community-average exposure, $\overline{E}_t$, in community time-series epidemiology. It is $\overline{E}_t$, not the random, pooled values of $E_{i,t}$, that need to have a statistically significant correlation with C_t for proper interpretation of community time-series epidemiology studies based on ambient monitoring data, as discussed further in Wilson et al. (2000) and Mage et al. (1999).

A critical assumption in the above analysis is that the risk varies linearly with C or E (i.e., β_c and β_E are constant). This assumption does not permit a threshold (a concentration below which there is no effect). It also includes the assumption that the appropriate metric for determination of a health response is the 24-h average PM mass concentration. Zeger et al. (2000) show that the likely consequence of using ambient concentrations instead of the risk-weighted average personal exposure measures is to underestimate the pollution effects. According to Zeger et al. (2000) the largest biases in inferences about the mortality-personal exposure relative risk will occur because of more complex errors between ambient concentration and daily-average personal exposure measures. It is important to note that both the Zeger et al. (2000) and the Dominici et al. (2000) error analyses used personal PM_{10} data from the PTEAM study data. However, effects of measurement error estimates may differ by particle size and composition. It is possible that $PM_{2.5}$, ultrafine particle measures, or another component of PM, may better reflect personal exposures to PM of outdoor origin. Finally, the seasonal or temporal variations in the measurement errors and correlations between different PM concentration measures and co-pollutants (e.g. SO_2, CO, NO_2, O_3) could influence the error analysis results reported by the investigators cited above.

5.6.5.2 Analysis of Exposure Measurement Errors in Long-Term Epidemiology Studies

The Six Cities (Dockery et al., 1993) and 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 epidemiologic 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 past exposures are more strongly associated with mortality than recent exposures, the measurement error for long-term averages could be higher, thus influencing 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 epidemiologic 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.

Another study that has examined the influence of measurement errors in air pollution exposure and health effects assessments is the one reported 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.

5.6.5.3 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-generated PM and nonambient PM, would reduce uncertainties in the analysis and interpretation of PM health effects data. Nevertheless, because ambient-generated PM is an integral component of total personal exposures to PM, statistical analysis 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 cross-sectional or time-series epidemiologic 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 PM toxic 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; these indicate that use of ambient PM concentrations as a surrogate for exposures is not expected to change the principal conclusions from PM epidemiologic studies, utilizing community average health and pollution data.

5.7 SUMMARY OF KEY FINDINGS AND LIMITATIONS

Exposure Definitions and Components

- Personal exposure (E) to PM mass or its constituents results when individuals come in contact with particulate pollutant concentrations (C) in locations or microenvironments (**μe**) 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 (E_t) can be expressed as the sum of various microenvironmental exposures that the person encounters during the course of a day.
- In a given **μe**, 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 (E_t) also can be expressed as the sum of contributions of ambient-generated (E_{ag}) and nonambient-generated (E_{nonag}) PM (i.e., $E = E_{ag} + E_{nonag}$). E_{nonag}, in turn, is composed of PM generated by indoor sources (E_{ig}) and PM generated by personal activities (E_{pact}) (i.e., $E_{nonag} = E_{ig} + E_{pact}$). E_{ag} is composed of exposures to

ambient PM concentrations while outdoors, $\sum_t C_a \Delta t_a$, and ambient PM that has infiltrated indoors, $\sum_t C_{ai} \Delta t_i$ while indoors (i.e., $E_{ag} = \sum_t C_a \Delta t_a + \sum_t C_{ai} \Delta t_i$).

- 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 has 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.
- The relative size of personal exposure to ambient-generated PM relative to nonambient-generated 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 and health outcome could depend on the concentration, composition, and toxicity of the PM originating from different sources. Application of source apportionment techniques to ambient, indoor, and personal PM composition data have identified the following general source categories of importance: 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 that
    - 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 impact the relation between indoor and ambient concentrations;
    - penetration and decay rates are a 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, such as the PTEAM study, or the longitudinal panel studies, which 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 temporally, their individual personal exposures may be correlated highly with ambient concentrations.

- Recent studies conducted by EPA of the elderly subjects living in a retirement facility in Baltimore and a group of elderly living in Fresno produced higher correlation coefficients between personal and ambient PM for daily-average correlations compared to longitudinal correlations. This supports earlier analyses showing the daily-average correlations are higher than pooled correlations.
- 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. But even for these studies, correlations varied by individual depending on their activities and on the microenvironments that they occupied.

Potential Sources of Error Resulting from Using Ambient Particulate Matter Concentrations in Epidemiologic Analyses

- There is, as yet, no clear consensus among exposure analysts as to how well ambiently measured PM concentrations represent a surrogate for personal exposure to total PM or to ambient-generated 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 epidemiologic 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 over 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-generated PM and nonambient-generated 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 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 epidemiologic 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 of the PM components.
- There are important differences in the relationship of ambient PM concentrations (C_a) with exposures to ambient PM (E_{ag}), and with exposures to nonambient PM (E_{nonag}). Various researchers have shown that E_{ag} is a function of C_a, 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, E_{nonag} is independent of C_a, 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 (RCS) 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, E_{nonag} is not expected to contribute to the relative risk estimates determined by regression of health responses on C_a.

- Using the PTEAM study data, analysis of exposure measurement errors in the context of time-series epidemiology 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.
- 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, it is impossible to ascertain at this point 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}. It is possible that various ultrafine particle measures, or other components of PM may be better exposure indicators for epidemiologic 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.
- Ordinarily, PM exposure measurement errors are not expected to influence the interpretation of findings from either the community time-series or long-term epidemiologic studies that have used ambient concentration data if they include sufficient adjustments for seasonality and key personal and geographic confounders.
- 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.

- Currently available studies on PM exposure measurement errors indicate that use of ambient PM concentrations as a surrogate for personal exposures is not expected to change the key conclusions derived from most of the recent epidemiologic studies on PM health effects.

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