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External Review Draft

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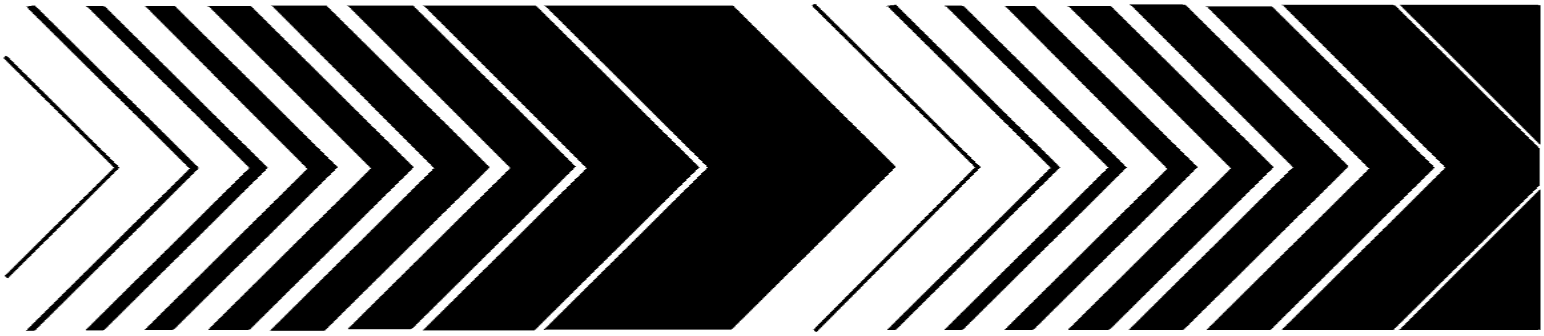
Air Quality Criteria for Particulate Matter

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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National Center for Environmental Assessment
Office of Research and Development
U.S. Environmental Protection Agency
Research Triangle Park, NC 27711

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 (U.S. 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 may reasonably be expected to endanger public health or welfare; (2) to issue air quality criteria for them which 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-yrs) review and revise, as appropriate, the criteria and NAAQS for a given listed pollutant or class of pollutants.

The original U.S. 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 ($150\ \mu g/m^3$, 24-h; $50\ \mu g/m^3$, annual ave.) were retained in modified form and new standards ($65\ \mu g/m^3$, 24-h; $15\ \mu g/m^3$, annual ave.) for particles $\leq 2.5\ \mu m$ ($PM_{2.5}$) were promulgated in July 1997.

This First External Review Draft of revised Air Quality Criteria for Particulate Matter assesses new scientific information that has become available since early 1996 through mid-1999. Extensive additional pertinent information is expected to be published during the next 6 to 9 months (including results from a vastly expanded U.S. 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. The present draft is being released for public comment and review by the Clean Air Scientific Advisory Committee (CASAC) mainly to obtain comments on the organization and structure of the document, the issues addressed, and the approaches employed in assessing and interpreting the thus far available new information on PM exposures and effects. Public comments and CASAC review recommendations will be taken into account, along with newly available information published or accepted for peer-reviewed publication by April/May 2000, in making further revisions to this document for incorporation into a Second External Review Draft. That draft is expected to be released in June 2000 for further public comment and CASAC review (September 2000) in time for final revisions to be completed by December 2000). Evaluations contained in the present document will be drawn upon 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 by July 2000 of decisions on potential retention or revision of the current PM NAAQS.

This document was prepared and 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. It describes the nature, sources, distribution, measurement, and concentrations of PM in both the outdoor (ambient) and indoor environments and evaluates the latest data on the health effects in exposed human populations, as well as environmental effects on: vegetation and ecosystems; visibility and climate; manmade materials; and associated economic impacts. Although not intended to be an exhaustive literature review, this document is intended to assess all pertinent literature through mid-1999.

The National Center for Environmental Assessment – Research Triangle Park, NC (NCEA-RTP) 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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Authors, Contributors, and Reviewers

CHAPTER 1. EXECUTIVE SUMMARY

Principal Authors

Dr. Robert Chapman—National Center for Environmental Assessment (MD-52),
U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Ms. Beverly Comfort—National Center for Environmental Assessment (MD-52),
U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Mr. William Ewald—National Center for Environmental Assessment (MD-52),
U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. Lawrence J. Folinsbee—National Center for Environmental Assessment (MD-52),
U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. J.H.B. Garner—National Center for Environmental Assessment (MD-52),
U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. Lester D. Grant—National Center for Environmental Assessment (MD-52),
U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. Dennis J. Kotchmar—National Center for Environmental Assessment (MD-52),
U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. David Mage—National Exposure Research Laboratory (MD-56), U.S. Environmental
Protection Agency, Research Triangle Park, NC 27711

Dr. Allan Marcus—National Center for Environmental Assessment (MD-52),
U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. Joseph P. Pinto—National Center for Environmental Assessment (MD-52),
U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. William E. Wilson—National Center for Environmental Assessment (MD-52),
U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Authors, Contributors, and Reviewers
(cont'd)

CHAPTER 2. INTRODUCTION

Principal Authors

Dr. Dennis J. Kotchmar—National Center for Environmental Assessment (MD-52),
U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. Lester D. Grant—National Center for Environmental Assessment (MD-52),
U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

CHAPTER 3. PHYSICS, CHEMISTRY, AND MEASUREMENT OF PARTICULATE MATTER

Principal Authors

Dr. William Wilson—National Center for Environmental Assessment (MD-52),
U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. Candis S. Claiborn—Washington State University, Laboratory for Atmospheric Research,
Department of Civil and Environmental Engineering,, P.O. Box 642910, Pullman, WA 99164

Contributors and Reviewers

Dr. Timothy Buckley—Johns Hopkins University, Department of Environmental Health
Sciences, 615 North Wolfe Street,, Baltimore, MD 21205

Ms. Lee Byrd—Office of Air Quality Planning and Standards (MD-14)
U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. Lyle Chinkin—Sonoma Technology, 1360 Redwood Way, Suite C
Petaluma, CA 94549

Dr. Steven Colome—Integrated Environmental Services, 5319 University Drive, #430
Irvine, CA 92612

Dr. Delbert Eatough—Brigham Young University, E 114 BNSN,
Department of Chemistry and Biochemistry, Provo, UT 84602

Authors, Contributors, and Reviewers
(cont'd)

Mr. William Ewald—National Center for Environmental Assessment (MD-52),
U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. Sheldon Friedlander—University of California at Los Angeles, Department of Chemical
Engineering, 5531 Boelter Hall, Los Angeles, CA 90095

Dr. Judith Graham—National Exposure Research Laboratory (MD-75)
U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. Lynn Hildemann—Stanford University, Civil and Environmental Engineering Department
Stanford, CA 94305

Mr. Jim Homolya—Office of Air Quality Planning and Standards (MD-14)
U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. Rudolf Husar—CAPITA, Washington University, Campus Box 1124
One Brookings Drive, St. Louis, MO 63130

Dr. Charles W. Lewis—National Exposure Research Laboratory (MD-47)
U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Mr. Tom McCurdy—National Exposure Research Laboratory (MD-56)
U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Mr. Frank McElroy—National Exposure Research Laboratory (MD-46)
U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. Haluk Ozkaynak—National Exposure Research Laboratory (MD-56)
U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Mr. Tom Pace—Office of Air Quality Planning and Standards (MD-14)
U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. Joseph Pinto—National Center for Environmental Assessment (MD-52)
U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. Richard Poirot—VT Air Program, Building 3 South, 103 South Main Street
Waterbury, VT 05671

Dr. Linda Sheldon—National Exposure Research Laboratory (MD-77)
U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Authors, Contributors, and Reviewers

(cont'd)

Dr. Helen Suh—Harvard School of Public Health, 665 Huntington Avenue
Boston, MA 02461

Mr. Robert Wayland—Office of Air Quality Planning and Standards (MD-15)
U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Mr. Dane Westerdahl—California Air Resources Board, 2020 L Street
Sacramento, CA 95814

CHAPTER 4. CONCENTRATIONS, SOURCES, AND EMISSIONS OF ATMOSPHERIC PARTICLES

Principal Authors

Dr. Joseph P. Pinto—National Center for Environmental Assessment (MD-52),
U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. William Wilson—National Center for Environmental Assessment (MD-52),
U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Contributors and Reviewers

Dr. Timothy Buckley—Johns Hopkins University, Department of Environmental Health
Sciences, 615 North Wolfe Street,, Baltimore, MD 21205

Ms. Lee Byrd—Office of Air Quality Planning and Standards (MD-14)
U. S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. Lyle Chinkin—Sonoma Technology, 1360 Redwood Way, Suite C
Petaluma, CA 94549

Dr. Steven Colome—Integrated Environmental Services, 5319 University Drive, #430
Irvine, CA 92612

Dr. Delbert Eatough—Brigham Young University, E 114 BNSN,
Department of Chemistry and Biochemistry, Provo, UT 84602

Mr. William Ewald—National Center for Environmental Assessment (MD-52),
U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Authors, Contributors, and Reviewers

(cont'd)

Dr. Sheldon Friedlander—University of California at Los Angeles, Department of Chemical Engineering, 5531 Boelter Hall, Los Angeles, CA 90095

Dr. Judith Graham—National Exposure Research Laboratory (MD-75)
U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. Lynn Hildemann—Civil and Environmental Engineering Department
Stanford University, Stanford, CA 94305

Mr. Jim Homolya—Office of Air Quality Planning and Standards (MD-14)
U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. Rudolf Husar—CAPITA, Washington University, Campus Box 1124
One Brookings Drive, St. Louis, MO 63130

Dr. Charles W. Lewis—National Exposure Research Laboratory (MD-47)
U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Mr. Tom McCurdy—National Exposure Research Laboratory (MD-56)
U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Mr. Frank McElroy—National Exposure Research Laboratory (MD-46)
U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. Haluk Ozkaynak—National Exposure Research Laboratory (MD-56)
U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Mr. Tom Pace—Office of Air Quality Planning and Standards (MD-14)
U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. Joseph Pinto—National Center for Environmental Assessment (MD-52), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. Richard Poirot—VT Air Program, Building 3 South, 103 South Main Street
Waterbury, VT 05671

Dr. Linda Sheldon—National Exposure Research Laboratory (MD-77)
U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. Helen Suh—Harvard School of Public Health, 665 Huntington Avenue
Boston, MA 02461

Authors, Contributors, and Reviewers
(cont'd)

Mr. Robert Wayland—Office of Air Quality Planning and Standards (MD-15)
U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Mr. Dane Westerdahl—California Air Resources Board, 2020 L Street, Sacramento, CA 95814

CHAPTER 5. HUMAN EXPOSURE TO AMBIENT PARTICULATE MATTER: RELATIONS TO CONCENTRATIONS OF AMBIENT AND NON-AMBIENT PM, AND OTHER AIR POLLUTANTS

Principal Authors

Dr. David Mage—National Center for Environmental Assessment (MD-52)
U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Contributors and Reviewers

Dr. Timothy Buckley—Johns Hopkins University, Department of Environmental Health
Sciences, 615 North Wolfe Street,, Baltimore, MD 21205

Ms. Lee Byrd U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. Lyle Chinkin—Sonoma Technology, 1360 Redwood Way, Suite C
Petaluma, CA 94549

Dr. Steven Colome—Integrated Environmental Services, 5319 University Drive, #430
Irvine, CA 92612

Dr. Delbert Eatough—Brigham Young University, E 114 BNSN,
Department of Chemistry and Biochemistry, Provo, UT 84602

Mr. William Ewald—National Center for Environmental Assessment (MD-52),
U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. Sheldon Friedlander—University of California at Los Angeles, Department of Chemical
Engineering, 5531 Boelter Hall, Los Angeles, CA 90095

Dr. Lawrence J. Folinsbee—National Center for Environmental Assessment (MD-52),
U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Authors, Contributors, and Reviewers
(cont'd)

Dr. Judith Graham—National Exposure Research Laboratory (MD-75)
U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. Lester D. Grant—National Center for Environmental Assessment (MD-52),
U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. Vic Hasselblad—29 Autumn Woods Drive, Durham, NC 27713

Dr. Lynn Hildemann—Civil and Environmental Engineering Department
Stanford University, Stanford, CA 94305

Mr. Jim Homolya—Office of Air Quality Planning and Standards (MD-14)
U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. Rudolf Husar—CAPITA, Washington University, Campus Box 1124
One Brookings Drive, St. Louis, MO 63130

Dr. Dennis J. Kotchmar—National Center for Environmental Assessment (MD-52),
U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. Charles W. Lewis—National Exposure Research Laboratory (MD-47)
U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. Allan Marcus—National Center for Environmental Assessment (MD-52),
U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Mr. Tom McCurdy—National Exposure Research Laboratory (MD-56)
U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Mr. Frank McElroy—National Exposure Research Laboratory (MD-46)
U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. Haluk Ozkaynak—National Exposure Research Laboratory (MD-56)
U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Mr. Tom Pace—Office of Air Quality Planning and Standards (MD-14)
U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. Joseph Pinto—National Center for Environmental Assessment (MD-52), U.S. Environmental
Protection Agency, Research Triangle Park, NC 27711

Authors, Contributors, and Reviewers
(cont'd)

Dr. Richard Poirot—VT Air Program, Building 3 South, 103 South Main Street
Waterbury, VT 05671

Dr. Linda Sheldon—National Exposure Research Laboratory (MD-77)
U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. Helen Suh—Harvard School of Public Health, 665 Huntington Avenue
Boston, MA 02461

Mr. Robert Wayland—Office of Air Quality Planning and Standards (MD-15)
U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Mr. Dane Westerdahl—California Air Resources Board, 2020 L Street, Sacramento, CA 95814

Dr. William Wilson—National Center for Environmental Assessment (MD-52),
U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. Jim Xue—Harvard School of Public Health, 665 Huntington Avenue, Boston, MA 02115

U.S. ENVIRONMENTAL PROTECTION AGENCY
PROJECT TEAM FOR DEVELOPMENT OF AIR QUALITY CRITERIA FOR PARTICULATE MATTER

Scientific Staff

Dr. Lester D. Grant—Director, National Center for Environmental Assessment (MD-52), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Mr. Randy Brady—Deputy, National Center for Environmental Assessment (MD-52), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. Lawrence J. Folinsbee—Health Coordinator, Chief, Environmental Media Assessment Group, National Center for Environmental Assessment (MD-52), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. William E. Wilson—Air Quality Coordinator, Physical Scientist, National Center for Environmental Assessment (MD-52), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. Dennis J. Kotchmar—Project Manager, Medical Officer, National Center for Environmental Assessment (MD-52), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. Robert Chapman—Technical Consultant, Medical Officer, National Center for Environmental Assessment (MD-52), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Ms. Beverly Comfort—Health Scientist, National Center for Environmental Assessment (MD-52), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Mr. William Ewald—Technical Project Officer, Health Scientist, National Center for Environmental Assessment (MD-52), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. David Mage—Technical Project Officer, Physical Scientist, National Center for Environmental Assessment (MD-52), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. Allan Marcus—Technical Project Officer, Statistician, National Center for Environmental Assessment (MD-52), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

U.S. ENVIRONMENTAL PROTECTION AGENCY PROJECT TEAM FOR DEVELOPMENT OF AIR QUALITY CRITERIA FOR PARTICULATE MATTER

(cont'd)

Dr. James McGrath—Technical Project Officer, Visiting Senior Health Scientist, National Center for Environmental Assessment (MD-52), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Dr. Joseph P. Pinto—Technical Project Officer, Physical Scientist, National Center for Environmental Assessment, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Technical Support Staff

Mr. Douglas B. Fennell—Technical Information Specialist, National Center for Environmental Assessment (MD-52), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Ms. Emily R. Lee—Management Analyst, National Center for Environmental Assessment (MD-52), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Ms. Diane H. Ray—Program Analyst, National Center for Environmental Assessment (MD-52), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Ms. Eleanor Speh—Office Manager, Environmental Media Assessment Branch, National Center for Environmental Assessment (MD-52), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Ms. Donna Wicker—Administrative Officer, National Center for Environmental Assessment (MD-52), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Mr. Richard Wilson—Clerk, National Center for Environmental Assessment (MD-52), U.S. Environmental Protection Agency, Research Triangle Park, NC 27711

Document Production Staff

Mr. John R. Barton—Document Processing Coordinator
OAO Corporation, Chapel Hill-Nelson Highway, Beta Building, Suite 210, Durham, NC 27713

Ms. Yvonne Harrison—Word Processor
OAO Corporation, Chapel Hill-Nelson Highway, Beta Building, Suite 210, Durham, NC 27713

U.S. ENVIRONMENTAL PROTECTION AGENCY PROJECT TEAM FOR DEVELOPMENT OF AIR QUALITY CRITERIA FOR PARTICULATE MATTER

(cont'd)

Ms. Bettye Kirkland—Word Processor
OAO Corporation, Chapel Hill-Nelson Highway, Beta Building, Suite 210, Durham, NC 27713

Mr. David E. Leonhard—Graphic Artist
OAO Corporation, Chapel Hill-Nelson Highway, Beta Building, Suite 210, Durham, NC 27713

Ms. Carolyn T. Perry—Word Processor
OAO Corporation, Chapel Hill-Nelson Highway, Beta Building, Suite 210, Durham, NC 27713

Ms. Veda E. Williams—Graphic Artist
OAO Corporation, Chapel Hill-Nelson Highway, Beta Building, Suite 210, Durham, NC 27713

Technical Reference Staff

Mr. R. David Belton—Reference Specialist
OAO Corporation, Chapel Hill-Nelson Highway, Beta Building, Suite 210, Durham, NC 27713

Mr. John Bennett—Technical Information Specialist
OAO Corporation, Chapel Hill-Nelson Highway, Beta Building, Suite 210, Durham, NC 27713

Mr. William Hardman—Reference Retrieval and Database Entry Clerk
OAO Corporation, Chapel Hill-Nelson Highway, Beta Building, Suite 210, Durham, NC 27713

Ms. Sandra L. Hughey—Technical Information Specialist
OAO Corporation, Chapel Hill-Nelson Highway, Beta Building, Suite 210, Durham, NC 27713

Mr. Jian Ping Yu—Reference Retrieval and Database Entry Clerk
OAO Corporation, Chapel Hill-Nelson Highway, Beta Building, Suite 210, Durham, NC 27713

1. EXECUTIVE SUMMARY

1.1 INTRODUCTION

1.1.1 Purpose of the Document

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

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

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

1.1.2 Organization of the Document

The present document is organized into nine chapters, as follows:

- This Executive Summary (Chapter 1) summarizes key points from the ensuing chapters.
- Chapter 2 provides a general introduction, including a brief summary of the history of the PM NAAQS and an overview of issues, methods and procedures used to prepare this document.
- Chapters 3 through 5 provide background information on air quality and exposure aspects, to help to place the succeeding discussions of PM effects into perspective.
- Chapter 6 discusses community epidemiology information and Chapter 7 discusses dosimetry and toxicology of PM.
- Chapter 8 provides an integrative synthesis of key points from those health chapters (6 & 7) and other preceding air quality and exposure chapters.
- Chapter 9 deals with environmental effects of PM on vegetation and ecosystems; visibility; climate; and manmade materials, as well as economic impacts of such effects.

It should be noted that new research results that have become available since early 1996 (when the last previous PM criteria assessment was completed) through mid-1999 are assessed in this First External Review Draft of the revised PM Air Quality Criteria Document (PM AQCD). Extensive further new research results, expected to be published during the next 6 to 9 mo (including many from a vastly expanded EPA PM Research Program) will be assessed in the Second External Review Draft of this document to be released in mid-2000 for public comment and CASAC review. Thus, key findings and conclusions summarized below must be considered to be only provisional and subject to change, as appropriate, due to consideration of new research in the next draft.

1.2 AIR QUALITY AND EXPOSURE ASPECTS

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

1.2.1 Chemistry and Physics of Atmospheric Particles

- Airborne PM is not a single pollutant, but rather is a mixture of many subclasses of pollutants with each subclass containing many different chemical species. Atmospheric PM occurs naturally as fine-mode and coarse-mode particles that, in addition to falling into different size ranges, differ in formation mechanisms, chemical composition, sources, and exposure relationships.
- Fine-mode PM is derived from combustion material that has volatilized and then condensed to form primary PM or from precursor gases reacting in the atmosphere to form secondary PM. New fine-mode particles are formed by the nucleation of gas phase species, and grow by coagulation (existing particles combining) or condensation (gases condensing on existing particles). Fine particles are composed of freshly generated nuclei-mode particles, also called ultrafine or nanoparticles, and an accumulation mode, so called because particles grow into and remain in that mode.
- Coarse-mode PM, in contrast, is formed by crushing, grinding, and abrasion of surfaces, which breaks large pieces of material into smaller pieces. These particles are then suspended by the wind or by anthropogenic activity. Energy considerations limit the break-up of large particles and small particle aggregates generally to a minimum size of about 1 μm in diameter. Mining and agricultural activities are examples of anthropogenic sources of coarse-mode particles. Fungal spores, pollen, and plant and insect fragments are examples of natural bioaerosols also suspended as coarse-mode particles.
- Within atmospheric particle modes, the distribution of particle number, surface, volume, and mass by diameter is frequently approximated by lognormal distributions. Aerodynamic diameter, d_{ae}, which depends on particle density and is defined as the diameter of a particle with the same settling velocity as a spherical particle with unit density (1 g/cm^3), is often used to describe particle size. Typical values of the mass median aerodynamic diameters (MMAD) are

0.05 to 0.07 μm for the nuclei mode, 0.3 to 0.7 μm for the accumulation mode, and 6 to 20 μm for the coarse mode. At high relative humidities or in air containing evaporating fog or cloud droplets, the accumulation mode may be split into a droplet mode (MMAD = 0.5 to 0.8 μm) and a condensation mode (MMAD = 0.2 to 0.3 μm).

- Research studies use (a) impactors to determine mass and composition as a function of size over a wide range and (b) particle counting devices to determine number of particles as a function of size. Such studies indicate an atmospheric bimodal distribution of fine and coarse particle mass with a minimum in the distribution between 1 and 3 μm d_{ae}. Routine monitoring studies generally measure thoracic particles or PM_{10} (upper size limited by a 50% cut at 10 μm d_{ae}). Research studies and new monitoring studies measure fine particles or $PM_{2.5}$ (upper size limited by a 50% cut point at 2.5 μm d_{ae}) and the coarse fraction of PM_{10}, i.e., the difference between PM_{10} and $PM_{2.5}$ ($PM_{10-2.5}$). Cut points are not perfectly sharp for any of these PM indicators; some particles larger than the 50% cutpoint are collected and some particles smaller than the 50% cutpoint are not retained.
- The terms “fine” and “coarse” were originally intended to apply to the two major atmospheric particle distributions which overlap in the size range between 1 and 3 μm diameter. Now, fine has come to be often associated with the $PM_{2.5}$ fraction and coarse is often used to refer to $PM_{10-2.5}$. However, $PM_{2.5}$ may also contain, in addition to the fine-particle mode, some of the lower-size tail of the coarse particle mode between about 1 and 2.5 μm d_{ae}. Conversely, under high relative humidity conditions, the larger fine particles in the accumulation mode may also extend into the 1 to 3 μm d_{ae} range.
- Three approaches are used to classify particles by size: (1) modes, based on formation mechanisms and the modal structure observed in the atmosphere, e.g., nuclei and accumulation modes (which comprise the fine-particle mode) and the coarse-particle mode; (2) cut point, based on the 50% cut point of the specific sampling device; (3) dosimetry, based on the ability of particles to enter certain regions of the respiratory tract; and (4) regulatory, based on instrument configuration or 50% cut-points, e.g., high volume sampler, PM_{10}, and $PM_{2.5}$.

1.2.2 Sources of Airborne Particles in the United States

- The chemical complexity of airborne particles requires that the composition and sources of a large number of primary and secondary components be considered. Major components of fine particles are: sulfate, strong acid, ammonium, nitrate, organic compounds, trace elements (including metals), elemental carbon, and water.
- Primary particles are emitted directly from sources. Secondary particles are formed from atmospheric reactions of sulfur dioxide (SO_2), nitrogen oxides (NO_x), and certain organic compounds. NO reacts with ozone (O_3) to form NO_2. SO_2 and NO_2 react with hydroxy radical (OH) during the daytime to form sulfuric and nitric acid. During the nighttime NO_2 reacts with ozone and forms nitric acid through a sequence of reactions involving the nitrate radical (NO_3). These acids may react further with ammonia to form ammonium sulfates and nitrates. Some types of higher molecular weight organic compounds react with OH radicals, and olefinic compounds also react with ozone, to form oxygenated organic compounds which nucleate or can condense onto existing particles. SO_2 also dissolves in cloud and fog droplets where it may react with dissolved O_3, H_2O_2, or, if catalyzed by certain metals, with O_2, yielding sulfuric acid or sulfates, that lead to PM when the droplet evaporates.
- Receptor modeling has proven to be a useful method for identifying contributions of different types of sources especially for the primary components of ambient PM. Apportionment of secondary PM is more difficult because it requires consideration of atmospheric reaction processes and rates. Results from western U.S. sites indicate that fugitive dust, motor vehicles, and wood smoke are the major contributors to ambient PM samples there, while results from eastern U.S. sites indicate that stationary combustion, motor vehicles and fugitive dust are major contributors to ambient PM samples in the East. Sulfate and organic carbon are the major secondary components in the East, while nitrates and organic carbon are the major secondary components in the West.
- Fine and coarse particles have distinctly different sources, both natural and anthropogenic. Therefore different control strategies are likely to be needed, depending on whether fine or coarse particles (or both) are selected for control.

1.2.3 Atmospheric Transport and Fate of Airborne Particles

- Primary and secondary fine particles have long lifetimes in the atmosphere (days to weeks) and travel long distances (hundreds to thousands of kilometers). They tend to be uniformly distributed over urban areas and larger regions, especially in the eastern United States. As a result, they are not easily traced back to their individual sources.
- Coarse particles normally have shorter lifetimes (minutes to hours) and only travel short distances (<10's of km). Therefore, coarse particles tend to be unevenly distributed across urban areas and tend to have more localized effects than fine particles. However, dust storms occasionally cause long range transport of the smaller coarse-mode particles.

1.2.4 Airborne Particle Measurement Methods

- Measurements of ambient PM mass and chemical composition are needed to determine attainment of standards; to guide attainment of a standard (including determination of source categories and validation of air quality models); and to determine health, ecological, and radiative effects. A comprehensive approach requires a combination of analytical techniques to assess: (1) mass, (2) crustal and trace elements, (3) water-soluble ionic species including strong acidity, (4) elemental carbon, and (5) organic compounds.
- There are no calibration standards for suspended particle mass; therefore, the accuracy of particle mass measurements cannot be definitively determined. The precision of particle mass measurements can be determined by comparing results from collocated samplers. When using different measurement techniques, samplers of different design or manufacturer, and, in some cases, when using identical systems of different age or cleanliness, substantial biases of 50% or more have been observed. Mass concentration measurements with a precision close to 10% have been obtained with collocated samplers of identical design and same time since cleaning.
- Available technology allows accurate (±10 to 15%) measurement of several of the major components of coarse and fine particles (crustal and trace elements, sulfates, and strong acidity). However, collection and measurement technologies for elemental carbon, organic carbon, and nitrates are not as well established.
- Semivolatile organic compounds and semivolatile ammonium compounds (such as NH_4NO_3) may be lost by volatilization during sampling. Such losses may be very important in

woodsmoke impacted areas for organic compounds or in agricultural and other areas where low sulfate and high ammonia lead to high NH_4NO_3 concentrations. Hence, while the Federal Reference Methods for PM_{10} and $PM_{2.5}$ give precise (± 10%) measurements of "equilibrated mass", loss of semivolatile PM and possible retention of some particle-bound water contribute to uncertainly in measurement of the mass of PM as it exists suspended in the atmosphere.

- Intercomparisons, using different techniques and samplers of different designs, coupled with mass balance studies (relating the sum of components to the measured mass), provide a method for gaining confidence in the reliability of PM measurements.

1.2.5 Ambient U.S. PM Concentrations: Regional Patterns and Trends

- Particle mass data have been collected at a number of rural, suburban, and urban sites across the United States by various local, state, and national programs. The data have been stored in the Aerometric Information Retrieval System (AIRS). Data have also been collected at remote sites as part of the IMPROVE and NESCAUM networks. An extensive analysis of this data was reported in the 1996 Air Quality Criteria Document for Particulate Matter (PM AQCD).
- Information on trends of $PM_{2.5}$ (fine) and $PM_{10\text{-}2.5}$ (coarse) were also examined for Philadelphia, several AIRS sites, the Harvard Six-City sites, and California sites. However, such data is still not sufficient, either in number of sites or number of years per site, to demonstrate differential trends in fine or coarse PM.

1.2.6 Human PM Exposure

Chapter 5 examines: ambient particulate matter (PM) air quality; that portion of ambient PM which penetrates into indoor microenvironments; and, to a lesser extent, the contributions of sources of non-ambient PM to total PM exposure. This is to aid in interpretation of acute and chronic epidemiology studies discussed in Chapter 6, in which ambient PM concentrations are assumed to be an indicator, or a surrogate, for mean community exposure to PM of ambient origin, or an individual's exposure to ambient PM. Thus, this chapter has three objectives:

(a) To provide a review of pertinent studies of personal exposures to total PM (ambient PM plus non-ambient PM).

(b) To evaluate linkages of human exposure to PM of ambient origin estimated from concentrations of PM measured at a fixed-site monitor located at some central location in a community under study.

(c) To quantify the contribution of PM of ambient origin to total personal PM exposure.

In meeting those objectives, Chapter 5 has reached the following provisional conclusions as supported by the evidence cited:

- Human exposure to PM of ambient origin for individuals in a community is often highly correlated ($R^2 > 0.5$) in time with concentrations of PM of ambient origin of the same size as measured in that community.
- Longitudinal correlation coefficients for ambient concentrations of fine PM ($AD \leq 2.5$ μm) with personal exposures to ambient fine PM are greater than the corresponding correlations for the coarse fraction of ambient PM_{10} (2.5 μm $< AD \leq 10$ μm), as shown by studies of ambient sulfate concentrations and sulfate exposures.
- People in a community surrounding an ambient monitoring station, over time, are exposed to relatively similar mixtures and concentrations of ambient $PM_{2.5}$.
- People in a community are exposed to widely different mixtures and concentrations of non-ambient PM due to the diversity of smoking habits, personal activities such as hobbies, residential furnishings and appliances, and varying occupations.
- Exposures to PM of indoor origin appear to be uncorrelated with exposures to PM of ambient origin.
- The correlation of a single individual's sequence of daily personal exposures to total PM and ambient PM concentrations will be greater than the correlation that would occur had a different person been monitored on each of the same days (e.g., one person monitored consecutively for n days vs sequentially monitoring n different people, each for one day, over n days).
- Ambient PM in the U.S. has average annual correlations with the ambient gaseous pollutants CO, ozone, NO_2, and SO_2 of order $r = 0.25$ with a standard deviation of order 0.25.
- Although exposures to PM from indoor sources and occupational activities may not be correlated with ambient PM concentrations, these non-ambient PM species may possibly act as effect modifiers by making subjects more or less susceptible to exposure to PM of ambient origin.

- There are only limited data available, from non-probability samples, to evaluate how well the exposures to PM of ambient origin for susceptible subgroups correlate with the ambient PM concentrations of similar AD size range as measured in their community.

The newly available PM exposure information, overall, appears to further substantiate that ambient PM measurements (especially for fine PM) made at community monitoring sites likely index well personal human exposures (both outdoors and indoors) to PM of ambient origin. The community monitoring data, used as the main PM exposure indices in PM community epidemiology studies, is not highly correlated with human exposure to PM from indoor sources, making it unlikely that exposure to PM from indoor sources confound reported ambient PM-health effects associations.

1.3 DOSIMETRY

Key findings derived from the assessment of dosimetry information include:

- Particles may be deposited in (a) the extrathoracic airways (i.e., mouth, nose, and larynx); (b) in airways of the tracheobronchial region; and (c) in the alveolar region where gas exchange occurs. There are differences in deposition mechanisms and dose distribution in each of these areas that are dependent on particle size and airway geometry. Whereas, impaction is an important deposition mechanism in large extra- and intrathoracic airways at higher flows, sedimentation and diffusion are more important at low flow rates in smaller airways.
- Respiratory tract deposition patterns are dependent on particle size and distribution (as indicated by the mass median aerodynamic diameter and the geometric standard deviation) within the inspired air. Biologic effects may be a function not only of particle mass deposition but also of particle number or the total surface area of the particles.
- Various host factors have been shown to influence particle deposition patterns, including airway dimensions (size and shape), breathing pattern (flow and volume), and the presence of obstructive or inflammatory airway disease. Particle deposition in the extrathoracic region is highest during nasal breathing, and is greatest in small children and least in adults. Increased total ventilation and increased oral breathing leads to greater deposition of coarse particles in

the thoracic airways. Obstructive airway disease, such as asthma, emphysema, and chronic bronchitis, results in increased deposition of particles in the lower respiratory tract.

- Acute effects of PM are probably best related to deposited dose, whereas chronic effects may be related to cumulative or retained dose. Retention of particles is a function of deposition site, clearance of particles by macrophages or the mucociliary system, and particle characteristics, especially solubility. Chronic effects may also arise from recurring cycles of pulmonary injury and repair.
- There are substantial differences among laboratory animal species with regard to the inhalability of different sized particles as well as quantitative and qualitative differences in airway geometry and branching patterns.
- Extrathoracic deposition of ultrafine particles (<0.100 μm) is very high, despite their small size. Estimates of deposition range from 50% for oral breathing to >90% for nasal breathing. Enhanced deposition of both ultrafine and coarse particles occurs at branching points within the intrathoracic airways.
- Clearance is either absorptive (dissolution) or nonabsorptive (transport of intact particles). Deposited particles may be dissolved in body fluids, taken up by phagocytic cells, or transported by the mucociliary system. Retained particles tend to be small (<2.5 μm) and poorly soluble, e.g., silica, metals).
- Tracheobroncial clearance has both a fast and a slow component. Translocation of poorly soluble PM to the lymph lodes takes a few days and is more rapid for smaller (<2 μm) particles; elimination rates of these retained particles are on the order of years. People with COPD have increased particle retention and use cough to augment mucociliary clearance.
- In order to extrapolate experimental results between different species, a number of factors must be considered such as: airway size; airway branching asymmetry; inhalability; deposition; deposition/surface area, hot-spots; number deposition versus mass deposition; dose-response; and clearance retention (where and how long).
- Mathematical models are available to predict deposition, clearance, and retention of particles. Two models, the ICRP and NCRP, were extensively discussed in the 1996 PM AQCD.

1.4 PARTICULATE MATTER HEALTH EFFECTS

1.4.1 Epidemiology Findings

The epidemiology evidence about the health effects of ambient PM has expanded greatly since the 1996 PM Air Quality Criteria Document (PM AQCD). The most important enhancements in information include:

- New studies of health endpoints using ambient PM_{10} and closely related mass concentration indices such as PM_{13} and PM_7;
- New studies on a variety of endpoints have evaluated effects of the ambient coarse PM fraction ($PM_{10-2.5}$), the ambient fine particle fraction ($PM_{2.5}$), and even ambient ultrafine particle mass concentrations (PM_1 and smaller);
- New studies in which the relationship of some health endpoints to ambient particle number concentrations were evaluated;
- Additional studies which evaluated the sensitivity of estimated PM effects to the inclusion of gaseous co-pollutants in the model;
- Preliminary attempts to evaluate the effects of air pollutant combinations or mixtures including PM components, based on empirical combinations (factor analysis) or source profiles;
- New studies of infants and children as a potentially susceptible population;
- Further studies of cardiovascular endpoints associated with PM exposures;
- New studies on asthma and other respiratory conditions exacerbated by PM exposure.

This additional information does not yet allow for full resolution of all outstanding key issues in PM air pollution epidemiology. Table 1-1 presents provisional conclusions about alternative hypothesis that may affect the interpretation and synthesis of epidemiology study results. The authors conclude that multiplicity of findings about PM health effects suggest that exposure to ambient PM at current concentrations may cause serious adverse health effects, but that the quantitative magnitude of the effects depends on several environmental and biological factors whose role is not yet known. That is, current levels of ambient PM may be harmful to human health, but not necessarily equally harmful everywhere or at all times.

Some more specific provisional key findings emerging thus far from assessment of new epidemiology study results in this draft document are:

TABLE 1-1. PROVISIONAL CONCLUSIONS ABOUT ALTERNATIVE HYPOTHESES THAT MAY AFFECT THE SYNTHESIS OF EPIDEMIOLOGY STUDIES

Alternative hypotheses	Adverse health effects depend only on current ambient PM, independent of co-factors	Adverse health effects depend on current ambient PM and on environmental co-factors
Adverse health effects depend only on ambient PM size range at current PM concentrations	Not likely. Adverse health effects from coarse particles may occur at some sites, not others.	Possible. Adverse health effects from ambient PM are different in sites where ambient PM has different co-factors with same PM range.
Adverse health effects depend on ambient PM with specific physical properties or current ambient PM composition	Possible. Adverse health effects from ambient PM of a given size may be different in sites where PM has different physical properties or composition with same PM size range.	Probable. Adverse health effects from ambient PM are different in sites where PM has different physical properties, composition, or co-factors, even in the same ambient PM size range

- New studies suggest that infants and children may represent an additional subgroup at special risk for ambient PM exposure effects. The new results most clearly indicate that children appear to be susceptible to respiratory effects associated with ambient PM exposures, including exacerbation of asthma and respiratory symptoms in school-age children. A few studies also report ambient PM to be associated with intrauterine growth reduction and low birth weight (known infant health risk factors) and excess infant mortality. However, some studies found that PM is not as good a predictor of these endpoints as other pollutants (e.g., CO), and no toxicologic evidence has yet been advanced to support biological plausibility of such effects due to ambient PM or to identify pathophysiologic mechanisms involved.
- Cardiovascular causes of death and hospitalization in older adults may also be a significant component of PM-attributable mortality, as well as respiratory causes
- PM health effects have been reported to be associated with several different ambient PM size fractions (ultrafine, fine, coarse), but some health effects may be absent from some ambient PM mass fractions under some circumstances.
- PM health effects may occur at different time scales for exposure to PM_{10} or $PM_{2.5}$, from (a) short -term responses to daily exposure through (b) larger excess mortality associated with

medium term exposures (15 to 120 day averages) to (c) excess morbidity or mortality associated with long-term (multi-year) exposures.

- Adverse health effects attributable to $PM_{2.5}$ in short-term exposure studies are at times seriously confounded by exposure to gaseous co-pollutants making it difficult to estimate, quantitatively that portion of the risk attributable to: PM acting alone; PM acting in combination with gaseous co-pollutants; the gaseous co-pollutants *per se*; or the overall ambient pollutant mix.

1.4.2 Toxicologic Responses to PM in Animals and Humans

Data on the toxicology of PM are derived from controlled inhalation exposure studies of humans and animals, intratracheal instillation studies in humans and animals, occupational studies, and ex vivo studies of human and animal cells grown in culture. The human or animal populations (cells) studied vary by age, health status, or other host factors. Exposures vary by duration, mass or number concentration, chemical composition and size of the PM in addition to other exposure variables (e.g., temperature, humidity, activity levels, etc.). Responses to PM in the respiratory tract are dependent on the physiological status of the host as well as on translocation of PM or PM constituents to other sites. Ex vivo studies provide important additional information regarding the mechanism of action of PM or PM constituents on cells or cellular components.

Responses to acidic aerosols (sulfuric acid, sulfates, nitrates) have been comprehensively reviewed in previous documents. Much of the newly available research focuses on combustion-related PM such as concentrated ambient particles (CAPs) from urban air or various forms of fly ash PM.

- Acute exposures to metal particles can cause inflammatory responses in the respiratory tract of humans and animals. The effective exposure levels are typically much higher than ambient air metal concentrations in the U.S. atmosphere. Endotoxin, a lipopolysacharide associated with bacteria, causes inflammation in human occupational exposures at concentrations that are also much higher than in the ambient air.
- Combustion-related particles (fly ash and urban air particles) cause a spectrum of responses in the airways of animals. These include inflammation, cellular injury, and increased permeability. Metal components (V, Cu, Zn, Fe, Ni) of combustion particles have been

implicated in the responses, possibly related to oxidant production and release of intercellular signaling molecules (cytokines).

- Cells primed by inflammatory mediators show increased cytokine responses to PM. Combustion-related particles may cause increased oxidant production in in vitro systems, presumably related to metal components of particles. Combustion-related particles cause damage to cells in vitro. Responses include impaired macrophage phagocytosis and altered permeability.

Susceptibility

- Chemically or pharmacologically treated rat "models of cardiorespiratory disease" as well as older rats demonstrate increased pulmonary responses to combustion-related particles.
- Diesel particulate matter and oil fly ash (ROFA) may augment responses to antigens in allergic animals or humans. These studies provide a plausible mechanism for an association between combustion PM exposure and exacerbation of asthma.
- Inhaled or instilled particles can have systemic effects, especially on the cardiovascular system which in certain circumstances can be lethal.

Mixtures

- Mixtures of ozone and PM (urban PM, sulfate aerosols, ultrafine carbon) may cause enhanced effects on lung cells, increased inflammation, and decrements in human lung function.

Mechanisms

- A number of studies indicate that reactive oxidant species (ROS) play a role in PM-induced responses. Catalysis of ROS is likely related to soluble metals in PM.
- ROFA and urban PM can induce apoptosis (programmed cell death) of human alveolar macrophages.
- Studies on ultrafine compared to fine particles indicate a greater response to ultrafines in terms of airway inflammation, an effect that appears to be related to their greater surface area.

1.4.3 Population Groups at Risk

Susceptibility can be affected by factors which influence dosimetry or the response of tissues to particle burdens. Host factors that may increase the susceptibility to PM include both changes in physiologic factors affecting respiratory tract deposition and pathophysiologic factors affecting response.

- Susceptible groups most clearly at special risk for PM effects include the elderly and those with cardiopulmonary disease, based on available epidemiology findings.
- Epidemiology findings indicate that risk of mortality and morbidity due to lower respiratory disease (e.g. pneumonia) is increased by ambient PM exposure. This may be due to exacerbation, by PM, of already existing respiratory disease. PM may also increase susceptibility to infectious disease by decreasing clearance, impairing macrophage function, or through other specific and nonspecific effects on the immune system. The epidemiologic findings also indicate that individuals with preexisting infectious respiratory disease (e.g., pneumonia) are at increased risk for PM effects.
- Epidemiologic findings indicate that ambient PM exposures are also associated with increased risk for mortality and hospitalization due to cardiovascular causes. Cardiac arrhythmia has been hypothesized as being involved in mortality due to acute PM exposure.
- Studies of infants and children indicate that they are a potentially susceptible population. Panel studies on asthma and other respiratory conditions show exacerbation by PM exposure. Children are susceptible to respiratory effects associated with PM exposure from pre-natal and post-natal effects through exacerbation of asthma and respiratory symptoms in school age children.

1.5 ENVIRONMENTAL EFFECTS

1.5.1 Vegetation and Ecosystem

- Human existence on this planet depends on the life-support service that ecosystems provide. Ecosystem structure and function play an essential role in providing two types of benefits to society. From the structural aspects (biodiversity, abundance, mass and arrangement of species), an ecosystem provides: (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.

- Ecosystems maintain clean water, pure air, a green earth, and a balance of creatures, the functions that enable humans to survive. The benefits they impart include absorption and breakdown of pollutants, cycling of nutrients, binding of soil, degradation of organic waste, maintenance of a balance of gases in the air, regulation of radiation balance, climate, and the fixation of solar energy.
- Concern has risen in recent years concerning the integrity of ecosystems because there are few ecosystems on planet earth today that are not influenced by humans. For this reason, understanding the effects of PM deposition and its impact on vegetation and ecosystems is of prime importance.
- The criteria pollutant presently defined as PM_{10} has no particular relevance to particulate effects on vegetation for which chemical composition is more relevant than mass. The PM whose effects on vegetation are considered in this chapter is not a single pollutant, but a heterogeneous mixture of particles of differing in size, origin, and chemical constituents. Exposure to a given mass concentration of PM_{10} may, depending on the particular mix of deposited particles, lead to widely differing phytotoxic responses. This variable has not been adequately characterized.
- 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. The range of particle sizes, the variety of chemical constituents in airborne PM, and the diversity of canopy surfaces, 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.

- Emphasis in this chapter has been placed on the effects of PM on natural plants and terrestrial ecosystems. Neither nitrate or sulfate deposition on crops is discussed as they are frequently added in fertilizers. Except for nitrogen and sulfur-containing compounds and their effects in acidic precipitation, information concerning the effects of PM on crops is not readily available.
- Particulate matter when transferred from the atmosphere to plant surfaces may cause direct effects when they (1) reside on the leaf, twig or bark surface for an extended period; (2) are taken up through the leaf surface; or indirect effects when (3) removed from the plant via suspension to the atmosphere, washing by rainfall, or by litter-fall with subsequent transfer to the soil.
- Deposition of PM on above-ground plant parts can have either a physical and or chemical impact, or both. The effects of "inert" PM are mainly physical, while 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 deposited particles and are usually of more importance than any physical effects. 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 would typically be experienced in the ambient environment.
- 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, iron, lead, and various smelting factories. Indirect impacts are usually the most significant because they can alter nutrient cycling in the soil and inhibit plant uptake of nutrients.
- Most PM deposited on vegetation eventually enters the soil environment which is one of the most dynamic sites of biological interaction in nature. The impact of particulate deposition on plants results from changes in the soil environment and plant nutrient uptake. These changes determine plant and ecosystem response.
- Bacteria and fungi in the soil have an important role in plant nutrition. Bacteria 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 the

uptake of mineral nutrients. The impact of nitrates, sulfates and metals in PM is determined by their affect on the growth and functions of the bacteria and fungi involved in making nutrients available for plant uptake.

- The major impact of PM on ecosystems is indirect and occurs in the soil through the deposition of nitrates and sulfates and the acidifying effects of the H+ ion associated with these compounds in wet and dry deposition.
- Intensive research over nearly a decade indicates that although the soils of most North American forests are nitrogen limited, there are forests that exhibit symptoms of excess nitrogen. Nitrogen saturation results in a progressive syndrome of concurrent responses to long-term, chronic nitrogen deposition. As nitrogen reaches saturation in temperate-zone forests, there is decrease in nitrogen mineralization and an increase in the trends of foliar Mg:N and Ca:Al ratios. Preliminary evidence suggests some forests may decline in productivity and experience greater mortality as a result of chronic nitrogen deposition.
- Increases in soil nitrogen plays a selective role. Plant succession patterns and biodiversity in some ecosystems are significantly affected by chronic nitrogen additions. 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. Studies also 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 has resulted in nitrophilous grass species replacing slower growing heath species. Over the past several decades the composition of plants in the forest herb layers 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.
- The effects of excessive deposition of nitrogen, particularly NH_3 and NH_4^+ ,deposition have lead to changes in Dutch heathlands via: (1) acidification of the soil and the loss of cations of K^+, Ca^{2+} and Mg^{2+}; and (2) nitrogen enrichment which results in increased plant growth rates and altered competitive relationships. Alteration of any of a number of parameters (e.g., increased nitrogen) can alter ecosystem structure and function.
- There is a major concern that soil acidification will result in nutrient deficiency. Growth of tree species can be affected when high aluminum to nutrient ratios limit uptake of calcium and magnesium. Calcium is essential in the formation of wood and the maintenance of cells, the

primary plant tissues necessary for tree growth. Calcium must be dissolved in the soil water to be taken up by plants. A major concern is that soil acidity will lead to nutrient deficiency. Acid deposition can increase the aluminum concentrations in soil water by lowering the pH in aluminum-rich soils through dissolution and ion-exchange processes. Aluminum in soil can 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 high Ca/Al ratios impair Ca and Mg uptake.

1.5.2 Particulate Matter-Related Effects on Materials

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

- The natural process of metal corrosion from exposure to environmental elements (wind, moisture, sun, temperature fluctuations, etc.) is enhanced by exposure to anthropogenic pollutants, in particular SO_2.
- Dry deposition of SO_2 enhances the effects of environmental elements on calcereous stones (limestone, marble, and carbonated cemented) by converting the calcium carbonate (calcite) in the stone to calcium sulphate dihydrate (gypsum). The rate of deterioration is determined by the SO_2 concentration, the stone's permeability and moisture content, and the deposition rate.
- Sulfur dioxide limits the life expectancy of paints by causing discoloration, loss of gloss, and loss of thickness of the paint film layer.
- A significant detrimental effect of particulate pollution is the soiling of painted surfaces and other building materials. Soiling is a degradation process requiring remediation by cleaning or washing, and depending on the soiled surface, repainting. Soiling decreases the reflectance of a material and reduces the transmission of light through transparent materials. Soiling may reduce the life usefulness of the material soiled.

1.5.3 Particulate Matter-Related Effects on Visibility

Visibility is the degree to which the atmosphere is transparent to visible light and the clarity (transparency) and the color fidelity of the atmosphere. The farthest distance at which a large black object can be distinquished against the horizontal sky is the visual range. For regulatory purposes, visibility impairment, any humanly perceptible change in visibility (light extinction, visual range, contrast, coloration), is classified into two principal forms: “reasonably attributable” impairment, attributable to a single source/small group of sources, and 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 (the sum of the light scattering coefficient and light absorption coefficient) and parameters related to the light-extinction coefficient (visual range and deciview scale), the light scattering coefficient, and fine particulate matter concentrations.
- Light scattering by gases is the major component of light extinction. Light absorption by gases is almost entirely due to NO_2, and is typically significant only near NO_2 sources. Light absorption by particles is primarily caused by elemental carbon.
- Visibility impairment or haziness is often associated with fine mass concentrations. Visibility impairment or haziness is greatest in the eastern United States and southern California. Haziness in the southeastern United States, caused by increased atmospheric sulfate, has increased by approximately 80% since the 1950s and is greatest in the summer months, followed by the spring and fall, and winter.
- 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. Nitrates account for 10 to 20% of the total extinction in other areas of the United States.
- 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 transported from southern California and the subtropics have contributed to regional haze in the Grand Canyon and other class I areas in the southwestern United States.
- Organics are the second largest contributors to light extinction in most areas in the United States. Organic carbon is the greatest cause of light extinction in the Pacific Northwest, Oregon, Idaho, and Montana, accounting for 40 to 45% of the total extinction. Organic carbon contributes between 15 to 20% to the total extinction in most of the western United States and 20 to 30% in the remaining areas of the United States.
- Light absorption by carbon is relatively insignificant but is highest in the Pacific Northwest (up to 15%) and in the eastern United States (3%).

1.5.4 Environmental and Economic Impacts of PM

- The four important categories of environmental costs and benefits of PM are: agriculture and forestry, cleaning and materials damage, visibility, and ecosystem functions. EPA has developed and applied cost methodologies to these cost categories in great detail, and its procedures have passed a number of scientific reviews.
- Any given level of particulate matter will be associated with resulting environmental effects that potentially have economic significance. Examples include the level of crop damage or visibility impairment that result from specified levels of PM. Defining the welfare effects of PM changes requires that baseline levels of effects be defined.
- Estimating benefits for visibility and for ecosystem services is a more difficult and less precise exercise because the effects are not valued in markets.
- Once endpoints reflecting physical and biological outcomes have been defined, several economic methods may be used to estimate economic damages. Some of the results of existing research were summarized for the major categories of endpoints.
- The measured economic costs of PM are particularly significant for reduced visibility, both in residential areas and in recreational areas with special value (e.g., the National Parks).
- It is possible that the costs imposed on ecosystems are significant as well. Making progress on measuring these ecosystem costs depends on improvements in linking environmental endpoints

to PM levels, and then on using these endpoints as a basis for improved techniques to elicit willingness to pay for changes in ecosystem quality.

2. INTRODUCTION

This document is an update of "Air Quality Criteria for Particulate Matter" published by the United States 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 thorough evaluation of that information most relevant to PM NAAQS criteria development, based on pertinent literature available through mid-1999. 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.

2.1 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 Administrator of the U.S. Environmental Protection Agency (EPA) 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

Administrator must consider available information to set secondary NAAQS that are based on the criteria and are requisite to protect the 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, weather, visibility, 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) of the CAA requires periodic review and, if appropriate, revision of existing criteria and standards. Also, an independent committee of non-EPA experts, the Clean Air Scientific Advisory Committee (CASAC), is to provide the EPA Administrator advice and recommendations regarding the scientific soundness and appropriateness of criteria and NAAQS for PM and other "criteria air pollutants."

2.2 HISTORY OF PREVIOUS PM CRITERIA/STANDARDS REVIEWS

On April 30, 1971 (Federal Register, 1971), EPA promulgated the original primary and secondary NAAQS for particulate matter (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 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 U.S. PM NAAQS. The primary standards for PM (measured as TSP) were 260 $\mu g/m^3$ (24-h average) not to be exceeded more than once per year, and 75 $\mu g/m^3$ (annual geometric mean). The secondary standard (measured as TSP) was 150 $\mu g/m^3$ (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 with notice of a final decision to revise the existing standards published in the Federal Register (Federal Register, 1987). In that decision, EPA changed the indicator for PM from TSP to PM_{10}. PM_{10} refers to particles with an upper 50% cut point of 10 μm aerodynamic diameter. Identical primary and secondary PM_{10} standards were set for two averaging times: 150 $\mu g/m^3$ (24-h ave.) with no more than one expected exceedance per year; and 50 $\mu g/m^3$ (expected annual arithmetic mean) averaged over 3 years.

2.2.1 The 1997 PM NAAQS 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, 1994), 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's 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 were then 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 U.S. EPA's Office of Air Quality Planning and Standards (OAQPS) and drawing upon 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 proposal for revision of the PM NAAQS. Taking into account information and assessments presented in the PM AQCD and the Staff Paper, 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 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 $\mu g/m^3$, with fractional parts of 0.05 or greater rounding up.

(3) 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 $\mu g/m^3$, with fractional parts of 0.5 or greater rounding up.

(4) The form of the 24-h PM_{10} (150 $\mu g/m^3$) 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 $\mu g/m^3$, 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 $\mu g/m^3$, 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 their chemical and physical properties, including behavior in the atmosphere. Detailed discussions of atmospheric formation, ambient concentrations, and health and welfare effects of PM, as well as quantitative estimates of human health risks associated with exposure to PM, can be found in the 1996 PM AQCD and in the 1996 OAQPS Staff Paper (U.S. Environmental Protection Agency, 1996b).

2.2.2 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) was also 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 emerging scientific information, which forms the criteria upon 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 plan. These PM research plans are outlined in the following section. 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.

PM Research Program

The EPA has broadened its ongoing PM research activities by developing, in partnership with other Federal agencies, a coordinated interagency PM research program. This interagency program will contribute to expanding scientific knowledge of PM health effects, as well as the development of improved monitoring methods and cost-effective mitigation strategies. The interagency effort is also promoting further coordination with other research organizations including 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. Workshops and the availability of relevant documentation are being announced in the Federal Register.

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 recently in 1999 (National Research Council, 1999).

The EPA's 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, will advance the scientific and technical bases for future decisions on the PM NAAQS and for the implementation of PM monitoring and control efforts.

2.3 CURRENT PM CRITERIA AND NAAQS REVIEW

2.3.1 Criteria Review Plans and Schedule

The EPA's plans for this current review of PM criteria are outlined in Table 2-1 below, together with target dates for key milestones. As with all NAAQS reviews, the purpose is to update the criteria and to determine whether it is appropriate to revise the standards in light of new scientific and technical information. Although the EPA concluded in its recent final rule on

TABLE 2-1. SCHEDULE FOR DEVELOPMENT OF THE CURRENT REVISED PARTICULATE MATTER AIR QUALITY CRITERIA DOCUMENT (PM AQCD)

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

Source: Modified from Federal Register (1997c).

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 $PM_{2.5}$, the EPA will continue to sponsor research to address these uncertainties even as this criteria review progresses as per Table 2-1.

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 Division. The development of the document has and will continue to involve substantial external peer review through public workshops involving the general aerosol scientific community, through iterative reviews of successive drafts by CASAC, and through 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. The schedule for this review will allow for consideration of relevant new peer-reviewed scientific studies published or accepted for publication from early 1996 (when the previous PM AQCD was completed) through mid-2000.

After the December 1999 CASAC meeting noted above in Table 2-1, EPA's Office of Air Quality Planning and Standards (OAQPS) will also start to prepare a Staff Paper (SP) for the Administrator, drawing on information in the newly revised PM AQCD. The SP will evaluate the 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 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 will also 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 to be promulgated by July 2002.

2.3.2 Methods and Procedures for Document Preparation

The procedures followed for developing this revised PM AQCD build on the knowledge and methods derived from the last PM, ozone, and CO AQCD preparation efforts. Briefly, the respective responsibilities for production of the present PM AQCD are as follows. An NCEA-RTP team has been appointed to be responsible for developing and implementing the project plan for preparation of the PM AQCD and inputs from individuals in other EPA program and policy offices identified as part of the EPA PM Work Group have been obtained. The resulting project 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, and 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 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. Draft 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 have been incorporated into this First External Review Draft of the PM AQCD now being released for public comment and CASAC review. Necessary revisions will be made on the basis of the public comments, CASAC recommendations, and newly emerging research results before a further Second External Review will be released in mid-2000 for public comment and CASAC review (Fall 2000). The final version of the newly revised PM AQCD will incorporate changes made in response to public comments and CASAC review of that Second External Review Draft.

New research results are being incorporated into this document as they become available. In order to foster presentation and publication of any new research findings not published during 1999, NCEA-RTP is working with the Air and Waste Management Association (AWMA) to hold an International Speciality Conference, entitled PM 2000: Particulate Matter and Health, in late January 2000, in Charleston, SC. The conference is being co-sponsored in cooperation with one or more government agencies or private organizations that also fund PM research. Topics to be covered will include 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 will be to facilitate having the latest scientific information available for incorporation into the final draft of the revised U.S. EPA PM Air Quality Criteria Document (AQCD) in time for the anticipated final CASAC review of the draft PM AQCD projected for Fall 2000. Arrangements will be made for PM 2000 presenters to submit written manuscripts at the conference and to have professional societies/journals prepared to expedite processing of the submitted papers through their peer-review processes, so that decisions on acceptance for publication can be made by April/May 2000. Given that extensive additional information is expected to be published during the next 6 to 9 mo as a result of the PM 2000 conference and elsewhere, the evaluations and findings set forth in this draft of the revised PM AQCD, overall, must be considered only provisional at this time.

2.3.3 Approach

The approach to organization and content of this revised PM AQCD is somewhat different from those used for previous criteria documents. Since the recent 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 data base has continued to evolve rapidly.

Detailed review of key new research was undertaken as an initial 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.

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 Project Team and through input from other EPA program and policy offices. Development of issue topics started with the last AQCD, staff paper, CASAC and public reviews, EPA's PM Research Needs Document, and from the standard promulgation process. Further identification and clarification of issues resulted from the National Research Council (NRC) review and report 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 has also played an important role in issue identification.

To aid in development of a concise document, compilation of summary tables of the relevant published literature and selective discussion of the literature was undertaken. Building on the previous PM AQCD, most of the scientific information selected for review and discussion in the text was from the literature published since completion of the previous PM AQCD (U.S. Environmental Protection Agency, 1996a).

2.3.4 Key Issues of Concern

Summarized below are several broad topics related to the main issues of concern to be addressed by this revised PM AQCD. 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}, $PM_{10\text{-}2.5}$, $PM_{2.5}$, and ultrafine particles. Chemical components include transition metals, acidity, sulphates, 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 due to coexposure to other pollutants such as O_3, SO_2, and CO and meterological factors.
   - Uncertainties due to confounding in epidemiologic studies (e.g., economic factors, demographic and lifestyle attributes, genetic susceptibility factors, occupational exposure, and 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-analysis.
3. *Biological Mechanisms of Action.* Evaluate data examining mechanisms for health outcomes of PM. Mechanistic information aids judgement 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 have also 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 (CAPs) studies. Newly available information will be examined from toxicology studies using devices which 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 may potentially 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 recently studied and provide evidence of increased deposition associated with lung disease.
   - Animal models of lung disease exposed to PM constituents suggest a role for PM in cardiac death.
5. *Environmental Effects.* Evaluation of 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 surface and for climate change.
6. *Background Information Topics Useful in Evaluating Health Risks.* Topics include:
   - 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 $PM_{10-2.5}$

- New data patterns of daily and annual concentrations for $PM_{2.5}$, $PM_{10-2.5}$, and PM_{10}

2.4 DOCUMENT CONTENT AND ORGANIZATION

The present document critically reviews and assesses relevant scientific literature on PM through mid-1999. 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) is generally 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 discussed in the text and presented in tables as well. Reports of lesser importance for the purposes of this document are typically only summarized in tables.

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 and 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, documentation of a previously unreported effect or mechanism. In reviewing and summarizing the literature, an attempt is made to present alternative points of view where scientific controversy exists.

The present document consists of 9 chapters. The Executive Summary for the entire document is contained in Chapter 1, followed by this general introduction in Chapter 2. Chapters 3 through 5 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 and factors affecting exposure of the general population. Chapters 6 through 8 evaluate information concerning the health effects of PM. Chapter 6 discusses epidemiological studies, and Chapter 7 discusses dosimetry of inhaled particles in the respiratory tract information on the toxicology of specific types of PM constituents, including laboratory animal studies and controlled human exposure studies. Chapter 8 integrates key information on exposure, dosimetry, and critical health risk issues derived from studies reviewed in the prior chapters. Lastly, Chapter 9 describes PM environmental effects on: vegetation and ecosystems; visibility; manmade materials; and climate, as well as economic impacts of such welfare effects.

Neither control techniques nor control strategies for the abatement of PM are discussed in this document, although some topics covered may be incidentally relevant to abatement strategies. Technologies for controlling PM emissions are discussed in other documents issued by EPA's Office of Air Quality Planning and Standards (OAQPS). Likewise, 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 OAQPS.

In addition, certain issues of direct relevance to standard setting are not explicitly addressed in this document, but are instead 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 summarized in the PM Staff Paper to be prepared by OAQPS and reviewed 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 Administrator, as mandated by the Clean Air Act.

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, such as information on estimated exposure, activity patterns, and personal habits. Such information is typically addressed in the Staff Paper developed by OAQPS.

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3. 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 Air Quality Criteria for Particulate Matter (AQC PM 96) (U.S. Environmental Protection Agency, 1996). Section 3.1 of this new version of the Air Quality Criteria for Particulate Matter 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 will be discussed. Emphasis will be placed on the differences between fine and coarse particles and the differences between the nuclei mode and the accumulation mode within fine particles.

Chapter 4 of the AQC PM 96 (U.S. Environmental Protection Agency, 1996) contained a review of the state-of-the-art of PM measurement technology. Since that time there has been considerable progress in understanding problems and errors in the measurement of PM mass, chemical composition, and physical parameters. There has also been some progress in developing new and improved measurement techniques. Therefore, a more extensive survey on measurement errors and newly developed measurement techniques is included in Section 3.2. For more detail and older references the reader is referred to Chapter 3 and 4 of the AQC PM 96 (U.S. Environmental Protection Agency, 1996).

3.1 PHYSICS AND CHEMISTRY OF PARTICULATE MATTER

3.1.1 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 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.

The composition and behavior of airborne particles are fundamentally linked with those of the surrounding gas. Aerosol is 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 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. Number size distributions are often 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 by 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 particles 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 closer to reality.

3.1.2 Physical Properties and Processes

3.1.2.1 Definitions of Particle Diameter

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, atmospheric particles often are not spherical. Therefore, their diameters are often described by an “equivalent” diameter, i.e., that of a unit density sphere which 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 particle density and is defined as the diameter of a spherical particle with equal settling velocity but a material 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), and Seinfeld and Pandis (1998).

3.1.2.2 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 aerodynamic diameter. 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. Size distribution studies using impactors give direct measurements of the aerodynamic diameter. The diameter of atmospheric particles range from 1 nanometer to 100 μ meters, 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 are usually given as geometric 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 .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, in future discussions, particle diameters, unless otherwise indicated, will be understood to refer to the aerodynamic diameter.

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 are often 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 $\log(D_p + \Delta D_p)$. It is not proper formally to take the logarithm of a dimensional quantity. However, one can think of the distribution as a function of $\log(D_p/D_{p0})$, where the reference diameter $D_{p0} = 1\ \mu m$ 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 3-1, 2, and 3 (Whitby, 1978; Whitby and Sverdrup, 1980). Figure 3-1 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 3-2. Figure 3-3 show 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, while most of the particle volume (and therefore most of the mass) is found in particles > 0.1 μm. The surface area peaks around 0.1 μm.

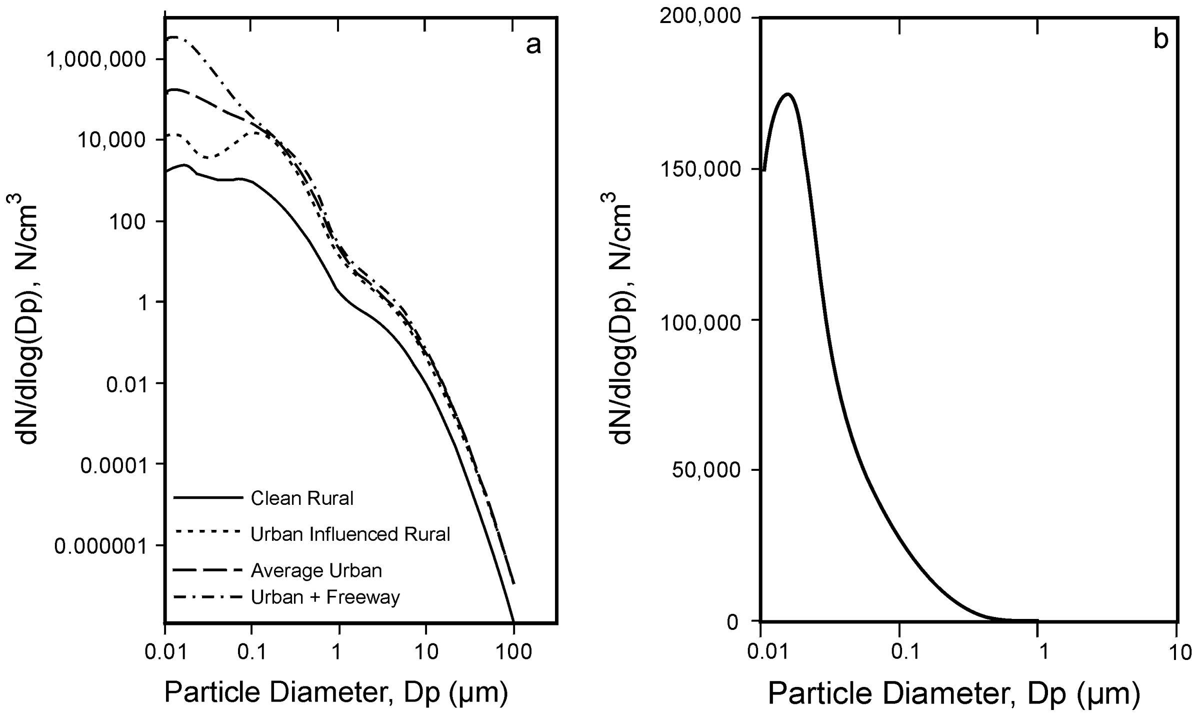

Figure 3-1. Number of particles as a function of particle diameter: (a) number concentrations are shown on a logarithmic scale to display the wide range by site and size; (b) number concentrations for the average urban distribution are shown on a linear scale for which the area under any part of the curve is proportional to particle number in that size range.

Source: Whitby and Sverdrup (1980).

An important feature of the mass or volume size distributions of atmospheric aerosol 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 1.0 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: nuclei, accumulation, and coarse. The three modes are most apparent in the freeway-influenced size distribution of Figure 3-2b and in the surface area distribution of Figure 3-3b. However, the nuclei mode, corresponding to particles below about 0.1 μm, may not be noticeable in volume or

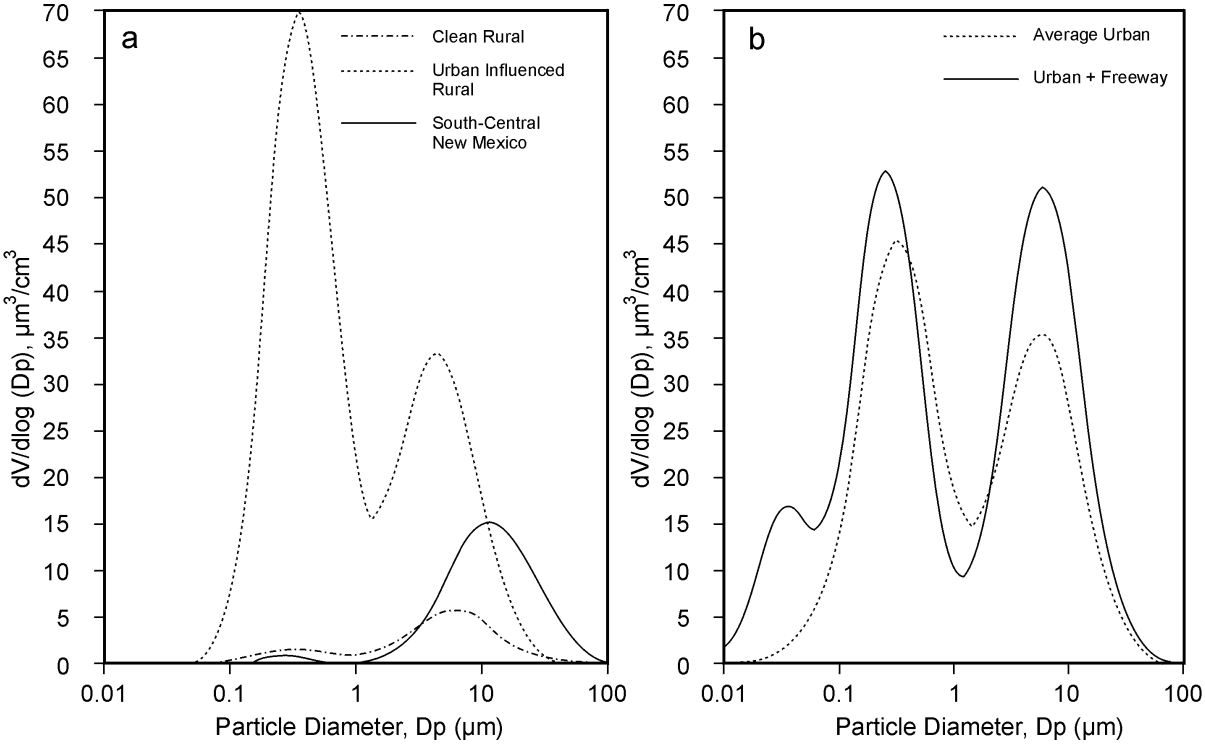

Figure 3-2. Particle volume distribution as a function of particle diameter: (a) for the averaged rural and urban-influenced rural number distributions shown in Figure 3-1 and a distribution from south central New Mexico, and (b) for the averaged urban and freeway-influenced urban number distributions shown in Figure 3-1.

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

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 see in arithmetic plots (Figures 3-1b and 3-3a) but can be seen in a logarithmic plot (Figure 3-1b). 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

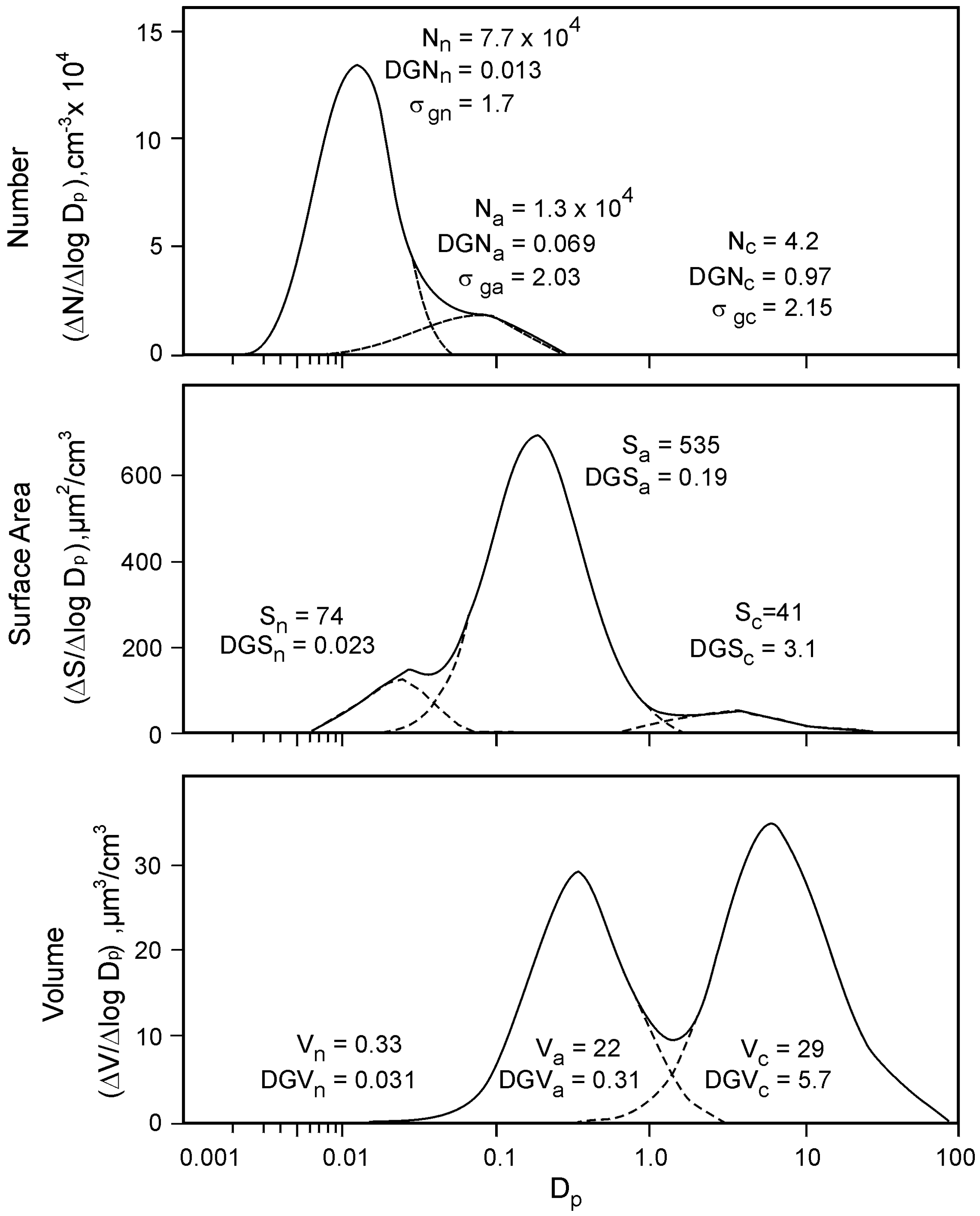

Figure 3-3. Distribution of coarse (c), accumulation (a), and nuclei or ultrafine (n), mode particles by three characteristics, volume (V), surface area (S), and number (N) for the grand average continental size distribution. DGV = geometric mean diameter by volume; DGS = geometric mean diameter by surface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

Source: Whitby (1978).

of western and midwestern locations during the 1970's (Whitby, 1978; Whitby and Sverdrup, 1980). No size-distribution studies of similar scope have been published since then. Newer results from particle counting techniques and impactor, size-segregation studies, including data from Europe (U.S. Environmental Protection Agency, 1996) and Australia (Keywood et al., 1999), show similar results.

Definitions of Particle Size Fractions

In the preceding discussion several subdivisions of the aerosol size distribution were identified. 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; (3) occupational 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 3-3. 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 3-4). 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 distribution, which generally occurs between 1 and 3 μm. These particles are usually mechanically generated.
>
> *Fine Mode:* The distribution of particles with diameters mostly smaller than the minimum in the particle mass distribution, which generally occurs between 1 μm 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 fraction 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 use ultrafine to refer to particles, generated in the laboratory, which are 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.

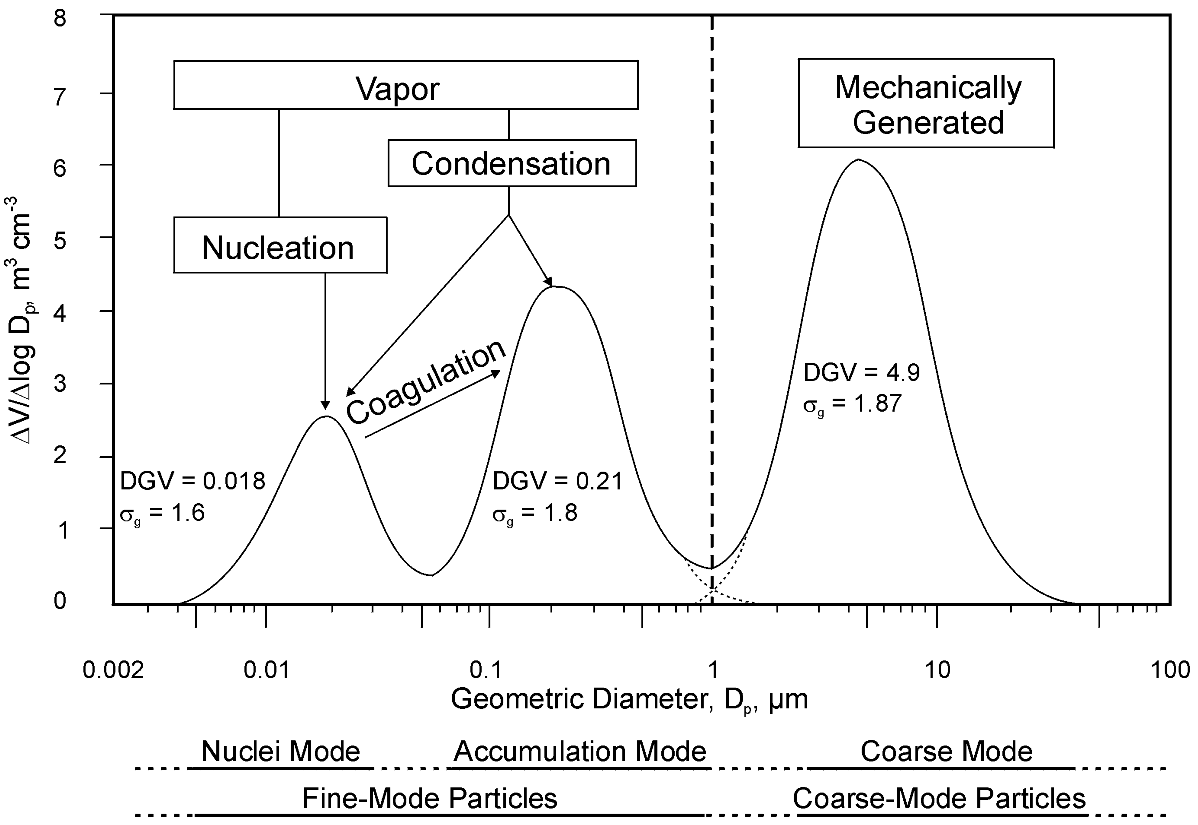

Figure 3-4. **Volume size distribution, measured in traffic, showing fine-mode and coarse-mode particles and the nuclei and accumulation modes within the fine particle mode. DGV (geometric mean diameter by volume, equivalent to volume median diameter) and σ_g (geometric standard deviation) are shown for each mode. Also shown are transformation and growth mechanisms (e.g., nucleation, condensation, and coagulation).**

Source: Adapted from Wilson and Suh (1997).

> *Accumulation Mode*: That portion of the fine particle fraction 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 3-4 and 3-5.

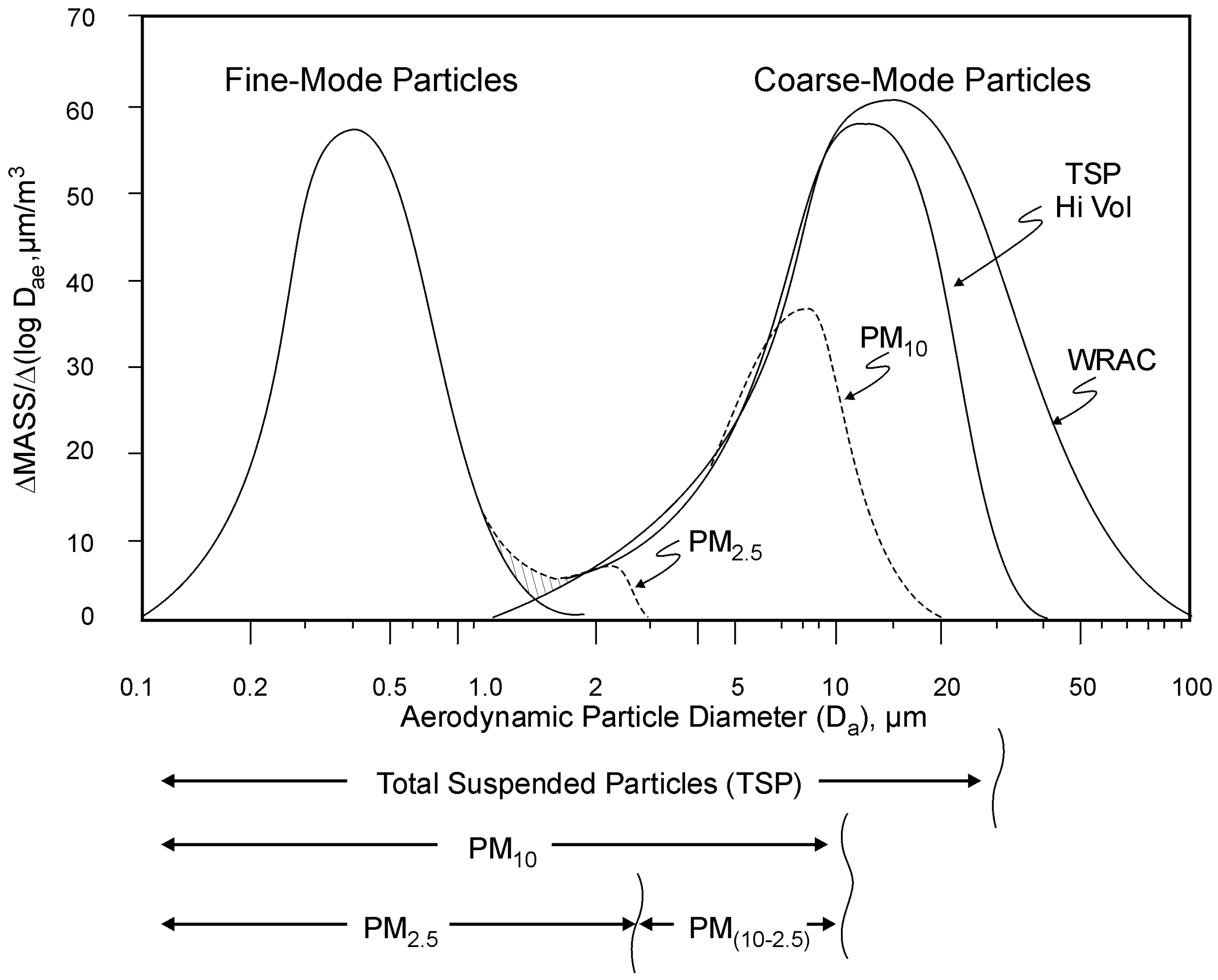

Figure 3-5. An idealized distribution of ambient particulate matter showing fine-mode particles and coarse-mode particles and the fractions collected by size-selective samplers.

Source: Adapted from Wilson and Suh (1997).

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. 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 have also been used.

Occupational Health 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 3-6.

Regulatory Size Cuts. In 1987, the NAAQS for PM were revised to use PM_{10}, rather than 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. 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

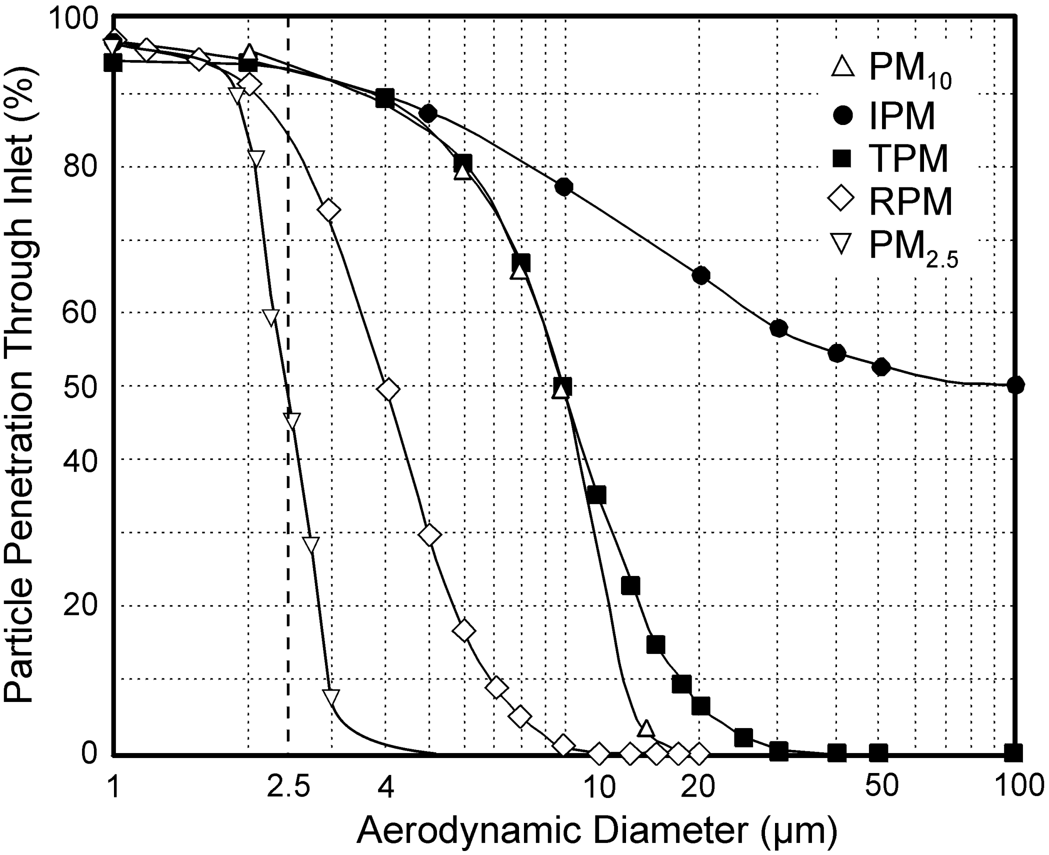

Figure 3-6. Specified particle penetration (size-cut curves) through an ideal (no-particle-loss) inlet for five different size-selective sampling criteria. PM $_{10}$ is defined in the Code of Federal Regulations (1991). PM $_{2.5}$ is also defined in the Federal Register (1997). Size-cut curves for 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).

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 PM$_{2.5}$ standard will increase regulatory concern with the sources of fine-mode particles.

Prior to 1997, the indicator for the NAAQS for PM was total suspended particulate matter (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. Heroic measures, such as those undertaken with the Wide Range Aerosol Classifier (WRAC), are required 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 3-5. 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 3-6.

An example of a $PM_{2.5}$ size-cut curve is also shown in Figure 3-6. 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, 1997a). Additional performance specifications are given in 40 CFR Parts 53 and 58 (Code of Federal Regulations, 1997b). 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). While these explanations may seen easier than (upper 50% cut point of x μm aerodynamic diameter), they are incorrect and misleading since they suggest an upper 100% cut point of x μm. This is illustrated in Figure 3-7 which shows the penetration cure 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.

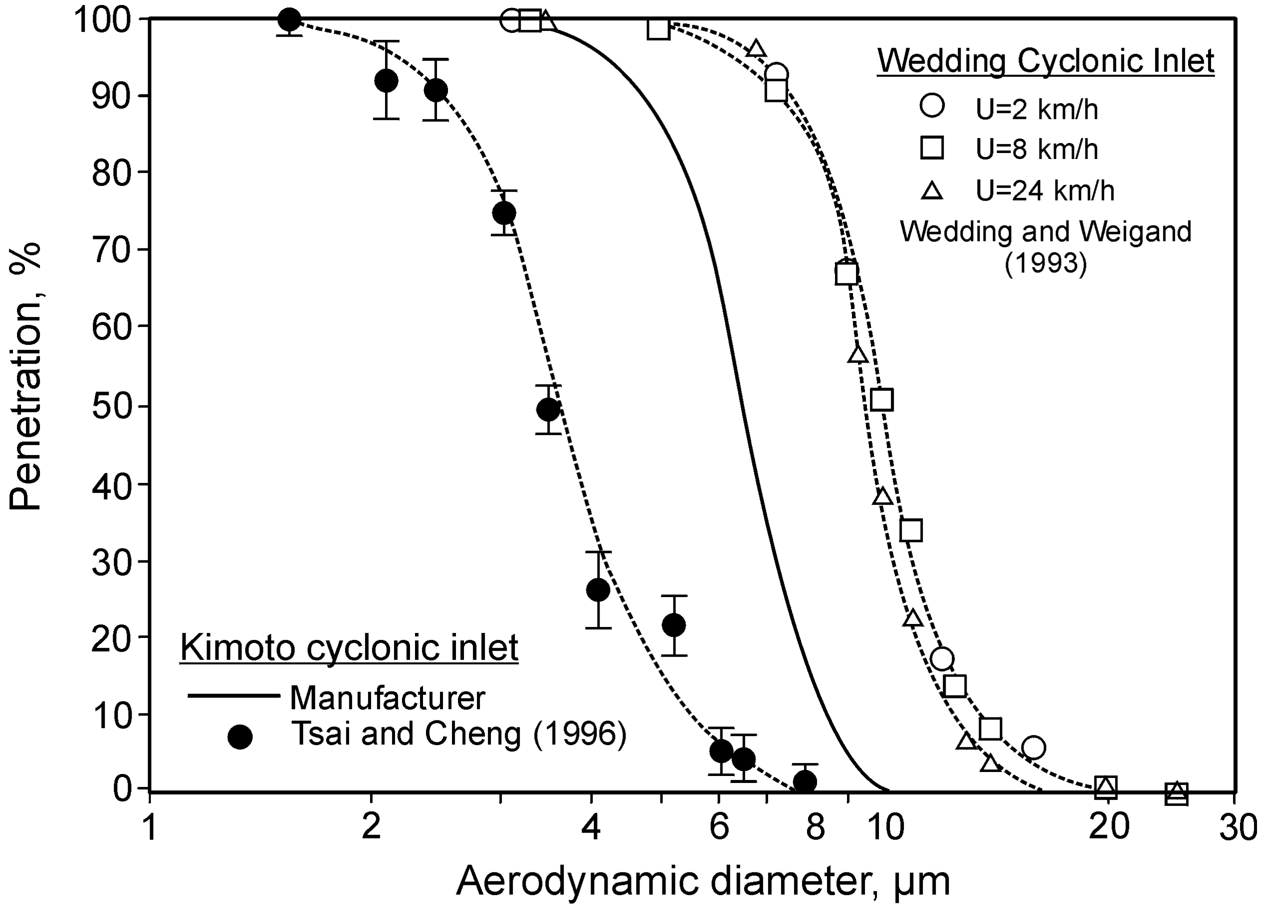

Figure 3-7. Comparison of penetration curves for two PM_{10} beta gauge samplers using cyclone inlets. The Wedding PM_{10} sampler uses the U.S. EPA definition of PM_x as x = 50% cut point. The Kimoto PM_{10} defines PM_x as x = the 100% cut point (or zero penetration).

Source: Tsai and Cheng (1996).

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, while 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 (since it contains some coarse-mode particles), $PM_{(10-2.5)}$ an indicator of the thoracic component of coarse-mode particles (since 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 3-6, 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}.

3.1.2.3 Nuclei-Mode Particles

Some further discussion of nuclei-mode particles is justified because of their possible health importance. The current $PM_{2.5}$ standard is based largely on the statistical association of health outcomes with particle mass. A recent epidemiologic study in Erfurt, Germany (Peters et al., 1997) found a better statistical association of asthma with particle number than with $PM_{2.5}$. Toxicologic studies (Oberdörster et al., 1992, 1994; Li et al., 1997; Lison et al., 1997) suggest that nuclei-size particles (diameter <about 0.1 μm) may be more toxic (on a $\mu g/m^3$ basis) than larger particles of identical composition. Recent studies by Oberdörster et al. (1995, 1999) suggest that some health outcomes may correlate better with particle surface area than with particle number or particle mass. The toxicologic studies did not use atmospheric particles. However, since nuclei-mode particles contribute the major portion of particle number and a significant portion of particle surface area, some further attention to nuclei 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 may also grow by coagulation as two particles combine to form one. Gas phase material condenses preferential 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 3-4). More information and references on formation and growth of fine particles may be found in the AQC PM 1966 (U.S. Environmental Protection Agency, 1966).

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.

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 can also be observed in cleaner, remote regions. Bursts of new particle formation in the atmosphere under clean conditions correspond to low aerosol surface area concentrations (Covert et al., 1992). High concentrations of nuclei mode particles can occur in regions corresponding to 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 which 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 may also 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 6.9 of the AQC PM 96 (U.S. Environmental Protection Agency, 1996)

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

(3) *Sulfates.* 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).

(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. Since 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 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 a decrease in the concentration of nuclei-mode particles. 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, 1996).

Since preliminary studies of the effects of ultrafine particles suggest the potential for enhanced toxicity of this size range, further research in this area is important. 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. 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.

3.1.3 Chemistry of Atmospheric PM

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, references, and the composition of PM, measured in a large number of studies in the U.S., may be found in AQC PM 96 (U.S. Environmental Protection

Agency, 1996). The composition and concentrations of PM are discussed in Chapter 4 of this document.

3.1.3.1 Chemical Composition and Its Dependence on Particle Size

Studies conducted in most parts of the U.S. 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 is also 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 pre-existing coarse particles.

3.1.3.2 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 which rapidly condense to form particles. This includes soot from diesel engines as well as compounds of As, Se, Zn, etc., condensed 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, 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.

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 is also 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., $SO_2 + 2NaCl + H_2O \rightarrow Na_2SO_3 + 2HCl\uparrow$.

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.

Formation of Secondary Organic PM

Atmospheric reactions, involving volatile organic compounds such as alkenes, aromatics, and terpenes (or any reactive organic gas which contains at least seven carbon atoms), yield organic compounds with low ambient temperature vapor pressures which nucleate or condense on existing particles to form secondary organic PM. While 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 may also initiate reactions and organic radicals may be nitrated by HNO_2, HNO_3, or NO_2. 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. Studies of the production of secondary organic PM in ambient air have focused on the Los Angeles Basin. Turpin and Huntzicker (1991) 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, and hydroperoxides); (2) adsorption of organic gases onto existing solid particles (e.g., polycyclic aromatic hydrocarbons); and (3) dissolution of soluble gases which 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 produced by 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 and estimates of the production rate of secondary organic PM in the Los Angeles airshed are provided in the previous AQCD for PM (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 aromatic compounds containing zero or one methyl and ethyl groups (i.e., toluene, ethylbenzene, and ethyltoluenes) and n-propylbenzene produce higher yields of secondary organic PM than did the oxidation of aromatic compounds containing two or more methyl groups (i.e., xylenes, di-, tri-, and 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.

Hoffmann et al. (1997) using the same framework described above 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 20-40% 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 μgm^{-3} ppb^{-1} and varied by almost a factor of two depending on the initial mixture.

Kao and Friedlander (1995) examined the statistical properties of a number of PM components in the South Coast Air Basin. They found that the concentrations of non-reactive, primary components of PM_{10} have approximately log normal frequency distributions and constant values of geometric standard deviations (GSDs) regardless of source type and location within their study area. However, aerosol constituents of secondary origin (e.g., $SO_4^=$, NH_4^+, and NO_3^-) were found to have much higher GSD's. Surprisingly, the GSD's 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 non-reactive 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 is 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 determine to what extent the results might be influenced by the evaporation of volatile constituents 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.
In addition, there is a high degree of uncertainty associated with all aspects of the calculation of secondary organic PM concentrations which 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 not 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, either the terpenes were being removed rapidly by some heterogeneous process or 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.

3.1.3.3 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 is generally 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 which 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 may also act as a carrier to convey soluble toxic species to the gas-exchange regions of the respiratory system, including species that would be removed by deposition in the upper airways if the 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 AQC PM 96 (U.S. Environmental Protection, Agency, 1996).

Briefly the interaction of particles with water vapor may be described as follows. As relative humidity increases, crystalline soluble salts in aerosol particles, such as $(NH_4)_2SO_4$, NH_4HSO_4, or NH_4NO_3, undergo a phase transition to become aqueous solution aerosols. 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 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 particle tends to follow the equilibrium growth curve. As relative humidity decreases, the particle follows the equilibrium curve to the deliquescence point. However, rather than crystallizing at the deliquescence relative humidity, the particle remains a solution in a supersaturated solution to considerably lower relative humidities. Ultimately the particle abruptly loses its water vapor (efflorescence), returning typically to the initial, stable 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 due to 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 3-8). A particle can grow to 5 times its dry diameter as the RH approaches 100% (Figure 3-9). 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) to remove particle-bound water (see 3.2 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, lost during equilibration, and 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, must all be made at the same RH if the results are to be comparable. These problems are addressed in more detail in Section 3.2 on Measurement of Particulate Matter.

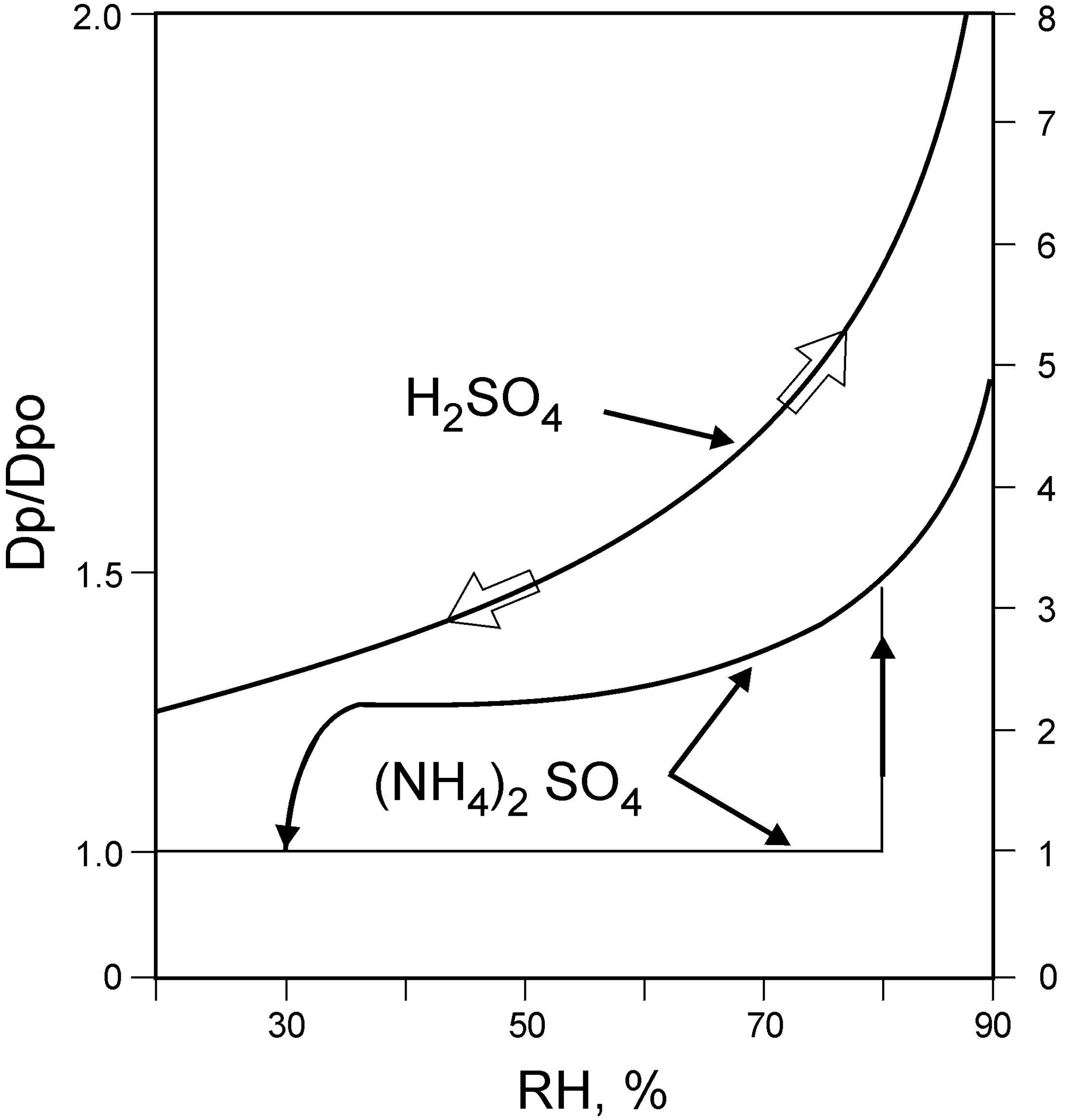

Figure 3-8. **Particle growth curves showing fully reversible hygroscopic growth of sulfuric acid (H_2SO_4) particles, deliquescent growth of ammonium sulfate [$(NH_4)_2 SO_4$] particles at about 80% relative humidity (RH), hygroscopic growth of ammonium sulfate solution droplets at RH greater than 80%, 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).

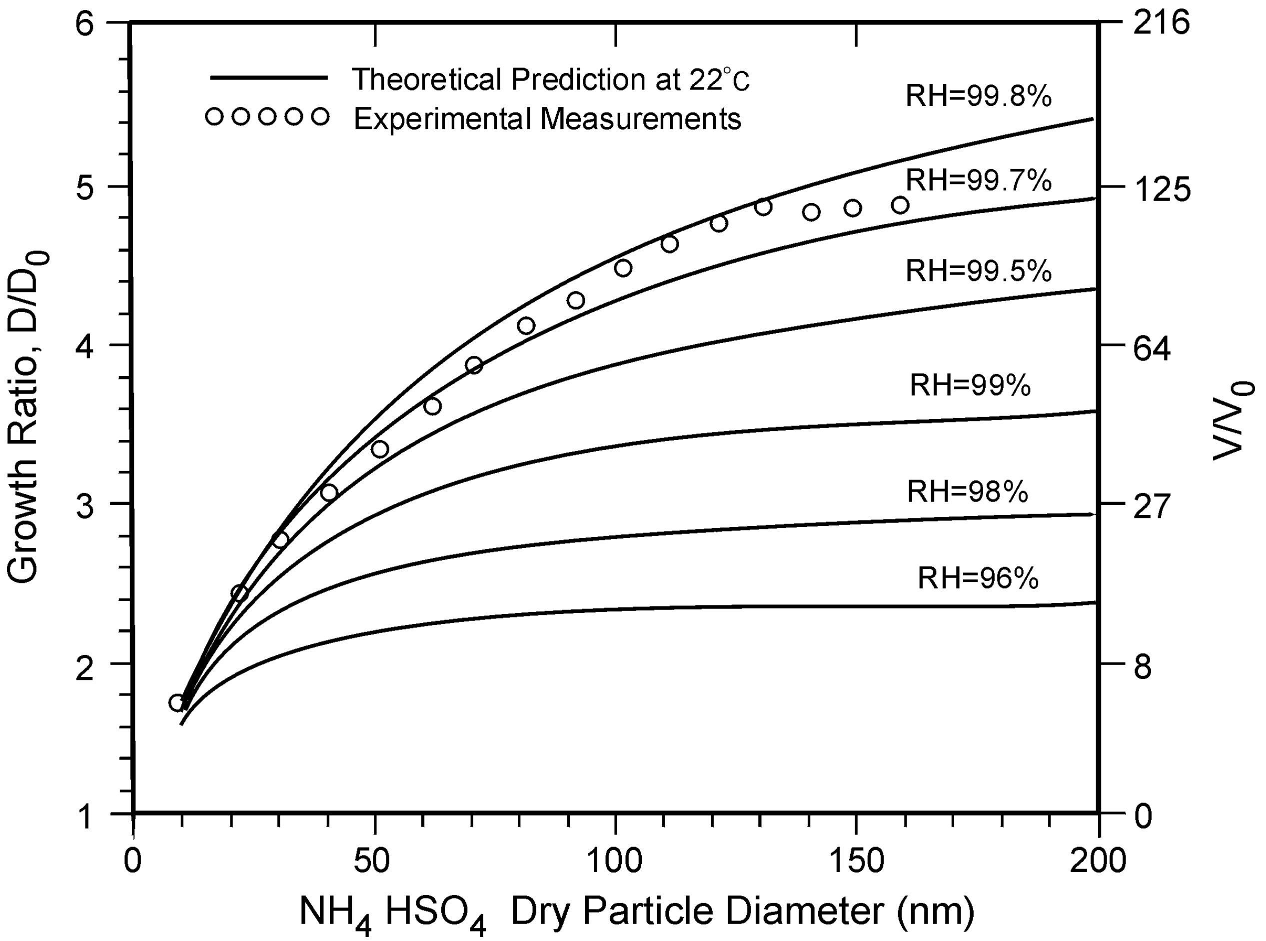

Figure 3-9. Theoretical predictions and experimental measurements of growth of NH_4HSO_4 and particles at relative humidity between 95 and 100%.

Source: Li et al. (1992).

3.1.3.4 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 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 which varies as the 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 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 and be removed. Falling rain drops, however, are not effective in removing accumulation-mode particles.

3.1.3.5 Particulate Matter and Acid Deposition

The EPA is required by law to set primary standards to product 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. 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 9.

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 acid 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 provide 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 may also be oxidized more slowly by dissolved oxygen 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 to fall out they will fall as rain and the particles will be removed from the atmospheric with potential effects on the materials, plants, or soil on which the rain falls. (Similar considerations apply to dew.) Atmospheric particles which nucleate cloud droplets may also contain other soluble or non-soluble materials such as metal salts and PNA organic compounds which 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 9.

Sulfuric acid, ammonium nitrate, and organic particles are also deposited on surfaces by dry deposition. The utilization of nitrate by plants leads to the production of acidity. Therefore, dry deposition of particles can also contribute to the ecological damages caused by acid deposition.

3.1.3.6 Particles as Carriers of Toxic Species

Wilson (1995) has suggested that particles could carry toxic species into the deep lung. "It is possible that water-soluble gases, which would be removed by deposition to wet surfaces in the upper respiratory system during inhalation, could dissolve in particle-bound water and be carried with the particles into the deep lung. Water-soluble gases in polluted air include oxidants such as O_3, H_2O_2, and organic peroxides; acid gases such as SO_2, HCl, HNO_3, HONO, and formic acid; and polar organic species such as formaldehyde." Friedlander and Yeh (1998) have discussed this possibility for peroxides. Wexler and Sarangapani (1998), quoted below, have discussed this process and investigated it quantitatively.

> Air pollutants are deposited in the human airway via two pathways—particle deposition and vapor deposition. In the absence of particles, vapors deposit at different locations in the lung depending on their solubility in mucus, which is over 99% water. High-solubility compounds, such as nitric acid or hydrogen peroxide, are rapidly removed in the upper airways while low-solubility compounds, such as oxygen or ozone, are less well removed and so penetrate to the alveoli. Pollutant deposition in the upper airways is less harmful than in the lower airways because

upper airways clearance is more rapid and the epithelium is protected by a mucus layer. As a result, low-solubility pollutants, such as ozone, may harm the alveoli, while high-solubility pollutants, such as nitric acid, do not reach these tissues.

In the presence of aerosol particles, this scenario changes. Under most ambient conditions, aerosol particles contain some liquid water so that soluble compounds are partitioned between the gas phase and the aerosol liquid-water phase. The degree of deposition via the gas compared to that via the particles is a function of a number of factors including the solubility of the compound and the liquid-water content of the aerosol. Since highly soluble compounds deposit in the upper airways, particles may provide a vector for deposition of these compounds in the lower airways. Lower-solubility compounds may persist in the vapor phase and so may deposit in lower airway segments.

As aerosols are inhaled, soluble vapors deposit on the mucus, disrupting the gas-particle equilibrium, and the compound begins to evaporate from the aerosol particles. If the evaporation is rapid, the pattern of deposition of the compound will not be influenced by the presence of the particles, i.e., the deposition pattern is essentially that of the vapor alone. If the evaporation is very slow compared to a breathing cycle, a significant amount of the compound will remain in the particle phase and the pattern of deposition may be shifted toward the pulmonary region by the particles.

Wexler and Sarangapani (1998) calculated the concentrations of a water-soluble gas, relative to its initial concentration, as a function of airway generation (a measure of penetration into the lung) for a range of Henry's law coefficients (a measure of solubility) for 0.1, 0.3, and 1 μm diameter particles, assuming that there is no resistence to evaporation of the gas from the particle-bound water. Wexler and Sarangapani conclude that, "Particles do not increase vapor deposition in human airways". This conclusion is based largely on the fact that only a very small fraction of the gas is dissolved in the particle-bound water for normal relative humidities. However, their calculations do show that soluble gases are carried to higher generation airways (deeper into the lung) in the presence of particles than in the absence of particles.

Underhill (1999) has pointed out that species such as SO_2 and formaldehyde either react to form different species ($SO_2 \rightleftharpoons H^+ + HSO_3^-$) or hydrates $\{HCHO + H_2O \rightleftharpoons CH_2(OH)_2\}$. These reactions reduce the concentration of the dissolved gas-phase species and provide a kinetic resistence to the evaporation of the dissolved gas. Thus, the concentration of the dissolved species may be greater than that predicted by the equilibrium calculations of Wexler and Sarangapani. Underhill further points out that Amdur (1957, 1960, 1966, 1969), Amdur and Mead (1958), and Amdur and Underhill (1968), in studies of the effects of particles and gases on pulmonary resistence in guinea pigs, observed synergistic effects between NaCl particles and SO_2 and HCHO, but not between NaCl and formic acid. The reaction rates for converting the reacted species back to the gas-phase compound is fast enough to maintain equilibrium conditions for formic acid, but not for SO_2 and HCHO.

It is also possible that toxic gases could be absorbed on solid particles thus be carried into the lungs. The gases might be desorbed in the higher temperature and relative humidity of the lung. If the toxic gas remains absorbed on the particle, it could be brought into direct contact with cells in the respiratory system. The thermal release of NO from ambient air and diesel particles has been studied (Ball et al., 1999) as well as the absorption of NO_2 on carbon particles (Kalberer et al., 1999). The partitioning of semivolatile organic compounds between the gas-phase and the liquid organic layer of an atmospheric particle has been investigated and modeled (e.g., Pankow et al., 1993; Pankow, 1994a,b; Jang et al., 1997). Less information is available on the kinetics of the partitioning process. However, Kamens and Coe (1997) have measured the rate of evaporation of polycyclic aromatic hydrocarbons (PAHs) from fresh diesel soot particles. For some PAHs the evaporation rates were slow enough (order of seconds) to allow particles to carry PAHs into higher generation airways. Kamens et al. (1999) also report calculations of desorption rates for certain products of the O_3 + α-pinene reaction from the secondary particles formed in the reaction. Muzyka et al. (1998) report that particulate matter from diesel exhaust contains absorbed benzene as well as polycyclic aromatic hydrocarbons (PAH) and nitro-PAH. Recent studies also suggest that a variety of allergens may be absorbed on atmospheric particles and carried into the lung and contribute to aggregation of allergy and asthma (Schappi et al., 1999; Ormstad et al., 1998).

3.1.3.7 Separation of Fine and Coarse Particles

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 AQC PM 96 (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 1.0 and 3 μm. However, the analysis of the existing data did demonstrate the important role of relative humidity in influencing the size of the fine particle mode and indicated that significant fine mode material is found above 1.0 μm only during periods of very high relative humidity.

Thus, a $PM_{2.5}$ sample will contain most of the fine mode material, except during periods of RH near 100 %. However, especially in conditions of low RH, it may contain 5 to 20 % of the coarse mode material below 10 μm in diameter. A $PM_{1.0}$ sample will prevent misclassification of coarse mode material as fine but under high RH conditions could result in some of the 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 amount of accumulation mode particles will be above 1 μm in diameter at RHs below 60% but a substantial fraction will grow above 1 μm for RH above 80% (Hitzenberger et al., 1997; McMurry and Stolzenberg, 1989; U.S. Environmental Protection Agency, 1996). As discussed in Section 3.2, some 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 require reduction of RH prior to collection. With such techniques $PM_{1.0}$ would be an appropriate cut-point.

Summary

The physical and chemical properties of ultrafine mode, accumulation mode, and coarse mode particles are summarized in Table 3-1.

3.2 MEASUREMENT OF PARTICULATE MATTER

The 1996 Air Quality Criteria Document for Particulate Matter (AQC PM 96) (U.S. Environmental Protection Agency, 1996) summarized sampling and analytical techniques for

TABLE 3-1. 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/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, 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/animal fragments Tire, break pad, road wear debris
Solubility:	Probably less soluble than accumulation mode	Largely soluble, hygroscopic and deliquescent	Largely insoluble and non-hygroscopic
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:	<1-10s of km	100s to 1000s of km	<1 to 10s of km (100s-1000s in dust storms)

Source: Adapted from Wilson and Suh (1997).

particulate matter (PM) and acid deposition that had appeared in the literature since the 1982 Air Quality Criteria for Particulate Matter (U.S. Environmental Protection Agency, 1982). Two other excellent reviews have been published in recent years by Chow (1995) and McMurry (1999). This section will concentrate on 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.

3.2.1 Problems in Measuring Particulate Matter

The decision by the US 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.

The US Federal Reference Methods (FRM) for $PM_{2.5}$ and PM_{10} provide relatively precise (±10 %) methods for determining the mass of material remaining on a Teflon filter after equilibration. However, numerous uncertainties remain as to the relationship between the mass and composition of material remaining on the filter, as measured by the FRMs, and the mass and composition of material that exists in the atmosphere as suspended PM. The goal of a PM indicator might be to accurately measure 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 treatment of semivolatile components; selection of an upper cut point; separation of fine-mode and coarse-mode PM; treatment of pressure, temperature, and relative humidity; and how to assess the reliability of the measurement technique. In many cases choices have been made by default and with inadequate 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.

3.2.1.1 Treatment of Semivolatile Components of PM

Current filtration-based mass measurements lead to significant evaporative losses, during and possibly after collection, of a variety of semivolatile components, i.e., species which 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 3-10.

Possible approaches that have been used to address the problem of potentially lost semivolatile components include the following 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 pre-concentration of the accumulation mode and reduction of ambient humidity.)
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 50ºC, beta gauge with heated inlet.)
3. Equilibrate collected material at fixed, near-room temperature and low relative humidity to remove particle-bound water. Accept loss of an unknown but possibly significant fraction of semivolatile PM. (Example: US Federal Reference Method and most filter-weighing techniques. There is also information to suggest that not all particle-bound water is removed by the equilibration process.)

The semivolatile artifact is composition dependent and has been shown to be significant in air sheds with high nitrate, wood smoke or secondary organic aerosols.

3.2.1.2 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).

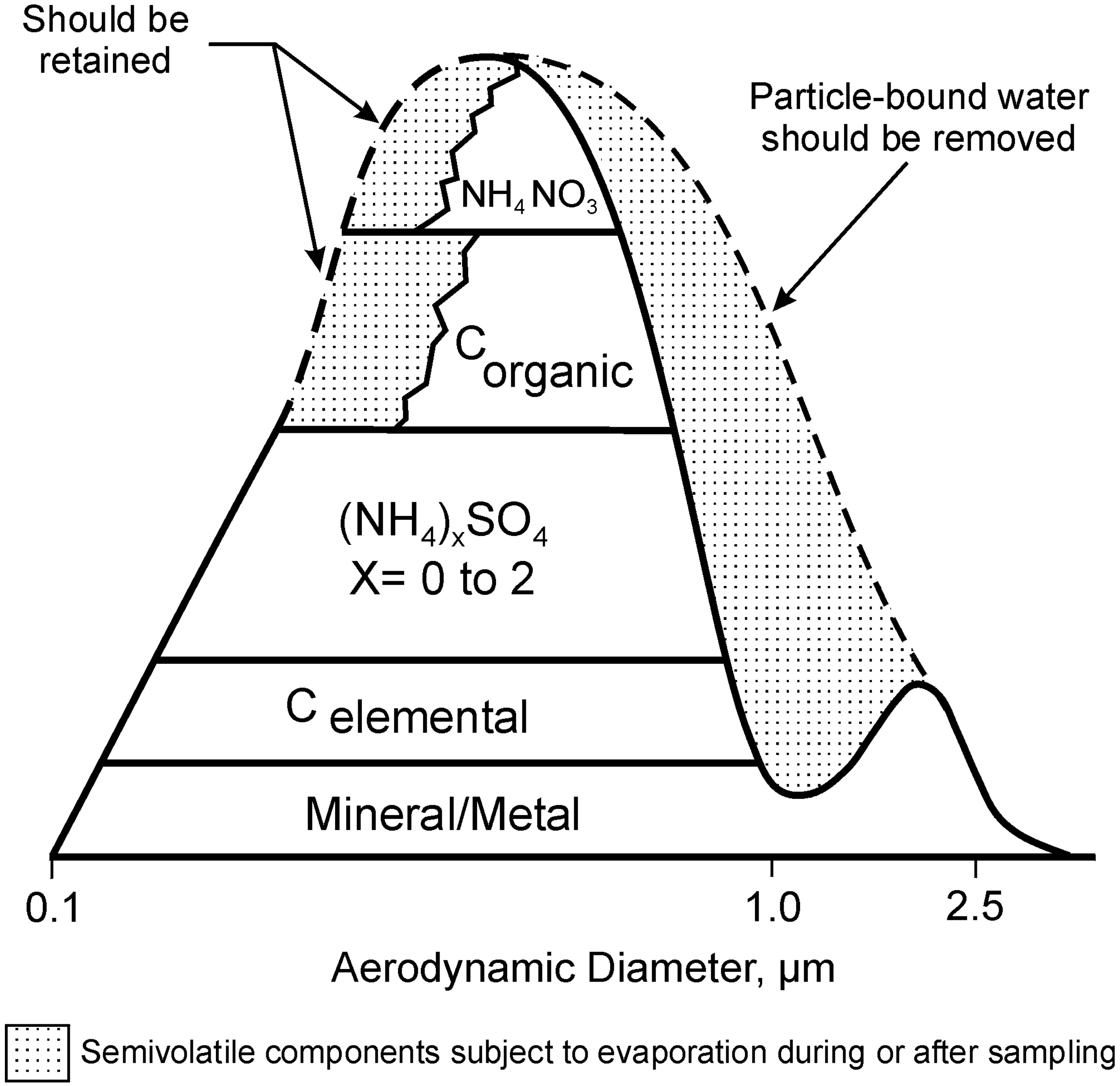

Figure 3-10. Schematic showing major nonvolatile and semivolatile components of $PM_{2.5}$. Semivolatile components are subject to partial to complete loss during equilibration or heating. The optimal technique was remove all particle-bound water but no ammonium nitrate or semivolatile organic PM.

A separation which 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 US 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 3-6 and Section 3.1.2.2.)

3.2.1.3 Separation of Fine-Mode and Coarse-Mode PM

Fine-mode and coarse-mode particles differ not only in size and morphology (e.g., smooth droplets vs 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.

At high relative humidity, such as that found in fog and clouds, hygroscopic fine-mode particles will increase in size due to accretion of particle-bound water. Some, originally sub-micrometer, 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. 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 and/or ammonium ions; sulfate in the coarse mode is associated with basic metal ions. The sources are different and the health effects are likely to 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.

The current practice of separating fine-mode and coarse-mode particles at 2.5 μm AD, while satisfactory for a health-based standard, does not provide an adequate separation for epidemiologic studies, especially in areas where winds cause high concentrations of wind blown soil, or for the determination of source categories to guide control strategy. A possible approach, which would provide much better separation of fine-mode PM and coarse-mode PM, would be to dehumidify the air stream to some fixed humidity that would remove all or most particle-bound water without evaporating semivolatile components and make the cut near 1 μm AD. (See Section 3.1.3.7.)

3.2.1.4 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.) (former EPA technique for PM_{10}).
b. Sample volume based on volumetric flow at ambient conditions of temperature and pressure (current EPA technique for $PM_{2.5}$ and PM_{10}).

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:

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:

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 the disaggregation of personal exposure into exposure to particles of ambient origin and exposure to particles of indoor origin.

3.2.1.5 No Way to Determine Accuracy

Precision and accuracy are normally used to describe the quality of a 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 material for suspended PM exists. Therefore, it is not possible to establish the 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. Measurement errors of concern in PM_{10} sampling that arise due to uncertainty tolerances in cutpoint; particle bounce and re-entrainment; impactor surface overloading; and losses to sampler internal surfaces were discussed in detail in the AQC PM 96 (U.S. Environmental Protection Agency, 1996). 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 primary calibration standards, because of the use of an operational definition of $PM_{2.5}$ as a surrogate for fine particles, and because of problems associated with trying to measure the mass of particles as they exist in the air rather than what remains after collection on a filter.

Because of the difficulties associated with determining the accuracy of PM measurements, the U.S. Environmental Protection Agency 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 $PM_{2.5}$ standards are defined with consistency of measurement technique, rather than accuracy of the true mass concentration measurement, in mind (McMurry, 1999). 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 subject field $PM_{2.5}$ sampler and a collocated $PM_{2.5}$ reference method audit sampler (McMurry, 1999). The Federal Reference Method (FRM) for $PM_{2.5}$ will be discussed in Section 3.2.3.3. The accurate measurement of the mass of PM suspended in the atmosphere was of concern in PM_{10} sampling and is of even greater concern for $PM_{2.5}$. 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 due to adsorption of organic vapors onto collected PM, filter media, or other sampler surfaces; neutralization of acid or basic vapors on either filter media or collected PM; and the role of particle-bound water in PM sampling.

The lack of a standard reference material or a primary calibration standard for PM suspended in the atmosphere has prevented any evaluation of accuracy. In the last 25 years, there have been advancements in the generation of monodisperse aerosols and classification, 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 little additional work in this area has been reported.

Methods validation was discussed in the previous AQC PM 96 (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, since only the material collected on the filter is included in the balance.

3.2.2 Why Measure Particles

3.2.2.1 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. PM standards are currently based on 24-hour measurements, with measurements every sixth day being used to estimate an annual average.

3.2.2.2 Implementation of a Standard

In order to develop State Implementation Plans, to reduce pollution in order 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 be measured. Also measurements are needed with shorter time resolution in order to match changes in pollution associated with diurnal changes in the boundary layer.

3.2.2.3 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 acute epidemiology, one-hour or continuous measurements may be needed as well as 24-hour measurements. For chronic epidemiologic studies, measurements which integrate over 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.

3.2.2.4 Determination of Ecological Effects

Measurement 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.

3.2.2.5 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.

3.2.2.6 PM Components/Parameters Which Need To Be Measured

The large variety of components of PM or PM parameters that need to be measured for various purposes are summarized in Table 3-2.

3.2.3 Problems Associated with Semivolatile Particulate Matter

It is becoming increasingly apparent that the semivolatile component of PM may significantly impact 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, due to changes in temperature, relative humidity, or composition of the aerosol, or due to pressure drop across the filter (McMurry, 1999). Semivolatile species may adsorb onto, or react with, filter media and/or collected PM, leading to a positive sampling artifact. 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

TABLE 3-2. PM 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

Crustal elements

Bioaerosols

Particle refractive index (real and imaginary)

Particle density

Particle size change with changes in relative humidity

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 have also 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) modeled the gas/particle partitioning of SVOC on inorganic, organic, and ambient smog aerosols.

Adsorption of organic vapors onto quartz filters has also been recognized as a source of positive sampling error. Although original experiments investigating this sampling artifact were typically carried out utilizing two quartz fiber filters deployed in series, the second quartz filter can indicate both gaseous VOC adsorbed on both filters (positive) artifact and SVOC evaporated from particles on the first filter and subsequently adsorbed on the second filter (negative artifact). 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., 1995a), as well as for sampling of gas and particulate phase organic acids (Lawrence and Koutrakis, 1996a,b), holds promise for improving our understanding of SVOC sampling artifacts.

Finally, Eatough et al. (1999) have reported on a batch sampler (the Particle Concentrator – Brigham Young University Organic Sampling System, or 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 will be discussed in more detail in Section 3.2.3.2.

3.2.3.1 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) will occur during sampling on Teflon filters. The impact on the accuracy of atmospheric particulate measurements from these volatilization losses will be even more significant for $PM_{2.5}$ than they are for PM_{10}. The FRM for $PM_{2.5}$ will suffer loss of nitrates, similar to the losses experienced with other simple filter collection systems. Sampling artifacts due to the loss of particulate nitrates will represent a significant problem in areas that experience high amounts of nitrogen species, like southern California.

Hering and Cass (1999) examined the errors in $PM_{2.5}$ mass measurements due to volatilization of particulate nitrate by looking at data from two field measurement campaigns conducted in southern California – the Southern California Air Quality Study (SCAQS, Lawson, 1990), and 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 collected particles onto a nylon filter, following a denuder to remove gaseous nitric acid. 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 due to volatilization of ammonium nitrate represented a significant fraction of the total $PM_{2.5}$ mass, and the fraction lost was higher during summer than during fall (17% versus 9% during the SCAQS study, and 21% versus 13% during the CalTech study) (Figure 3-11). Hering and Cass (1999) found that nitrate obtained from Teflon filter samples was on average 28% lower than that obtained by denuded nylon filters.

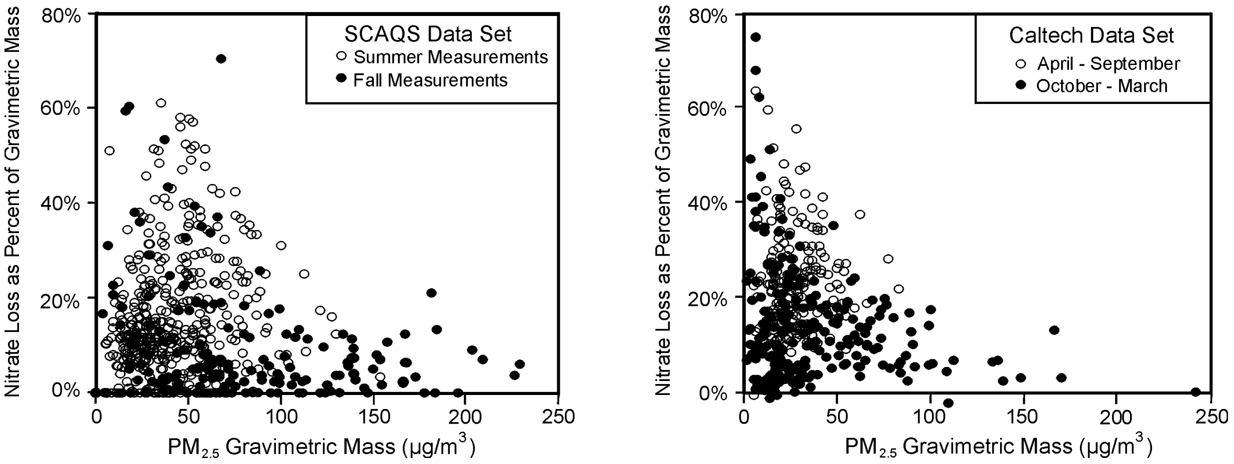

Figure 3-11. Amount of ammonium nitrate volatilized from Teflon filters, expressed as a percentage of the measured $PM_{2.5}$ mass, for the SCAQS and CalTech studies, for spring and fall sampling periods.

Source: Herring and Cass (1999).

Hering and Cass (1999) also analyzed these data by extending the evaporative model developed by Zhang and McMurry (1987). The extended model utilized by Hering and Cass (1999) takes into account dissociation of collected particulate ammonium nitrate on Teflon filters into nitric acid and ammonia, via three mechanisms: 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), heating of the filter substrate above ambient temperature by sampling, and pressure drop across the Teflon filter. For the sampling systems modeled, the flow-induced pressure drop was measured to be less than 0.02 atmospheres, 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, and higher during the day compared to night, and were reasonably consistent with modeled predictions.

Finally, during the SCAQS study, particulate samples were also collected using a Berner impactor and greased Tedlar substrates, in size ranges from 0.05 to 10 mm 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.

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 as a gas. 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 U.S., therefore, loss of nitrate will be a bigger problem in the western U.S. than in the eastern U.S. However, as SO_2 emissions are reduced in the eastern U.S., nitrate may become a larger fraction of the suspended PM.

3.2.3.2 Semivolatile Organic Compounds

Although there is less information on losses of semivolatile organic compounds (SVOC), it is known that these species can similarly be lost from Teflon filters due to volatilization, and can also cause the $PM_{2.5}$ mass to be significantly underestimated. 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. It has been shown that attempting to correct for the losses of SVOC during sampling by deploying a second quartz filter directly behind either a quartz or Teflon filter can significantly underestimate the volatilization losses (e.g., Eatough et al., 1993). 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; the fraction of the total fine particulate matter that this loss represents was not given. At present, there are limited data available specifically on the fraction of $PM_{2.5}$ mass lost during sampling onto Teflon filters due to volatilization of organic species, and even less on the regional differences in the effects of volatilization losses of SVOC. Cui et al. (1998) found that losses of SVOC from particles in the Los Angeles Basin during the summer were greater during the day than at night. Cui et al. (1998) determined that on average, 42 and 62% of the particulate organic material was semivolatile organic compounds lost from particles during sampling for daytime and nighttime samples, respectively.

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, for example, polycyclic aromatic hydrocarbons (PAHs) and polycyclic organic matter, which has been identified as a hazardous air pollutant. PAHs have also been suggested as alternative particulate tracers for automobile emissions, since 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 are also emitted during biomass burning, including burning of cereal crop residues and wood fuels (Jenkins et al., 1996; Roberts and Corkill, 1998). The semivolatile PAHs are also of interest in ambient PM studies, because of their potential for causing both positive and negative sampling artifacts if not properly accounted for. Several investigators have observed that collection of particles on a filter can result in underestimation of particulate organic compounds due to 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., 1995a; Finn et al., 1999). Positive sampling artifacts can also occur due to the adsorption of gases onto the filter materials (e.g., Gundel et al., 1995a). There appears to be a larger positive artifact due to 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., 1999).

Phase distribution of semivolatile organic species has been the subject of several studies that have employed denuder technology (see Gundel et al., 1995a; Gundel and Lane, 1999) to directly determine the phase distributions while avoiding some of the positive and negative sampling artifacts associated with using backup quartz filters. For measuring particulate phase organic compounds, the denuder-based sampling system is a definite improvement over the filter/adsorbent collection method (Turpin et al., 1993). Some researchers 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 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 due to sampling and analytical effects. Results on field studies using their sampling system have not been published.

Losses of the SVOC fraction of particulate organic matter occurring during sampling were investigated by Eatough et al. (1995), who found that on average losses of 35% of the POM in samples collected at a site in southern California resulted. In this study, 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 Lpm) 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 Lpm). 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 4 systems (each with a flowrate of 200 Lpm). Particle size cuts of 2.5, 0.8, and 0.4 mm are achieved by virtual impaction, and the sample subsequently flows through a denuder, then is split, with the major flow (150 Lpm) 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, Utah, 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% due to volatilization losses of SVOC from the quartz filters.

Six-hour daytime samples and 9-hour nighttime samples were collected with the BIG BOSS sampler in the LA Basin in September of 1994 (Cui et al., 1998). During this study, Cui et al. (1998) determined that an average of 42 and 62% of organic PM was SVOC lost from the particles during daytime and nighttime sampling, respectively. The negative sampling artifact associated with SVOC losses was an order of magnitude larger than the positive quartz filter artifact that results due to adsorption of gas phase organic material.

The BIG BOSS sampler developed by Eatough and colleagues (Eatough et al., 1999) has been used to determine the total carbonaceous material collected by the quartz filters and the charcoal impregnated filter (CIF) by temperature programmed volatilization (TPV) and for GC analyses of extractable material from the XAD-II sorbent beds. In TPV, a portion of the sample is continuously heated from ambient temperature to 800 C in a mixed nitrogen/oxygen air stream, and the volatilized gases are converted to CO2 in a catalytic furnace and detected as CO2. The TPV analysis gives a measure of the EC and OC. To thermally desorb the CIF, a pure nitrogen stream is used as the carrier gas, to avoid oxidative decomposition of the CIF substrate, as well as the collected organic material. To determine organic compounds collected on the XAD-II substrate, the sorbent is solvent extracted with dichloromethane and analyzed via GC and GC-MS. In this way, aromatic compounds, paraffins, organic acids, and esters have been detected (quantities were not reported) in samples collected at Azusa (Los Angeles Basin, CA) and in Philadelphia (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, UT, they found that the majority of the n-nitroso and nitrite organic compounds that were present in fine particulate matter were semivolatile organic compounds that could be evaporated from the particles during sampling. They found particulate n-nitroso compound concentrations ranging between <1 and 3 nmoles/m^3, and gas-phase n-nitroso compound concentrations in the same range. Particulate organic nitrite concentrations were found in the range of <1 to ~5 nmoles/m^3, and gas-phase concentrations as high as 10 nmoles/m^3 were found.

Turpin et al. (1993) developed a sampling system 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 their 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 has been evaluated for the collection of PAH.

Gundel et al. (1995a) recently developed a technique for the direct determination of phase distributions of semivolatile polcyclic aromatic hydrocarbons, rather than phase distribution determination using difference method, using annular denuder technology. That technique has been applied to characterizing PAHs in environmental tobacco smoke (Gundel et al., 1995b), and to ambient air sampling (Lane and Gundel, 1996). The method developed by Gundel et al. (1995a), called the integrated organic vapor/particle sampler (IOVPS), uses a cyclone inlet with a D_{50} cutpoint of 2.5 mm. 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 IOVPS, which operates at 10 Lpm, 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., 1995a) 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.

Gas-phase PAH concentrations in indoor laboratory air ranged from 0.4 (0.1 – 0.6) ng/m^3 for anthracene to 338 (162 – 545) ng/m^3 for naphthalene. In ETS, gas-phase PAHs ranged from 0.4 (0.2 – 1.1) ng/m^3 for benz(a)anthracene to 1099 (784 – 1690) ng/m^3 for naphthalene. In ETS, the fraction of PAHs in the particle phase was less than 0.11 for most, except for fluoranthene (38% in particle phase); pyrene (18%); benz(a)anthracene (99%); and chrysene (97%).

Particulate phase PAHs have been measured by Gundel and Lane (1999) using sorbent-coated diffusion denuders (IOVPS). A series of 6 IOVPS were used sequentially over a 24-hr period to measure PAH phase distributions near a roadway in Berkeley, CA. Particulate fractions of PAH varied from 7 to 91% and were higher during colder periods. Gundel and Lane also reported that roughly two third of particulate PAH fluoranthene, pyrene, benz[*a*]anthracene and chrysene were found on the post-filter denuders, so that it is likely that considerable desorption from the collected particles took place. The IOVPS has also been used by Kamens and associates to study semivolatile PAH and nitro-PAH, and dioxins, primarily in smog chamber studies. Fan et al. (1996a) found that particulate phase nitro-PAH decayed quickly in sunlight, and that degradation by ozone was important at night (Fan et al., 1996b). In a study of the atmospheric behavior of dioxins, Penisse and Kamens (1996) found that, under high particle loadings (TSP concentrations ranging from 1 to 7 mg/m^{-3}), the tetra and pentachlorinated dioxins and furans partitioned into the gas phase.

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 denuder tubes of length 60, 90, and 120 cm. 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 significantly impacted 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 of 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 hours.

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 mm 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.

3.2.3.3 Use of Denuder Systems To Measure Semivolatile Compounds

Much progress has been made to date in the design of diffusion denuder systems for the measurement and characterization of both the particulate and gaseous phases of semivolatile compounds. Some of the recent research has focused upon 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 loses by absorption in impactor coatings.

Reducing the Size of Denuders

Diffusion denuder systems have been used in a number of studies aimed at quantifying both gaseous and particulate pollution. The typical denuder configuration is an annular diffusion denuder tube of significant length (e.g., 26.5 cm for 10 Lpm, Koutrakis et al., 1988). A more compact design based upon a honeycomb configuration was shown to significantly increase the capacity (Koutrakis et al., 1993). However, in intercomparisons with an annular denuder/filter pack system (Koutrakis et al., 1988), significant losses of ammonia and nitric acid were observed for the honeycomb configuration, and 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 of 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 – 8% losses of HNO_3 observed, and –4 – 2 % losses of NH_3 observed). The highest inlet losses were observed for HNO_3 lost to PFA surfaces (14 – 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. Since 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 seconds (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 seconds.

Effect of Diffusion Denuders on the Positive Quartz Filter Artifact

Denuder systems may be useful to reduce artifact reactions between gases and either the filter substrate or collected particles (Durham et al., 1978). Annular denuder systems, coupled with filter packs employing both Teflon and nylon filters, have been used to study ammonium nitrate, nitric acid, and ammonia in the vapor and aerosol phases (e.g., Benner et al., 1991). To account for the volatilization losses of semi-volatile 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 was also suggested as a method to collect semi-volatile organic compounds. However, it was noted that these methods (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). At the time of the previous AQC PM 96 (U.S. Environmental Protection Agency, 1996), some investigators were beginning to examine the phase partitioning of SVOC and accounting for the vapor phase SVOC, the particulate organic matter captured on the filter, and any SVOC that was subsequently lost from the filter by volatilization. Eatough et al. (1993) measured both adsorption and volatilization artifacts by using a sampling train that consisted of a diffusion denuder followed by a filter pack followed by a sorbent bed. The effects of face velocity and pressure drop across the filter were noted, and sampling systems optimizing these parameters to minimize artifacts were discussed. Gundel et al. (1995a,b) have also used sorbent-coated diffusion denuders to examine the phase distributions of semi-volatile organic compounds.

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 at 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.

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 which 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 and/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 since reactive gases are removed by the charcoal denuder which proceeds the particle collection filter. The implication from these studies is that, if the organic material lost from particles is important to respiratory health problems, then the traditional PM measurement techniques based upon integrated filter sampling followed by equilibration and gravimetric analysis may significantly underestimate the concentrations of POM. Moreover, it appears that the negative sampling artifact associated with volatilization losses from quartz filters is usually much greater than the positive sampling artifact that would be associated with adsorption of SVOC vapors onto quartz fiber filters. Because of the redistribution of SVOC between phases and the potential for chemical changes that occur during sampling, it may be necessary to use diffusion denuders or diffusion separation systems like those described in this section to adequately characterize particulate organic matter in ambient air.

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 was 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 9-stage low pressure Berner impactor followed by analysis by ion chromatography and found a strong temperature dependency on the redistribution. Bunz et al. 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 polar (hydrocarbons and chlorinated hydrocarbons) and non-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 upon 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, upon 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 upon an inorganic salt content of 1 to 2%, while 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.

Adsorption by Impactor Coatings

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 in particulate sampling is placed upon chemical speciation. Allen et al. (1999) 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. (1999) 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. Similarly, the use of coating solutions, especially those that contain organic liquids, in denuder systems may lead to adsorption of volatilized coating solution components on the downstream filters (Finn et al., 1999).

3.2.3.4 Particle-Bound Water

It is generally desirable to collect and measure ammonium nitrate and semivolatile organic compounds. However, for many measurement 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 is due to 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 3-8 and 3-9 show the change in diameter of sulfate particles as a function of relative humidity. Figure 3-8 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 upon 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 precisely observed. They also reported that, at relative humidities between 81 and 89%, the water content of ammonium sulfate aerosols (by mass) was 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 - 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 conclude 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 upon 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 mm) 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 hours. 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) which 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, 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 generated aerosol and on an ambient $PM_{2.5}$ sample collected in RTP, NC. The ambient aerosol sample was also analyzed for chemical constituents. It is interesting to note that while 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, due to 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 3-12. 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).

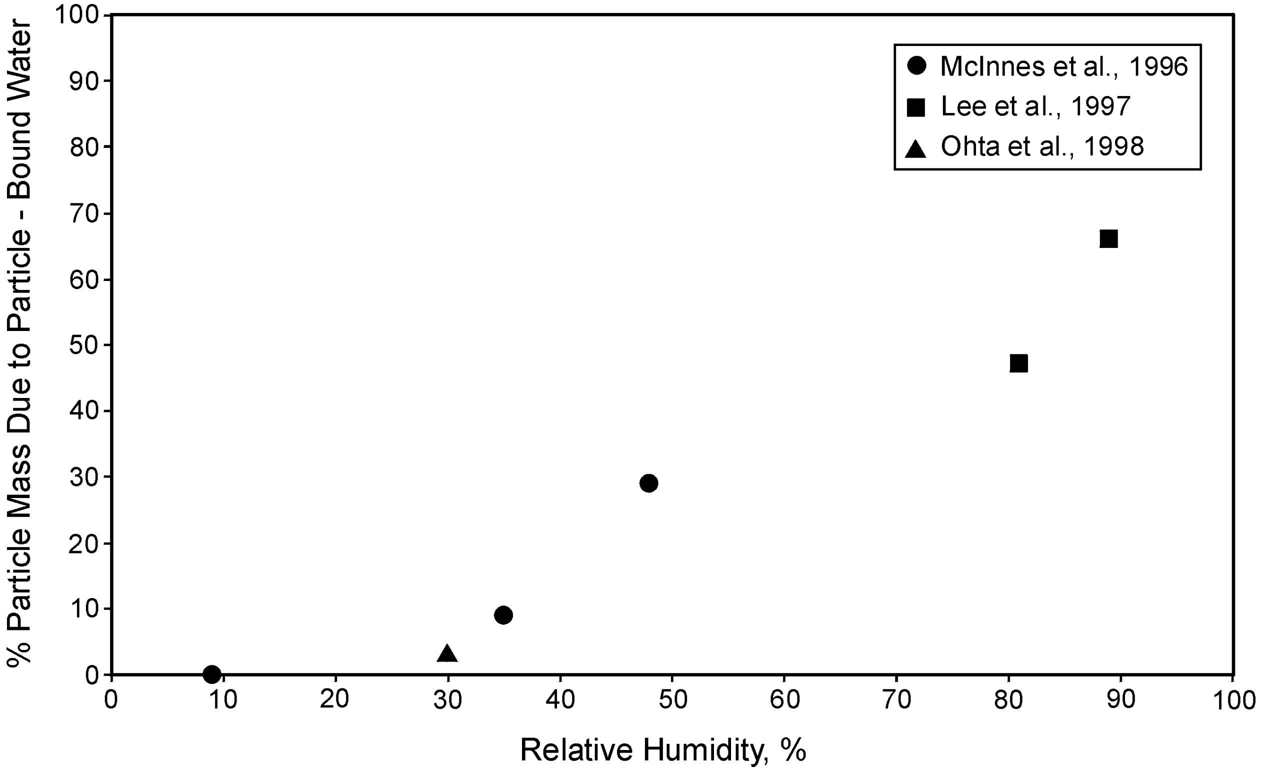

Figure 3-12. Aerosol water content expressed as a mass percentage, as a function of relative humidity.

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

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 at the stage for which the cut size was 0.047 mm, 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 - 15 mm in Vienna, Austria using a 9-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 mm 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. The “less” hygroscopic particles sampled in Los Angeles did not grow to within the experimental uncertainty (±2%) 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, CA was dependent upon 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 effects of RH on adsorption of semivolatile organic compounds is discussed elsewhere in this chapter. Saxena et al. (1995) observed that particulate organic compounds can also 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 non-urban site (Grand Canyon, AZ) 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.

Non-equilibrium issues may become of important for the TDMA, as well as for other methods of measuring water content. While 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.

3.2.4 EPA Monitoring Programs

3.2.4.1 The Federal Reference Methods (FRM) for Equilibrated Mass

Federal Reference Methods (FRM) have been specified for measuring PM_{10} (Federal Register, 1987) and for measuring $PM_{2.5}$ (Federal Register, 1997). The FRM for PM_{10} has been discussed in previous AQC for PM 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. Sample volumes are adjusted to standard conditions (1 atm and 25 °C). Measurement precision for 24-hr samples must be ± 5 $\mu g/m^3$ for PM_{10} concentrations below 80 $\mu g/m^3$, and 7% above this (McMurry, 1999).

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, while other aspects have performance specifications. The $PM_{2.5}$ FRM sampler consists of a PM_{10} inlet, an oil-soaked impaction substrate to remove particles larger than 2.5 mm, and a 47-mm polytetrafluoroethylene (PTFE) filter with a particle collection efficiency greater than 99.7%. The sample duration is 24 hours, during which the sampler temperature is not to exceed ambient temperatures by more than 5 °C. Filters are weighed before and after sampling at relative humidities in the range of 30 – 40%, but controlled to within ± 5%. For sampling conducted at ambient relative humidity less than 30%, mass measurements at relative humidities down to 20% are permissible (McMurry, 1999).

The FRM also allows for Class I, II, and III equivalent methods for $PM_{2.5}$. 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-hr integrated filter samplers that are subjected to subsequent moisture equilibration and gravimetric mass analysis." Class III equivalent methods include filter-based methods having other than a 24-hr collection interval or non-filter-based methods such as beta attenuation, harmonic oscillating elements, and nephelometry (McMurry, 1999).

The strength of the $PM_{2.5}$ FRM is that specification of all details of the sampler design ensures that measurements at all locations should be comparable. However, the FRM requires maintenance because of the oil-soaked impaction substrate that could otherwise become loaded with coarse particles. Failure to do so could lead to coarse particle bounce, thus artificially increasing the fine particle concentrations. Moreover, the specification of a PM_{10} inlet requires the oil-soaked impaction substrate to collect all particles between 2.5 and 10 mm – if an inlet with a smaller cutpoint diameter were specified, coarse particle bounce could potentially be reduced, and perhaps the maintenance frequency could be reduced (McMurry, 1999).

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 re-entrainment 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 re-entrainment problems have since been dealt with voluntarily by the manufacturers by recommending operational procedures including oiling of impact surfaces and regular cleaning. The AQC PM 96 (U.S. Environmental Protection Agency, 1996) concluded that the PM_{10} sampling systems can be designed such that concentration measurements are within ±10% of the true concentrations. For $PM_{2.5}$, cutpoint tolerances are not expected to affect the mass concentration as much as for PM_{10}, since the 2.5 mm cutpoint generally occurs near a minimum in the mass distribution (e.g., Figure 3-5).

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 AQC PM 96 (U.S. Environmental Protection Agency, 1996). These included 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) losses (e.g., Eatough et al., 1993); and relative humidity effects (e.g., Keeler et al., 1988). Due to conversion of SO_2 and nitrogen oxides to particulate sulfates and nitrates, respectively, on glass fiber filters, according to the previous AQC PM 96 (U.S. Environmental Protection Agency, 1996), TSP concentration measurements could be inflated by as much as 10 to 20 mg/m^3. Losses of particulate nitrates, chlorides, and/or ammonium from quartz fiber filters were noted during storage or during sampling by several researchers (e.g., Witz et al., 1990). Although losses of fine particle nitrates from Teflon filters were reported by several investigators, there was some evidence that the nitrate artifacts were minor except in California (Malm et al., 1994), and unquantifiable with the current theory. Similarly, significant losses of particulate organic compounds on quartz filters were observed by Eatough et al. (1993). Adsorption of organic vapors onto the filter or collected particulate matter was also observed to cause a positive sampling artifact during the Carbonaceous Species Methods Intercomparison Study (Hering et al., 1990), so that in regions where a significant fraction of the ambient PM mass is organic, there may be significant positive or negative errors in the mass concentration measurement.

3.2.4.2 Speciation Monitoring

In addition to FRM sampling to determine compliance with PM standards, EPA requires States to conduct speciation sampling primarily to determine source categories and trends. The current samplers include three filters: Teflon for equilibrated mass and elemental analysis, a Nylon filter with a nitric acid denuder to collect nitrate, and a quartz fiber filter for elemental and organic carbon (but without any correction for positive or negative artifacts due to adsorption of organic gases or the quartz filters or evaporation of semivolatile organics from the collected particles.

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 and receptor sample characterization should be performed using the same analyses. A considerable amount of receptor modeling work has been conducted with CMB and using elemental analyses coupled with OC/EC and some ionic species (e.g., Watson et al., 1994; Hidy and Venkataraman, 1996; McLaren and Singleton, 1996; Vega et al., 1997). Recent developments in receptor modeling include using organic analyses for tracers of specific sources (Benner et al., 1995), and very detailed organic analyses for source fingerprinting (Rogge et al., 1991, 1993a,b,c,d, 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 and will not be discussed further, here.

Statistical models based upon factor analysis or principal component analysis have the advantage of not requiring detailed source characterization but the drawback is that they require a large data set of receptor sample analyses. These statistically based models have an additional benefit in that they can also 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) reported on a principal component analysis (PCA) study conducted at Niwot Ridge, Colorado, during which organic constituents of atmospheric aerosols were measured, along with physical and meteorological data. Organic compounds were thermally desorbed from the aerosol particles at 250 C in a pure helium atmosphere, separated by gas chromatography, and identified by mass spectrometry. Veltkamp et al. (1996) did not report desorption recoveries or calibration procedures. For each of 48 samples, 31 variables, including 18 particulate organic compounds, along with 11 organic and inorganic vapor species (e.g., NO, NO_2, HNO_3, HONO, PAN, H_2O_2, etc.) wind direction and time of day were used as variables in a principle component analysis. Several factors were identified that served to distinguish various sources, and 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 in 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) discussed 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, MD, and determined the size distribution of soot from the trucks.

Elemental Analyses

X-ray emission, either stimulated by X-rays (X-ray fluorescence, XRF) or by proton beams (Proton Induced X-ray Emission, PIXE) are standard techniques for non-destructive analysis of certain elements. Some newer techniques with some advantages have become available in recent years.

Instrumental Neutron Activation Analysis (INAA). Instrumental neutron activation analysis (INAA) was mentioned briefly in the previous AQC PM 96 and will be expanded upon 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 the advantage of having a 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 due to self-attenuation of the X-rays due to particle size effect.

Atomic Absorption Spectrophotometry (AAS). Atomic Absorption Spectrophotometry (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-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 $r^2 \sim 0.84 - 0.98$. Both atmospheric inputs and emissions were found to have followed downward trends for Pb. For the period of 1987 to 1988, 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 waste, and medical waste incineration, the contribution from which has increased).

Inductively Coupled Plasma – Mass Spectroscopy (ICP-MS). Keeler and Pirrone (1996) also used inductively coupled plasma – mass spectroscopy (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.

Elemental/Organic Carbon, Soot, or Particulate Organic 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 AQC

PM 96 (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 U.S. 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 oxidation of $CaCO_3$. In the thermal apparatus used by Lavanchy et al. (1999), a filter sample is placed in a moveable sample boat and, prior to insertion into the 340°C oven, the sample is flash heated in the 650 °C oven for one minute, in order to minimize charring. It then is inserted into the first stage of a two-stage oven, in which OC is oxidized to CO_2 at 340°C in the presence of O_2 for 42 minutes. The filter is then moved into the second stage oven, in which EC is oxidized at 650 °C, for 32 minutes. This temperature is reported to be sufficient to completely oxidize EC, but with only about 1% of the $CaCO_3$ being oxidized (Lavanchy et al., 1999; Petzold et al., 1997). In order 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. They also reported detection limits of 1.3 μg for EC and 1.8 μg for OC.

The thermal/optical transmission method (TOT) was mentioned briefly in the AQC PM 96 (U.S. Environmental Protection Agency, 1996), as being similar to the TOR with the exception that light transmission rather than reflectance is monitored on the filter throughout the analysis. 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) and has gained significantly in popularity since then, and so will be described in more detail, here. The OC/EC method described by Birch and Cary (1996) is a TOT method similar to the TOR method described in the AQC PM 96 (U.S. Environmental Protection Agency, 1996) in that temperature and atmospheric control are used to accomplish carbon speciation; several temperature steps are utilized; carbon evolved is converted to methane and quantified with FID; and light transmission, rather than reflectance, off the filter is measured during the analysis. In thermal/optical methods, the optical feature allows for correction for pyrolytic char generated during the analysis. The OC/EC 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 3-13, 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 the volatilization of any remaining complex organic compounds so they are not apportioned to the EC phase.

Black carbon (BC) is also 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 upon thermal properties, while BC is based upon 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^2 g^{-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^2 g^{-1} (Hintzenberger et al. [1996] and references therein). The absorption coefficient, (B_a), is defined as absorption per mass concentration and can be calculated given the sample filter area, the total deposited mass, and

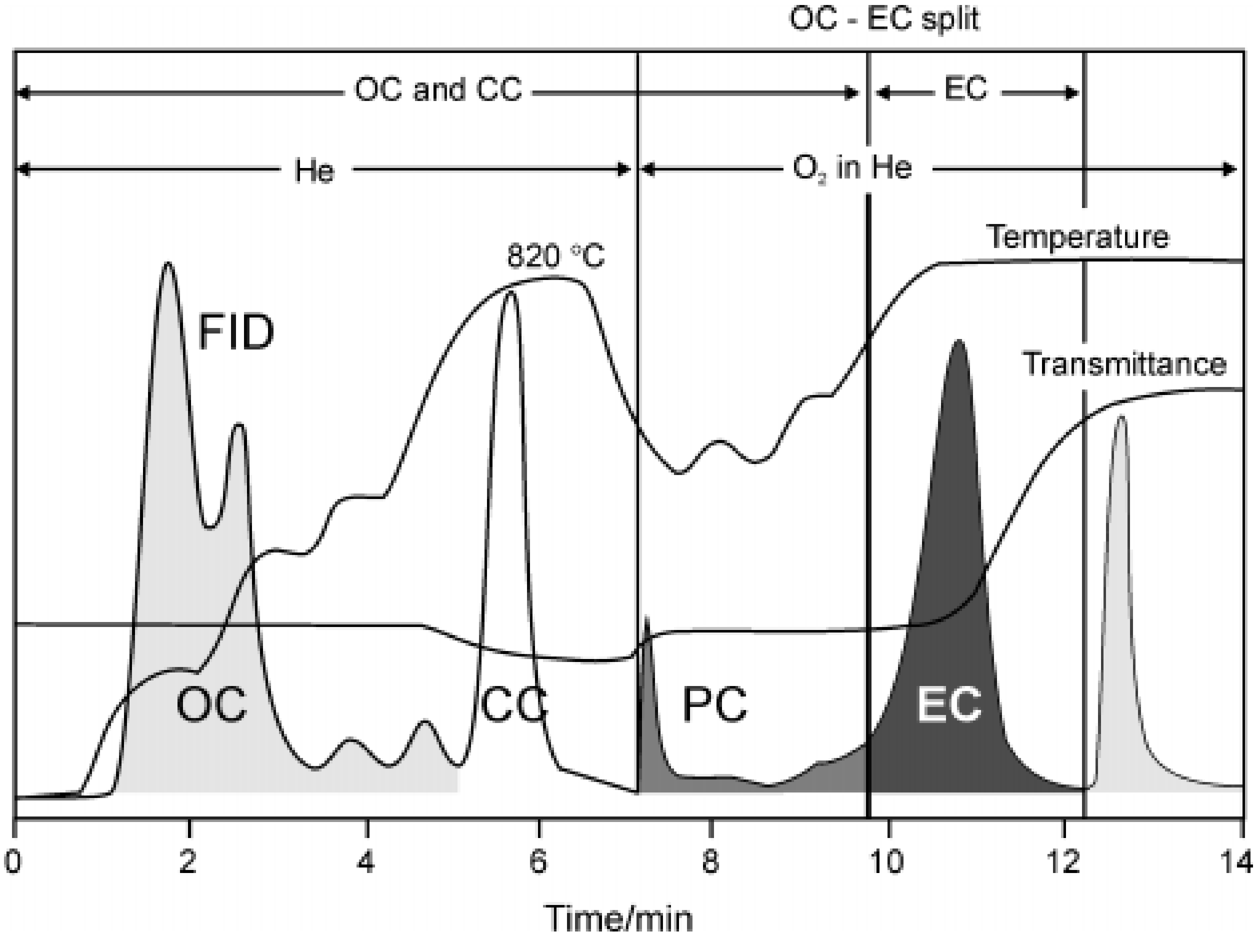

Figure 3-13. This thermogram, for a sample containing rock dust (a carbonate source) and diesel exhaust, shows three traces that correspond to temperature, filter transmittance, and FID detector response. Peaks correspond to organic (OC), carbonate (CC), pyrolytic (PC), and elemental (EC) carbon. The final peak is a methane calibration peak.

Source: Birch and Cary (1996).

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^2 g^{-1} have been used (Hintzenberger 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 (Hintzenberger et al. (1996), and references therein) and so it is essential that accurate values for B_a are available. Hintzenberger 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 upon samples collected during a 10-day period in May 1994, they determined that the usually assumed value of 10 m^2 g^{-1} was also applicable to aerosol BC occurring in Vienna.

In 1986, the Carbonaceous Species Methods Comparison Study (CSMCS) was conducted in Los Angeles, CA, during which a number of methods for the measurement of this species were intercompared. The CSMCS was mentioned in the previous AQC PM 96 (U.S. Environmental Protection Agency, 1996), however it is interesting to add that 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 comparisons between organic carbon measurements exhibited considerably less agreement.

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 concentration 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.

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 minutes. The analyzer is comprised 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.

In 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.

3.2.5 Continuous Monitoring

The U.S. EPA expects that 100 local agency monitoring sites throughout the States will operate continuous PM monitors. However, EPA has not yet provided any guidance regarding what continuous monitoring technique to use. All currently available continuous measurements of suspended particle mass share the problem of dealing with semivolatile PM components. In order not to include particle-bound water as part of the mass, the particle bound water must be removed by heating or dehumidification. However, heating also causes 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.

3.2.5.1 TEOM

The advantages of continuous PM monitoring, and the designation of the Tapered Element Oscillating Microbalance (TEOM) as an equivalent method for PM_{10}, has led to the deployment of the TEOM at a number of air monitoring sites. The TEOM is also 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 federal reference methods sample at the ambient temperature. Thus, the TEOM may not provide data equivalent to the FRM due to 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 the implications for fine particle measurements were examined by researchers at CSIRO Atmospheric Research in Australia (Ayers et al., 1999). That group compared 24-hr 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 U.S. and Mexico were compared with 24-hr 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 portion 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}. Moreover, they suggested that this difference is likely to be larger for $PM_{2.5}$ than it is for PM_{10} (Allen et al., 1997).

3.2.5.2 RAMS

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., 1999; Obeidi and Eatough, 1999) 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. Since 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 3-14.

3.2.5.3 CAMM

Koutrakis and colleagues (Koutrakis et al., 1996; Wang, 1997) have developed the Continuous Ambient Mass Monitor (CAMM), a technique for the continuous measurement of

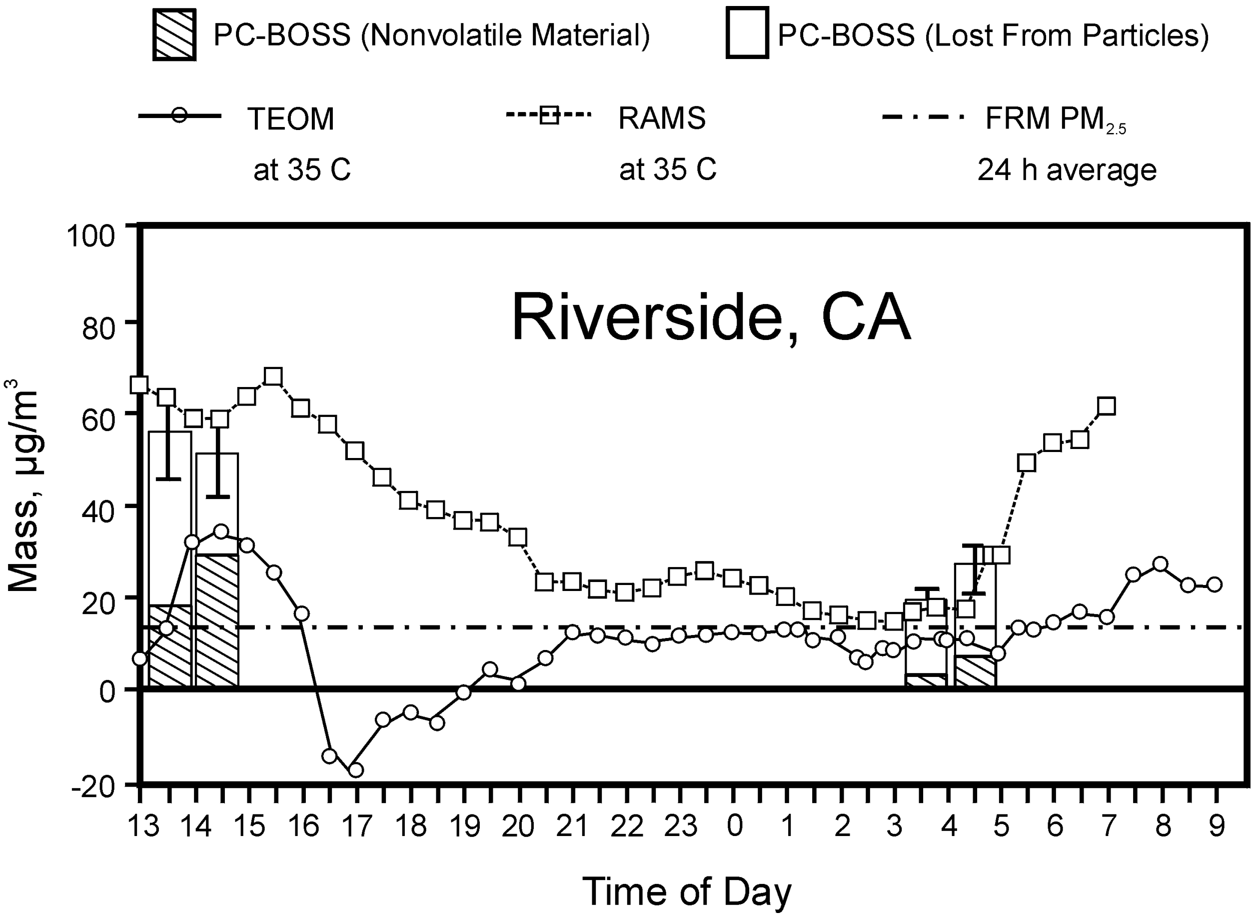

Figure 3-14. Comparison of mass measurements with collocated RAMS (real-time data), PC-BOSS (1-hour data), FRM $PM_{2.5}$ sampler (24-hour data) and a conventional TEOM monitor (real-time data). The semivolatile fine particulate matter is sampled with the RAMS and PC-BOSS, but not with the TEOM monitor 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. (1999).

ambient particulate matter mass concentration, based upon 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 mm) 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 accurately controlled. 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 were the pressure drop measurement is made to avoid artifacts due to semivolatile components.

3.2.5.4 Light Scattering

The evaporation of ammonium nitrate aerosol in a heated nephelometer was examined by Bergin et al. (1997). This is potentially of concern because the nephelometer operates in part by heating the ambient aerosol to a low reference relative humidity of 40%, in order to measure the light scattering intrinsic to the aerosol rather than including atmospheric relative humidity. Bergin et al. conducted laboratory experiments at low relative humidity (~10%) and as a function of temperature (300 – 320K), 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 due to evaporation for typical field conditions. The model estimates for their worst-case scenario suggest that the decrease in the aerosol scattering coefficient could be roughly 40%. Under most conditions, however, they estimate that the decrease in aerosol scattering coefficient is generally expected to be less than 20%.

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 for the size range of 0.016 to 0.7 mm, and a TSI aerodynamic particle sizer for the size range of 0.7 to 30 mm. 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, which is consistent with the notion that PM_{10} mass measurements would provide less information about ultrafine particles.

3.2.5.5 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 has also 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 particular 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 seven percent lower. This suggests that the mild heating in the beta gauge causes losses comparable to those due to equilibration, although the differences could be due to 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%.

3.2.5.6 Measurements of Individual Particles

A new technique, aerosol time-of-flight mass spectroscopy (ATOFMS), has demonstrated the ability for real-time measurement of correlated size and composition profiles of individual atmospheric aerosol particles (Noble and Prather, 1996; Gard et al., 1997). 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. 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 know 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 3-15.

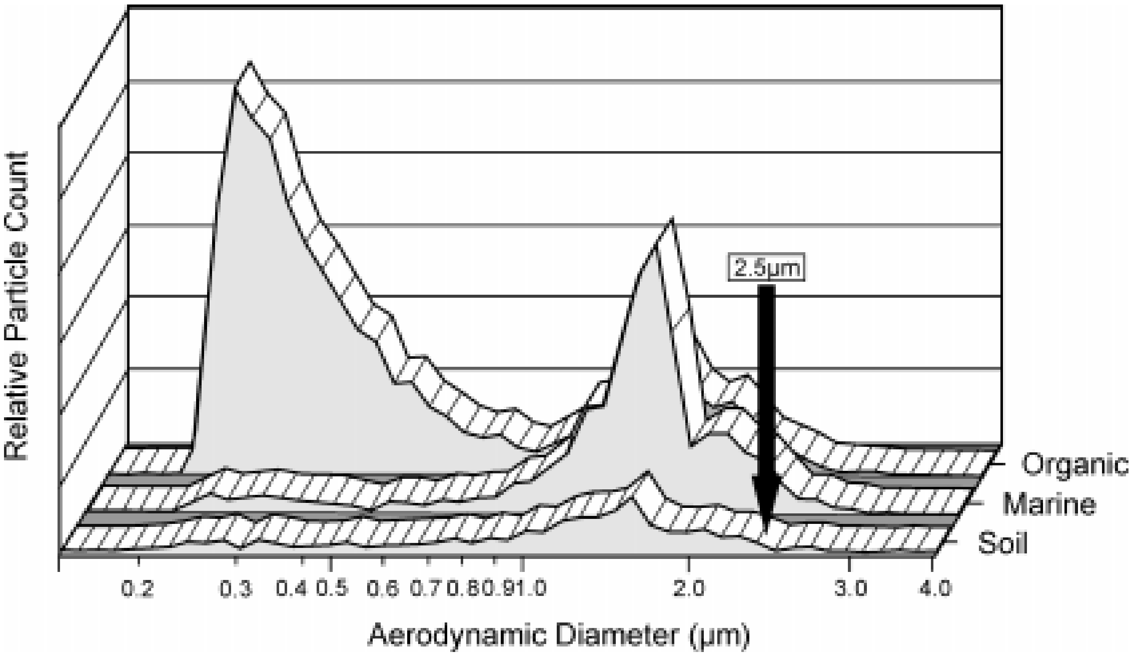

Figure 3-15. Size Distribution of particles divided by chemical classification into organic, marine, and crustal.

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

3.3 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 is 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 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. 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 which would have the same physical behavior, 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, while most of the particle volume (and therefore most of the mass) is found in particles greater than 0.1 μm. The surface area peaks around 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, are almost always 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 use ultrafine to refer to particles, generated in the laboratory, which are 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.

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) 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 the 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 3-4 and 3-5.

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 preferential 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 which 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, 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 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. 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 which varies as 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 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 acid deposition and PM concentrations. Sulfuric acid, ammonium nitrate, and organic particles are also deposited on surfaces by dry deposition. The utilization of nitrate by plants leads to the production of acidity. Therefore, dry deposition of particles can also contribute to the ecological damages caused by acid deposition.

It has been proposed that particles could act as carriers to transport toxic gases into the deep lung. Water-soluble gases, which would be removed by deposition to wet surfaces in the upper respiratory system during inhalation, could dissolve in particle-bound water and be carried with the particles into the deep lung. Equilibrium calculations indicate that particles do not increase vapor deposition in human airways. However, their calculations do show that soluble gases are carried to higher generation airways (deeper into the lung) in the presence of particles than in the absence of particles. In addition, species such as SO_2 and formaldehyde react in water, reducing the concentration of the dissolved gas-phase species, and providing a kinetic resistence to the evaporation of the dissolved gas. Thus, the concentration of the dissolved species may be greater than that predicted by the equilibrium calculations. Toxic species, such as NO, NO_2, benzene, polycyclic aromatic hydrocarbons (PAH), nitro-PAH, and a variety of allergens may be absorbed on solid particles and carried into the lungs.

The decision by the US 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.

The US Federal Reference Methods (FRM) for $PM_{2.5}$ and PM_{10} provide relatively precise (±10 %) methods for determining the mass of material remaining on a Teflon filter after equilibration. However, numerous uncertainties 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 measure what exists as a particle in the atmosphere, 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. Reasons for measuring particles include: attainment of a standard, implementation of a standard, determination of health effects, determination of ecological effects, and determination of radiative effects.

Current filtration-based mass measurements lead to significant evaporative losses, during and possibly after collection, of a variety of semivolatile components, i.e., species which 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. Other areas where choices must be made in designing an aerosol indicator include selection of an upper cut point; separation of fine-mode and coarse-mode PM; and treatment of pressure, temperature, and relative humidity.

It is becoming increasingly apparent that the semivolatile component of PM may significantly impact the quality of the measurement, and can lead to both positive and negative sampling artifacts. Negative artifacts, due to loss of ammonium nitrate and semivolatile organic compounds, may occur during sampling, due to changes in temperature, relative humidity, or composition of the aerosol, or due to pressure drop across the filter. Negative artifacts may also occur during handling and storage due to evaporation. Positive artifacts occur when volatile species adsorb onto, or react with, filter media and/or collected PM.

The loss of particulate nitrate may be determined by comparing nitrate collected on a Teflon filter to that collected on a nylon filter (which absorbs nitrate) preceded by a denuder to remove nitric acid. In two studies, the $PM_{2.5}$ mass lost due to volatilization of ammonium nitrate was found to represent a significant fraction of the total $PM_{2.5}$ mass (9% to 21%. The fraction lost was higher during summer than during fall. The nitrate obtained from Teflon filter samples was on average 28% lower than that obtained from denuded nylon filters. In these studies samples were extracted immediately after sampling. Therefore, losses that might occur during handling, storage, and equilibration were avoided. Semivolatile organic compounds (SVOC) can similarly be lost from Teflon filters due to volatilization during or after collection. Such losses can cause the $PM_{2.5}$ mass to be significantly underestimated. 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.

Much progress has been made to date in the design of diffusion denuder systems for the measurement and characterization of both the particulate and gaseous phases of semivolatile compounds. Some of the recent research has focused upon 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 due to changes in temperature and relative humidity, and identifying possible loses by absorption in impactor coatings.

It is generally desirable to collect and measure ammonium nitrate and semivolatile organic compounds. However, for many measurement 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 is due to particle-bound water. Calculation and measurements indicate that aerosol water content is strongly dependent upon composition but that liquid water could represent a significant mass fraction of aerosol concentration at relative humidities above 60%.

Federal Reference Methods (FRM) for equilibrated mass have been specified for PM_{10} and $PM_{2.5}$. In addition to FRM sampling 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: Teflon for equilibrated mass and elemental analysis, a Nylon filter with a nitric acid denuder to collect nitrate, and a quartz fiber filter for elemental and organic carbon (but without any correction for positive or negative artifacts due to adsorption of volatile organic compounds on the quartz filters or evaporation of semivolatile organic compounds from the collected particles.

The U.S. EPA expects that 100 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 continuous measurements of suspended particle mass share the problem of dealing with semivolatile PM components. In order not to include particle-bound water as part of the mass, the particle bound water must be removed by heating or dehumidification. However, heating also causes loss of ammonium nitrate and semivolatile organic components. Potential candidates for continuous measurement of mass include the Tapered Element Oscillating Microbalance (TEOM), which determines non-volatile mass by measuring the change in frequency of a vibrating quartz tube with a filter on the end; the Real-Time total Ambient Mass Sampler, RAMS, based on diffusion denuder and TEOM monitor technology, which attempts to determine nonvolatile plus semivolatile mass by using a charcoal impregnated filter (CIF) to collect any semivolatile species lost from the particles during sampling (all gas phase compounds that can be adsorbed by a CIF must be removed from the sampling stream prior to the TEOM monitor); the Continuous Ambient Mass Monitor (CAMM), a technique based upon the measurement of pressure drop increase with particle loading across a membrane filter; and a variety of techniques based on light scattering or measurement of particles mass on a filter by absorption of beta radiation. In addition to continuous mass measurement a number of techniques for continuous measurement of sulfate or semicontinuous measurements of nitrate and elements have been demonstrated. More recently, a new technique, aerosol time-of-flight mass spectroscopy (ATOFMS), that has demonstrated the ability for real-time measurement of correlated size and composition profiles of individual atmospheric aerosol particles.

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4. CONCENTRATIONS, SOURCES, AND EMISSIONS OF ATMOSPHERIC PARTICLES

4.1 INTRODUCTION

The present chapter incorporates material from Chapters 5 (Sources and Emissions of Atmospheric Particles) and Chapter 6 (Environmental Concentrations) of the previous document, Air Quality Criteria (CD96) for Particulate Matter (U.S. Environmental Protection Agency, 1996) and presents updates to these materials where available.

Information on ambient concentrations of particles in various size ranges (PM_{10}, $PM_{2.5}$, $PM_{10\text{-}2.5}$) and their chemical composition, based on specific field studies, is presented in Section 4.2. The results of field studies will be used to characterize the spatial and temporal variability in PM and its components in selected urban areas in geographically diverse regions of the United States as they become available.

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 4.3. Since 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 4.4. Estimates of contributions of various sources to ambient PM levels given by source apportionment studies are presented in Section 4.5. Information about the composition of emissions from various sources is given in Appendix A.

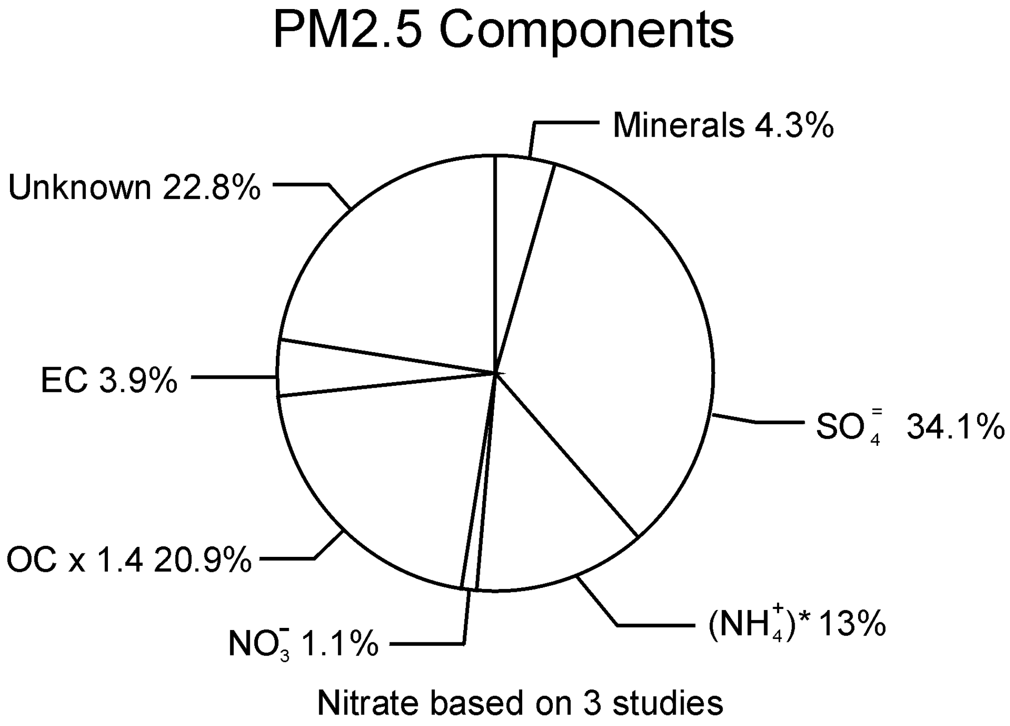
4.2 TRENDS AND PATTERNS IN AMBIENT PARTICULATE MATTER $PM_{2.5}$ CONCENTRATIONS AND TRENDS

A significant amount of data for characterizing PM_{10} mass concentrations and trends exists and that available up to about 1994 was presented in CD96. However, data sets for characterizing $PM_{2.5}$ and $PM_{(10-2.5)}$ mass or trends are not as extensive. Results from the small number of recent studies in which daily mass and composition measurements are available for extended periods will be discussed in this section. Sources of data on $PM_{2.5}$ (fine) and $PM_{(10-2.5)}$ (coarse), which were discussed in CD96, include EPA's Aerometric Information Retrieval System (AIRS) (Aerometric Information Retrieval System, 1995), IMPROVE (Eldred and Cahill, 1994; Cahill, 1996), The California Air Resources Board (CARB) (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 with only a small amount of PM_{10} data.

Summary tables giving the results of field studies which 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 CD96. The summary tables included data for mass, organic carbon, elemental carbon, nitrate, sulfate, and trace elements. The results of sixty six studies were separated and presented for the eastern, western and central United States. The data for the broad compositional categories given above from these studies are summarized in pie-chart form in Figures 4-1a, 4-1b, and 4-1c. The mean ratio of $PM_{(10-2.5)}$ to $PM_{2.5}$ from these studies was 0.33 in the East, 0.92 in the central United States, and 0.89 in the West.

PM_{10} Concentrations and Trends

Nationwide PM_{10} levels declined by 20% between 1988 and 1994 (U.S. Environmental Protection Agency, 1996). The United States was divided into seven regions and on a regional basis, reductions ranged from 17% in the Southeast to 33% in the Southwest. The estimated ratio of $PM_{2.5}$ to PM_{10} ranged from 0.38 to 0.70 in the seven regions considered. Darlington et al. (1997) extended this analysis to include 1995. Their analysis indicated a nationwide average PM_{10} level of 34 $\mu g/m^3$ in 1988 declining to 26 $\mu g/m^3$ in 1995, corresponding to an overall



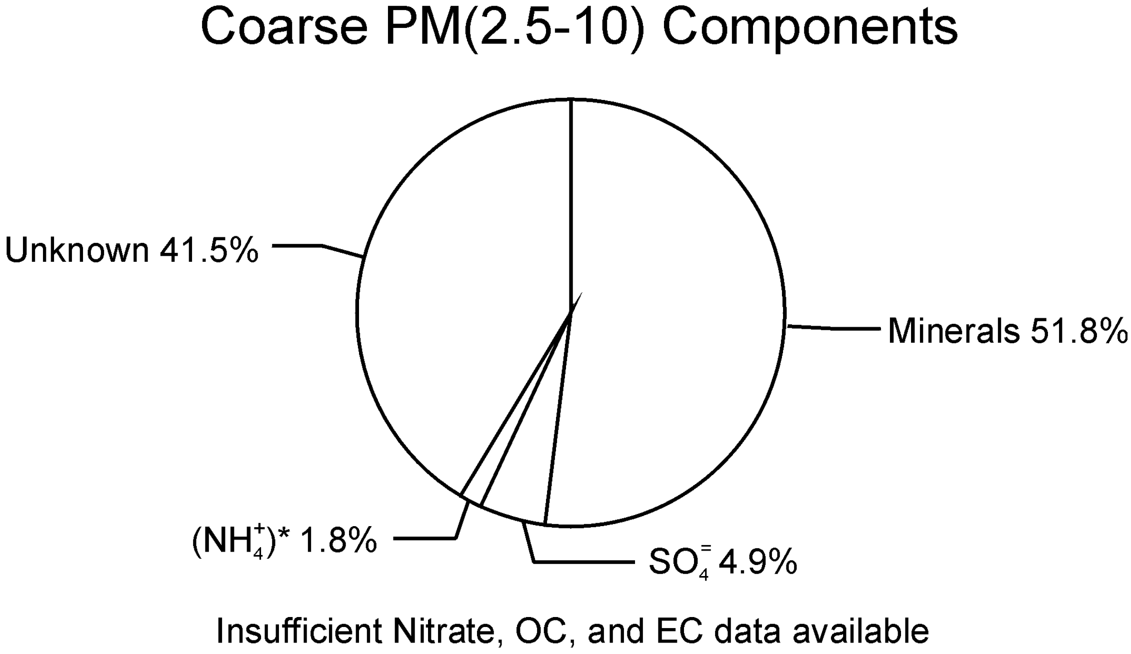
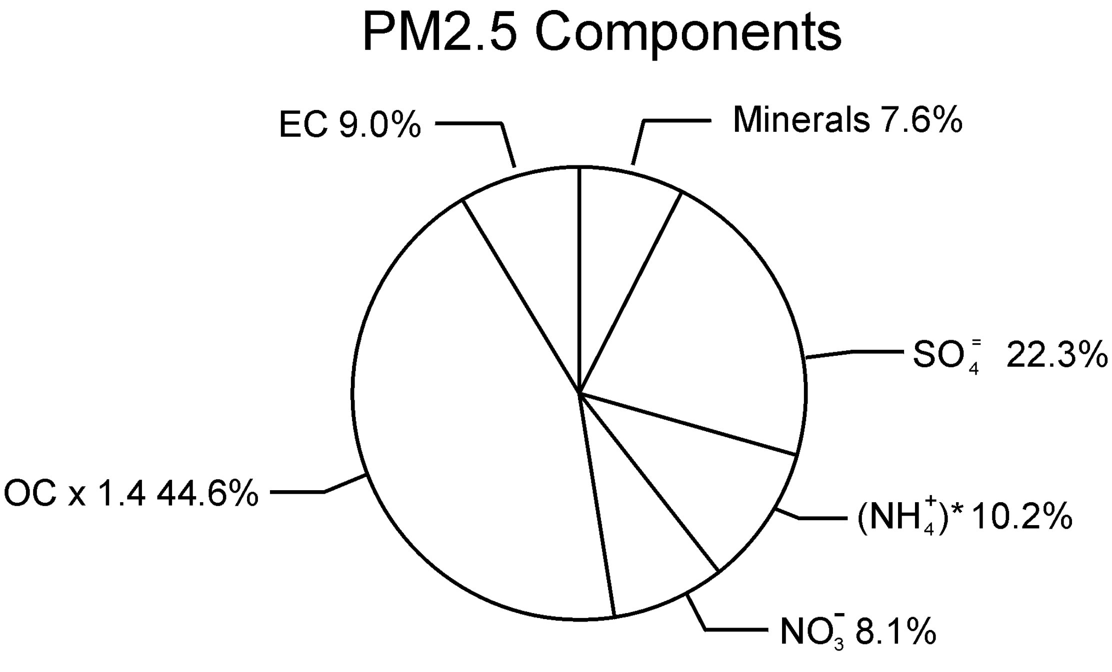
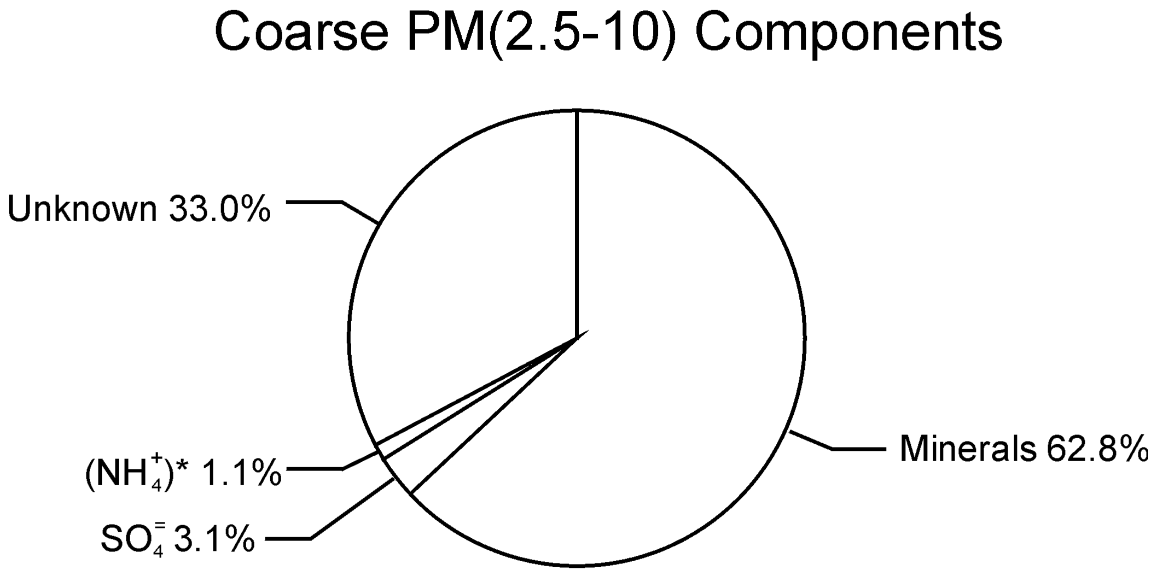


Figure 4-1a. Major constituents of particles measured at sites in the eastern United States. $(NH_4^+)^*$ represents the concentration of NH_4^+ that would be required if all $SO_4^=$ were present as $(NH_4)_2SO_4$ and all NO_3^- as NH_4NO_3. Therefore, $(NH_4^+)^*$ represents an upper limit to the true concentration of NH_4^+.

Source: U.S. Environmental Protection Agency (1996).



Reconstructed sum = 124.8%



Insufficient Nitrate, OC, and EC data available

Figure 4-1b. Major constituents of particles measured at sites in the central United States $(NH_4^+)^*$ represents the concentration of NH_4^+ that would be required if all $SO_4^=$ were present as $(NH_4)_2SO_4$ and all NO_3^- as NH_4NO_3. Therefore, $(NH_4^+)^*$ represents an upper limit to the true concentration of NH_4^+.

Source: U.S. Environmental Protection Agency (1996).

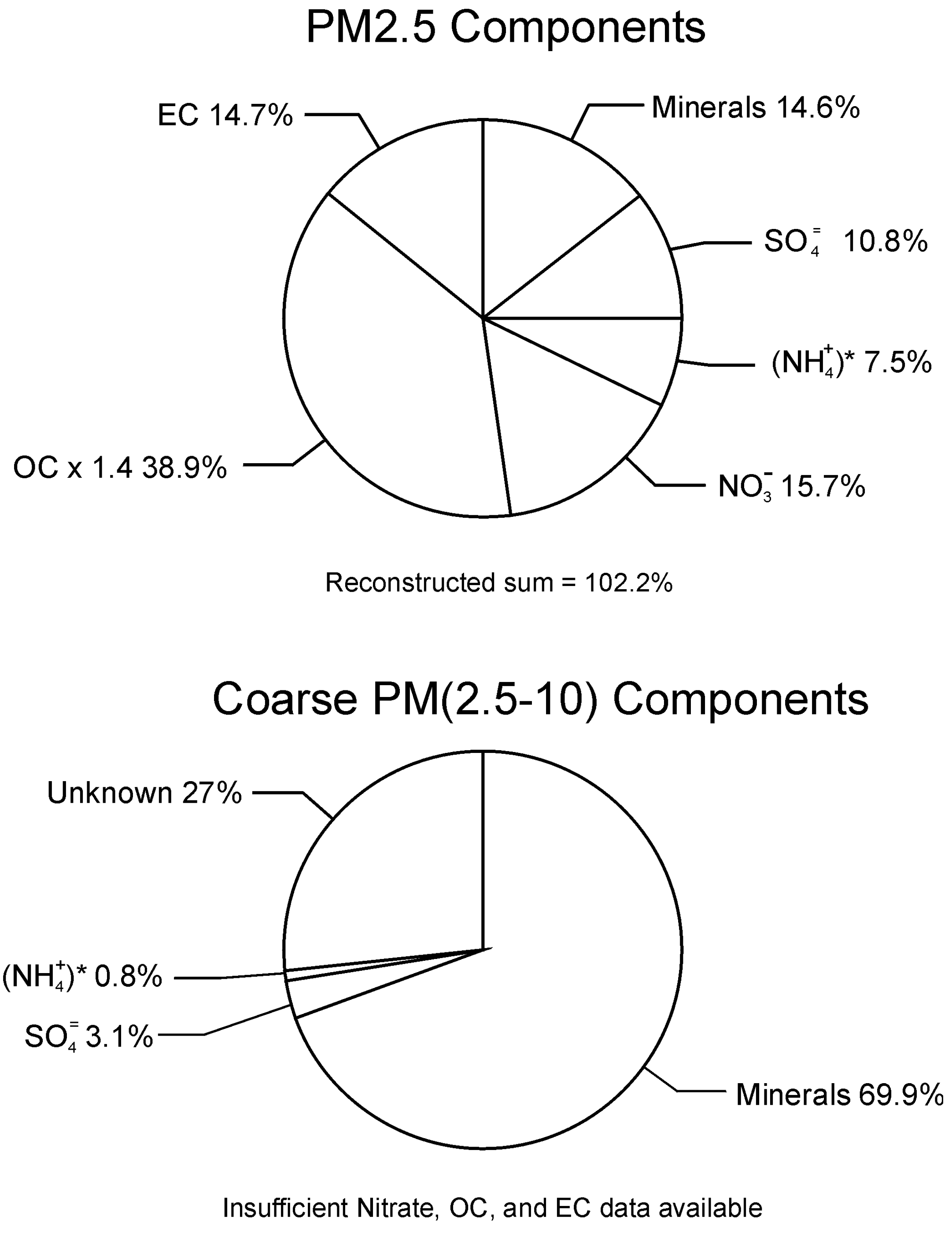


Figure 4-1c. Major constituents of particles measured at sites in the western United States. $(NH_4^+)^*$ represents the concentration of NH_4^+ that would be required if all $SO_4^=$ were present as $(NH_4)_2SO_4$ and all NO_3^- as NH_4NO_3. Therefore, $(NH_4^+)^*$ represents an upper limit to the true concentration of NH_4^+.

Source: U.S. Environmental Protection Agency (1996).

reduction of 24% or 3.4% per year. They also found that the 95th percentile value declined from 69 μg/m^3 in 1988 to 52 μg/m^3 in 1995.

$PM_{2.5}$ data have been collected continuously since 1994 as part of the children's health study in twelve 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 decrease 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. Information regarding $PM_{2.5}$ levels mainly in non-urban areas across the United States is shown in Figure 4-2. Sufficient data are not yet available to permit the calculation of nationwide trends or average levels of $PM_{2.5}$ or $PM_{(10-2.5)}$, however some general conclusions can be reached. Darlington et al. (1997) proposed that since 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 and that these factors affected fine particles more strongly than coarse particles because fine particles can be transported over longer distances.

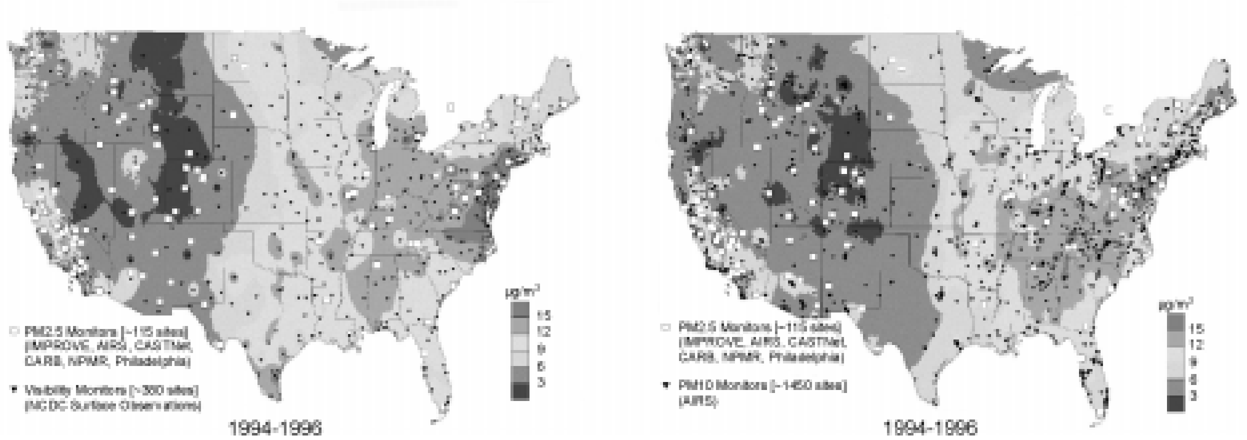


Figure 4-2. Annual average $PM_{2.5}$ concentration (1994-96).

Source: CAPITA, 1999.
(Available http://llcapita.wuste,edu/CAPITA/Capita Reports/Capita Activities 98-99/CAPITA Activities_98_99/)

A few attempts to infer "background" levels of $PM_{2.5}$ and PM_{10} have been made. The background levels most relevant to the present criteria document include (1) a "natural background" which excludes all anthropogenic sources anywhere in the world, and (2) a "natural and uncontrollable anthropogenic background" which includes anthropogenic sources outside of North America in addition to (1). Annual average natural background levels (1) of PM_{10} have been estimated to range from 4 to 8 μg/m^3 in the western United States and 5 to 11 μg/m^3 in the eastern United States. Corresponding $PM_{2.5}$ levels have been estimated to range from 1 to 4 μg/m^3 in the western United States and from 2 to 5 μg/m^3 in the eastern United States (U.S. Environmental Protection Agency, 1996). Twenty-four hour 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.

Data for characterizing the daily and seasonal variability of $PM_{2.5}$ mass and composition will be discussed in 4.2.1, the interrelations and correlations among the various PM components and parameters will be discussed in 4.2.2, the spatial variability of various PM components will be discussed in 4.2.3, new data on $PM_{2.5}$ mass from EPA compliance network will be discussed in 4.2.4, and trends of $PM_{2.5}$ mass in rural air will be discussed in 4.2.5.

4.2.1 Daily and Seasonal Variability

Information, useful for relating ambient concentrations to health effects, can be obtained by analyzing long time series of concentration data at a single site. Collocated 24-hour $PM_{2.5}$ and PM_{10} filter samples were collected at a site in southwestern Philadelphia, PA from May 1992 through April 1995 (Koutrakis, 1995). The $PM_{2.5}$ filters were analyzed by X-ray fluorescence (XRF) spectroscopy at EPA for the three years. This unique data set was collected on a nearly daily basis, thereby allowing an assessment of day-to-day variability in aerosol concentrations and relationships. EPA has also obtained similar data bases for at least one year from Phoenix, AZ and Baltimore, MD. $PM_{2.5}$ and $PM_{(10\text{-}2.5)}$ mass data were also collected at a number of sites in California (California Air Resources Board, 1995). The data collected at Philadelphia and at Riverside-Rubidoux, CA were presented in CD96 and are shown here for completeness.
In addition, the compositional data obtained at the Philadelphia and Phoenix sites will be presented in Section 4.2.2 and spatial relations among PM components in Philadelphia will be presented in Section 4.2.3.

The data for Philadelphia are presented as box plots showing the lowest, lowest tenth percentile, lowest quartile, median, highest quartile, highest tenth percentile, and highest $PM_{2.5}$ values in Figure 4-3. The four three-month averaging periods shown (March-May, June-August, September-November, December-February) correspond to the so-called climatological or meteorological seasons.

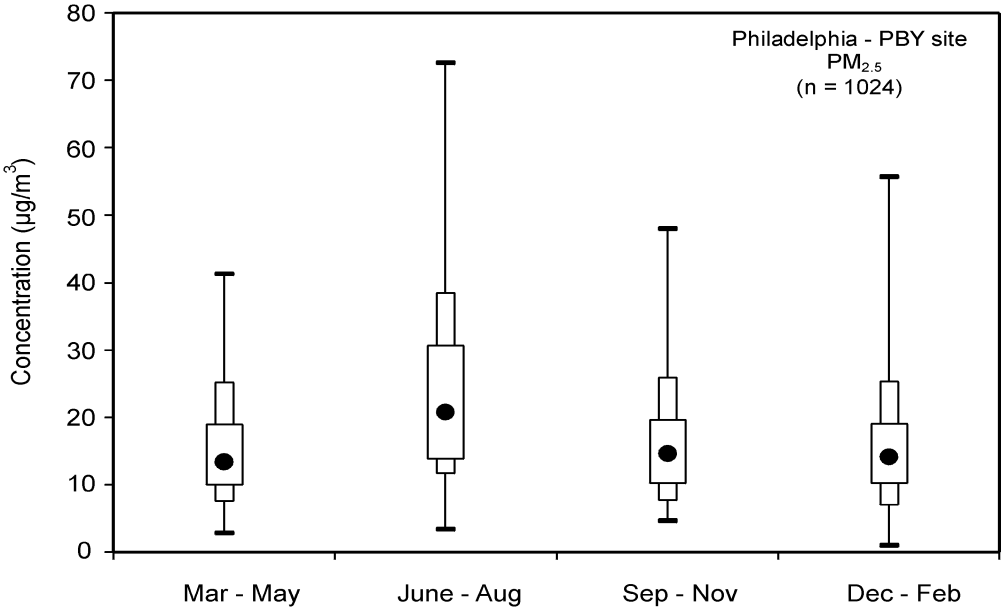


Figure 4-3. Concentrations of $PM_{2.5}$ measured at the PBY site in southwestern Philadelphia. The data show the lowest, lowest tenth percentile, lowest quartile, median (black circles), highest quartile, highest tenth percentile, and highest $PM_{2.5}$ values.

Frequency distributions for $PM_{2.5}$ are shown in Figure 4-4 for Philadelphia. Concentrations predicted from the log-normal distribution, using mean values and geometric standard deviation derived from the data, are also shown. Frequency distributions of particle concentrations at several sites in the South Coast Air Basin (Kao and Friedlander, 1995) have also been shown to be approximated reasonably well by log-normal distributions.

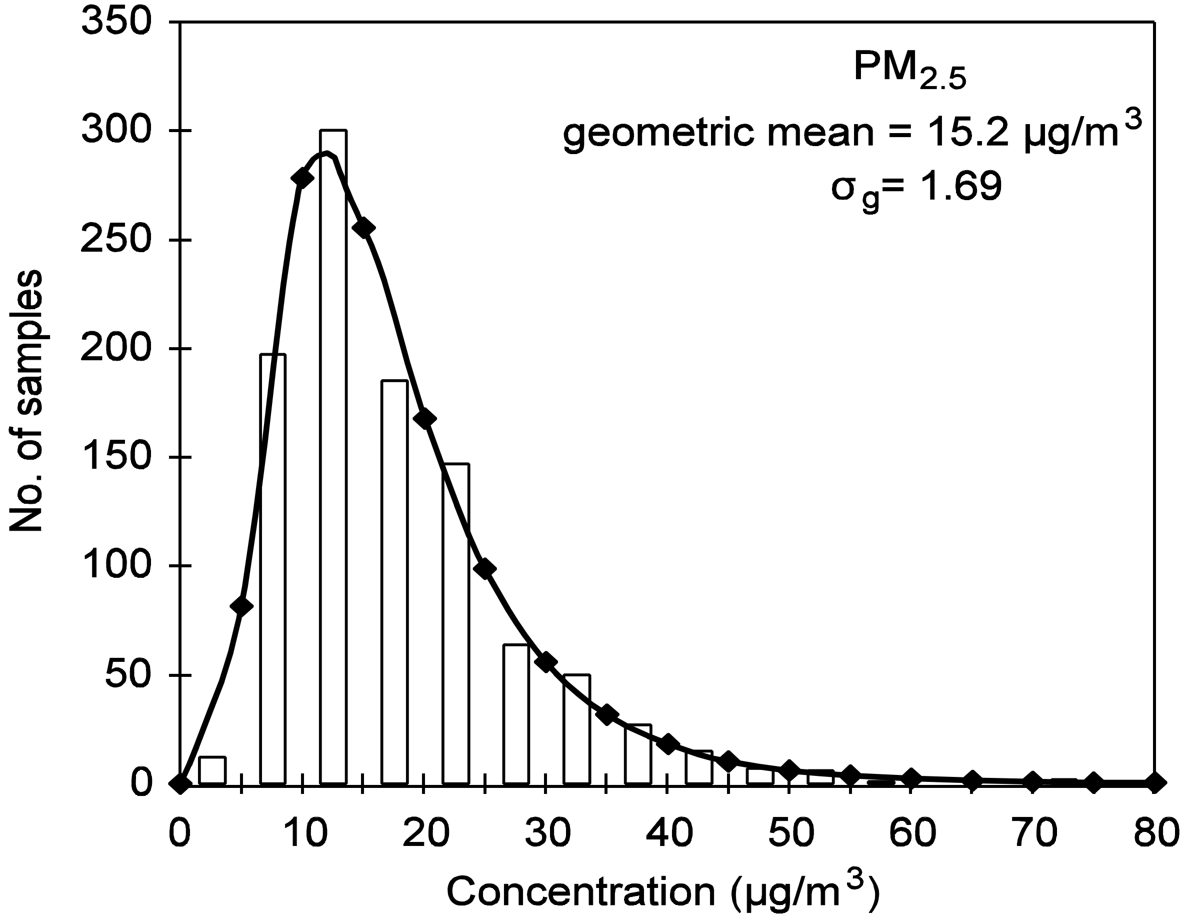


Figure 4-4. Frequency distribution of $PM_{2.5}$ concentrations measured at the PBY site in southwestern Philadelphia. Log-normal distribution fit to the data shown as solid line.

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 are 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}.

Different conclusions could be drawn about data collected elsewhere in the United States. $PM_{2.5}$ concentrations obtained in Phoenix, AZ are summarized in Figure 4-5 and frequency distributions of $PM_{2.5}$ concentrations obtained in Phoenix are shown in Figure 4-6. Day-to-day concentration differences in this data set are 2.9 ± 3.0 $\mu g/m^3$ with a maximum day-to-day

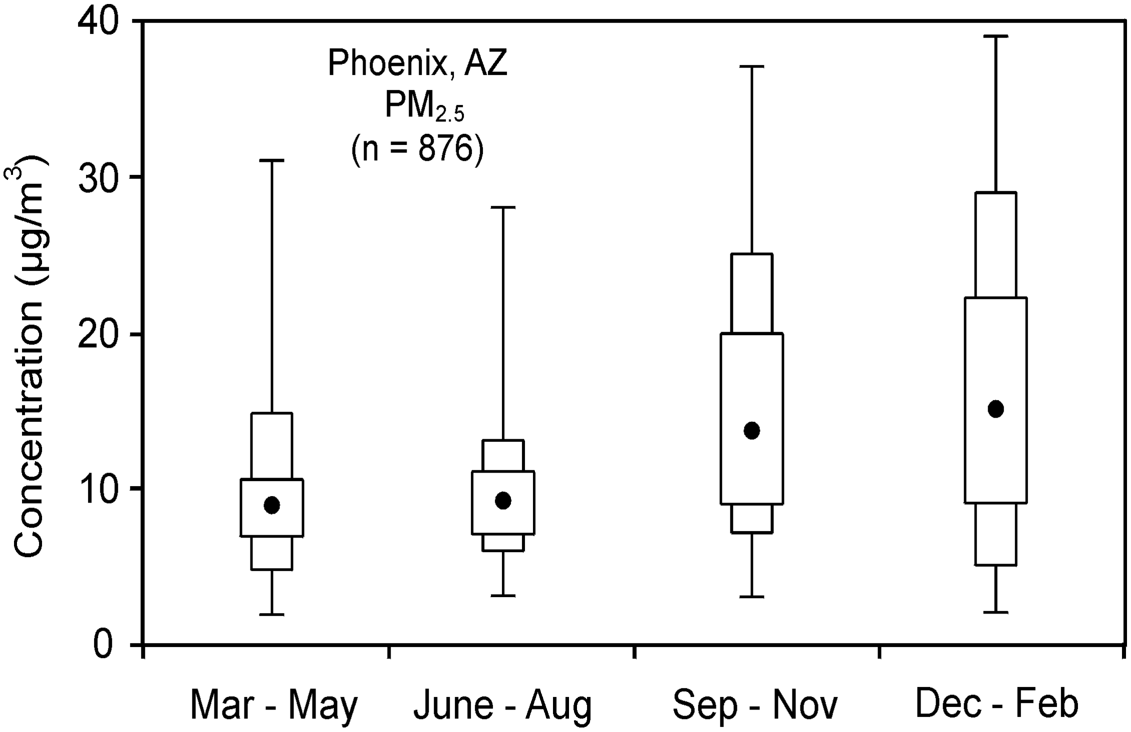


Figure 4-5. Concentrations of $PM_{2.5}$ measured at the EPA site in Phoenix, AZ. The data show the lowest, lowest tenth percentile, lowest quartile, median (black circles), highest quartile, highest tenth percentile, and highest $PM_{2.5}$ values.

concentration difference of 23 μg/m^3. $PM_{2.5}$ and $PM_{(10\text{-}2.5)}$ data were obtained at a number of sites in California on a sampling schedule of every six days with dichotomous samplers (California Air Resources Board, 1995). Data for $PM_{2.5}$ are summarized in box plot form in Figure 4-7. The frequency distribution of $PM_{2.5}$ concentrations obtained at Riverside-Rubidoux from 1989 to 1994 is shown in Figure 4-8. It can be seen that the data are not as well fit by a log normal distribution as can the data shown in Figures 4-4 and 4-6, mainly as the result of a significant number of days with $PM_{2.5}$ >100 μg/m^3 (Figure 4-7).

An examination of the data from Philadelphia, PA, 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 Philadelphia and appear to drive the daily and seasonal variability in PM_{10} concentrations there.

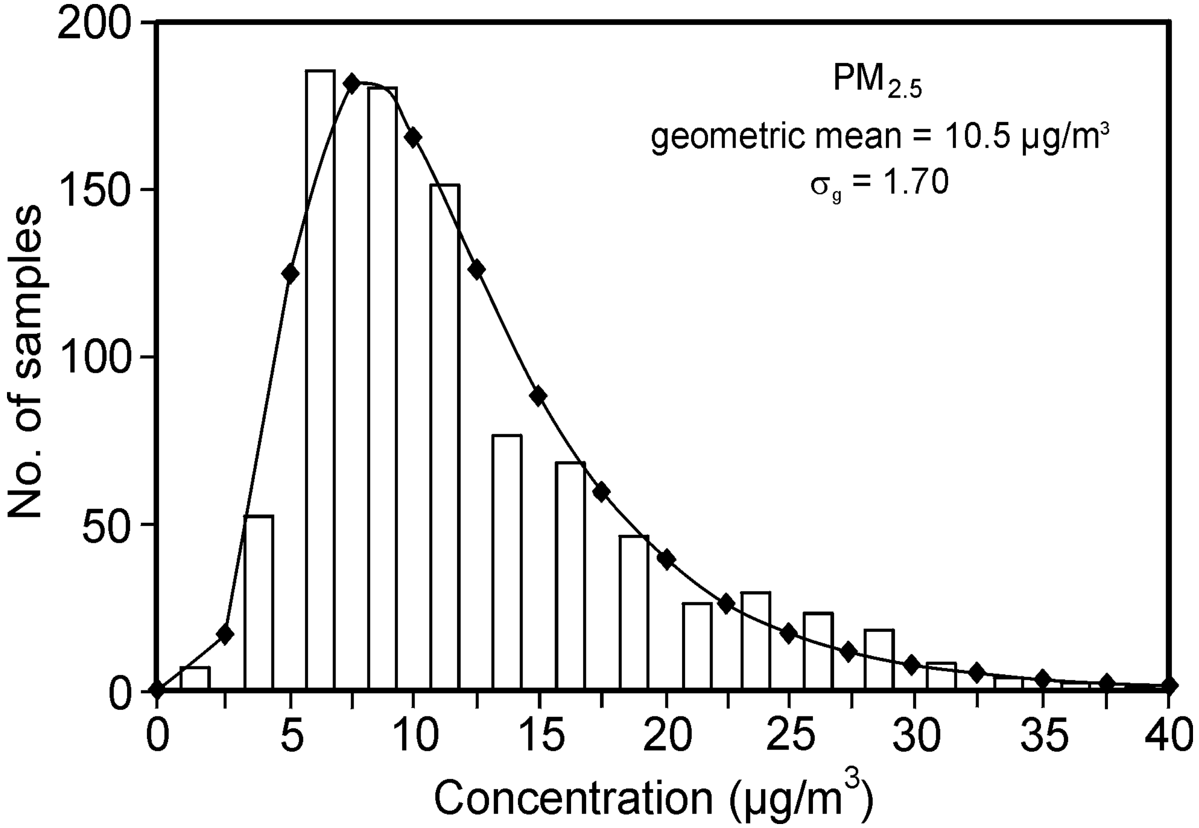


Figure 4-6. Frequency distribution of $PM_{2.5}$ concentrations measured at the EPA site in Phoenix, AZ.

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} mass is much larger in Philadelphia (0.72) 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 Philadelphia or Phoenix sites. Many of these differences could reflect the more sporadic nature of dust suspension at Riverside. These considerations demonstrate the hazards in extrapolating conclusions about the nature of variability in aerosol characteristics inferred at one location to another.

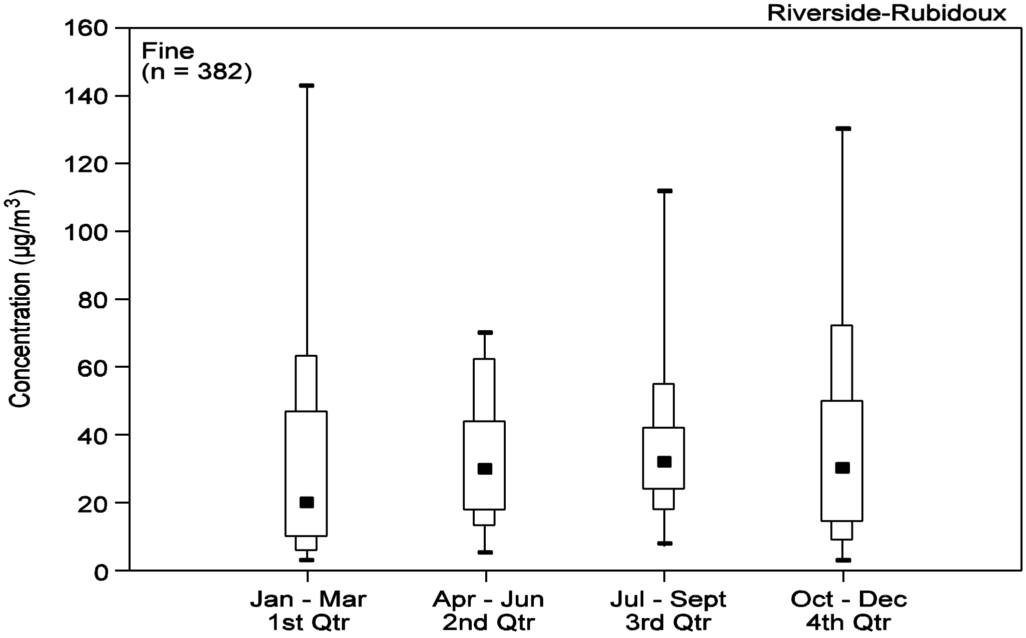


Figure 4-7. Concentrations of $PM_{2.5}$ measured at the Riverside-Rubidoux site. The data show the lowest, lowest tenth percentile, lowest quartile, median (black squares), highest quartile, highest tenth percentile, and highest $PM_{2.5}$ values.

4.2.2 Relations Between Mass and Chemical Component Concentrations

Time series of elemental composition data for $PM_{2.5}$ particles have been obtained at a few locations across the United States. The filter samples that were collected at the PBY site in southwestern Philadelphia and were used in the construction of Figures 4-3 and 4-4 were also analyzed by X-ray fluorescence. 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 4-1. Also shown in Table 4-1 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 U.S. EPA facility in Research Triangle Park, NC. As can be seen from inspection of Table 4-1, 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, while it is very small for abundant elements such as S.

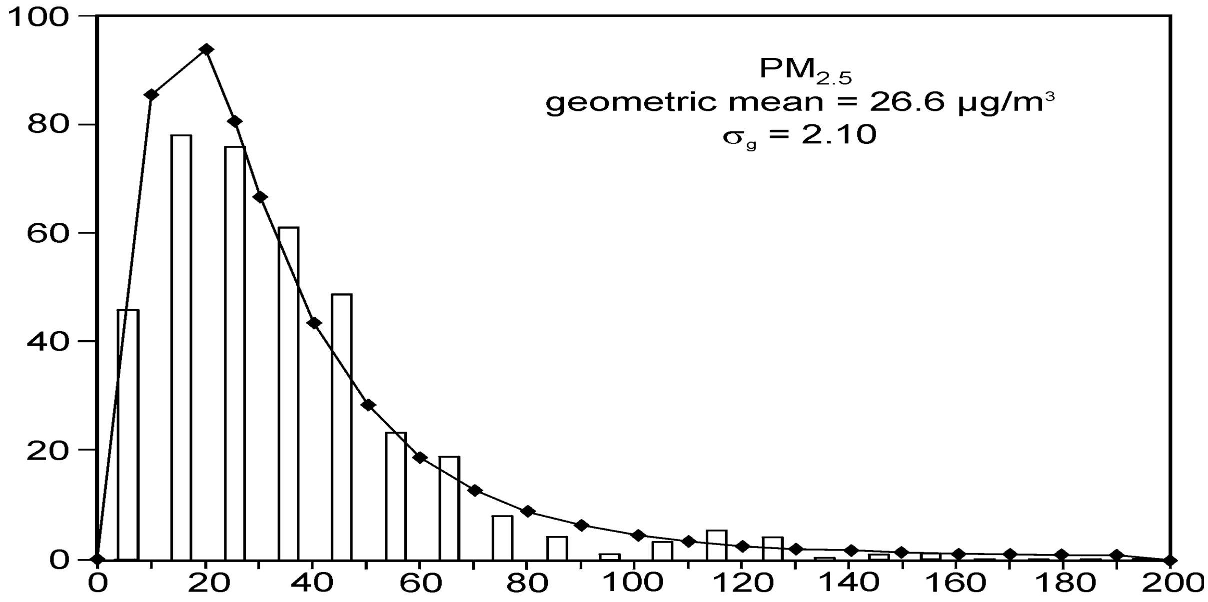


Figure 4-8. Frequency distribution of $PM_{2.5}$ concentrations measured at the Riverside-Rubidoux site.

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 while 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 due, at least partly, to higher sulfate concentrations. Correlation coefficients between $SO_4^=$ and $PM_{2.5}$ were 0.97 during the summer of 1993. Similar 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, Fe) are higher relative to $PM_{2.5}$ mass in the Phoenix data set compared to the Philadelphia data set. Sulfur is very highly correlated with $PM_{2.5}$ ($r = 0.92$) in the Philadelphia data set while it is only weakly correlated ($r = 0.16$) with $PM_{2.5}$ in the Phoenix data set. Toxic 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 while 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

TABLE 4-1. CONCENTRATIONS OF $PM_{2.5}$ ($\mu g/m^3$) 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[1]		Phoenix, AZ[2]	
	Concentration	r	Concentration	r
$PM_{2.5}$	17.0 ± 0.8 $\mu g/m^3$	1	9.4 ± 0.5 $\mu g/m^3$	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

[1] n = 1105
[2] n = 643

with $PM_{2.5}$, especially when the analytical uncertainty is high relative to concentration, e.g., for trace metals such as Co.

4.2.3 Spatial Variability

Three methods for comparing the chemical composition of aerosol databases obtained at different locations and times were discussed by Wongphatarakul et al. (1998). Log - log plots of chemical concentrations obtained at pairs of sampling sites accompanied by the coefficient of divergence (COD) were examined as a way to provide an easily visualized means of comparing two data sets[1]. Examples comparing downtown Los Angeles with Burbank and with Riverside Rubidoux are shown in Figures 4-9 and 4-10, 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 $PM_{2.5}$ and contributions from different source categories obtained at various sites in the South Coast Air Basin (SoCAB) Study are shown in Table 4-2. In Wongphatarakul et al. (1998), crustal material (crust), motor vehicle

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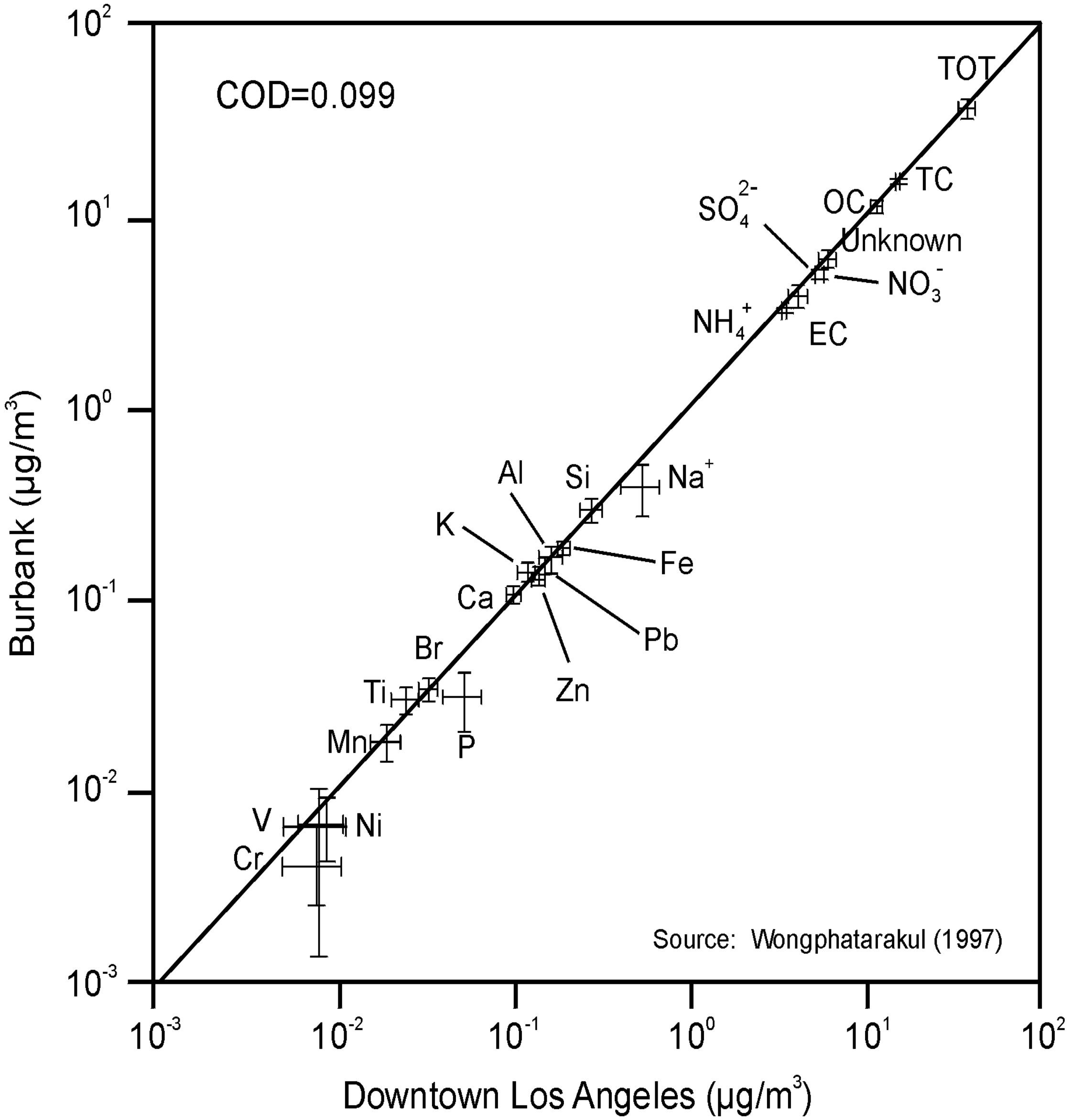
[1] The COD for two sampling sites is defined as follows:

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

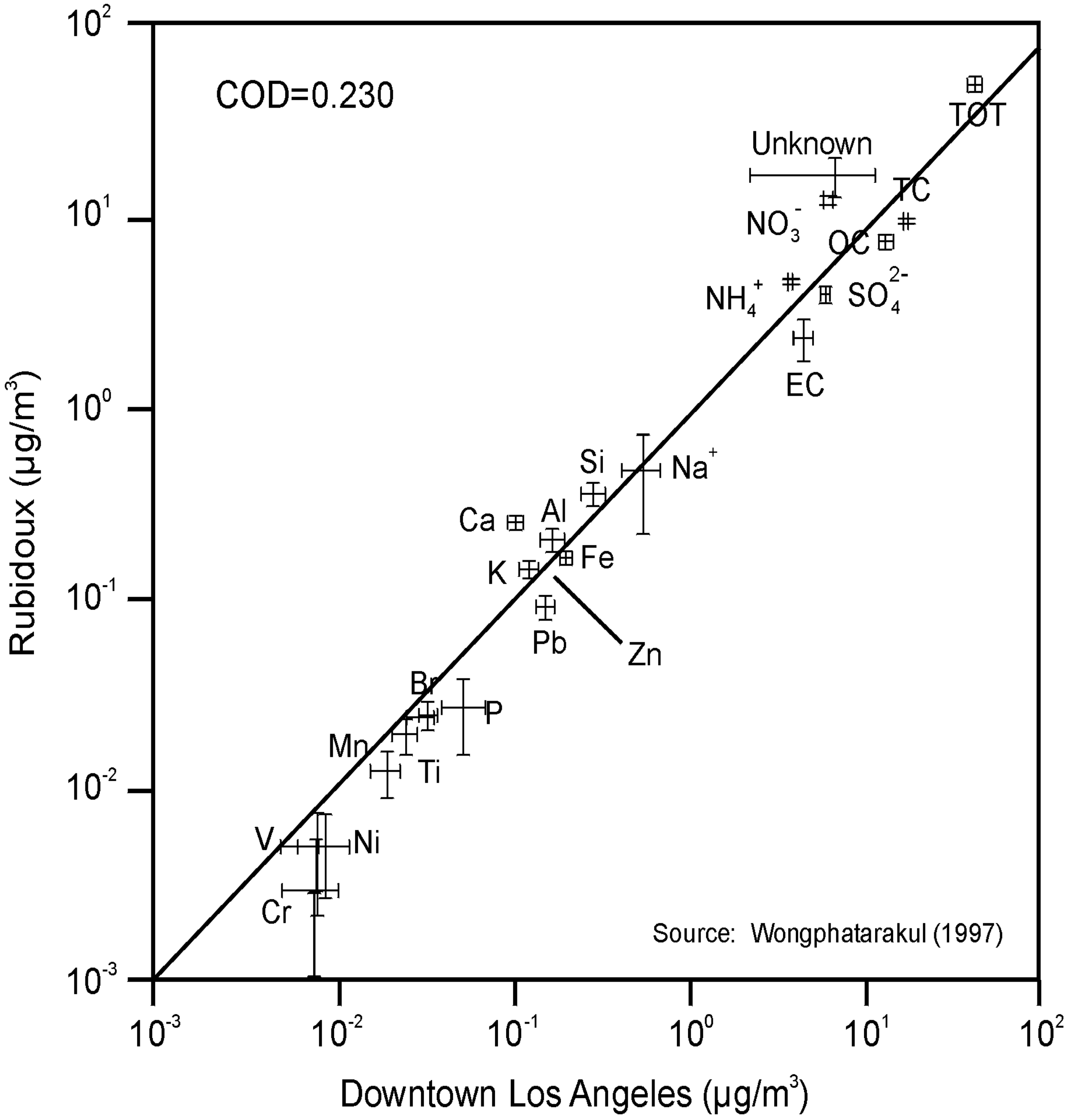
where x_{ij} represents the average concentration for a chemical component i at site j, j and k represent two sampling sites and p is the number of chemical components.



*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 4-9. $PM_{2.5}$ chemical components in downtown Los Angeles and Burbank (1986)* have similar characteristics.

Source: Wongphatarakul (1997).



*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 4-10. 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 7).

Source: Wongphatarakul (1997).

TABLE 4-2. CORRELATION COEFFICIENTS FOR SPATIAL VARIATION OF $PM_{2.5}$ MASS AND DIFFERENT SOURCES FOR PAIRS OF SAMPLING SITES IN SoCAB (1986)

	R_{tot}	$R_{crustal}$	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).

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 4-2. Total $PM_{2.5}$ (tot) varies in a similar fashion among Friedlander, 1995). Values of R_{sec} and R_{mv} are much higher than those for $R_{crustal}$ and $R_{residual\ oil}$ throughout the SoCAB suggesting a more uniform distribution of the contributions from secondary PM formation and automobiles than from crustal material and localized stationary sources.

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). The same relations were also found during the summer of 1994 at four monitoring sites as part of a separate study (Pinto et al., 1995). The results from these studies strongly suggest that $PM_{2.5}$ and $SO_4^=$ concentrations are spatially uniform throughout the Philadelphia area, and that variability in PM_{10} levels is caused largely by variability in $PM_{2.5}$ (Wilson and Suh, 1997). However, not enough data are available from regional sites to define the total areal extent of the spatial homogeneity in $PM_{2.5}$ and $SO_4^=$ concentrations observed in the urban concentrations $SO_4^=$. Correlation coefficients in Philadelphia air for $PM_{2.5}$, crustal components (Al, Si, Ca, Fe), the major secondary component (sulfate), organic carbon (OC) and elemental carbon (EC) are shown in Table 4-2a. Because these data were obtained after Pb had been phased out of gasoline, a motor vehicle contribution could not be extracted.

TABLE 4-2a. 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}
Castor Ave. and Roxboro	0.92	0.52	0.98	0.88	0.84
Castor Ave. and NE Airport	0.93	0.47	0.99	0.88	0.77
Castor Ave. and Broad St.	0.93	0.57	0.99	0.85	0.89
Roxboro and NE Airport	0.98	0.67	0.98	0.83	0.82
Roxboro and Broad St.	0.95	0.90	0.98	0.86	0.79
NE Airport and Broad St.	0.95	0.69	0.99	0.84	0.63

Source: Pinto et al. (1995).

4.2.4 Urban Concentrations and Patterns from the New $PM_{2.5}$ Compliance Network

4.2.5 Trends and Patterns

4.2.5.1 Visual Range/Haziness

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).

Visual range i.e., the maximum distance at which an observer can discern the outline of an object, is an understandable and for many purposes an appropriate measure of the optical environment. It has the disadvantage, however, of being related inversely to aerosol concentration. It is usual, therefore, to convert visual range to a direct indicator of fine mode. particle concentration. The quantitative measure of haziness is the extinction coefficient, B_{ext}, defined as B_{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. Husar et al. (1994) use K=1.9 in accordance with the data given by Griffing (1980). The extinction coefficient is in units of km^{-1} and is proportional to the concentration of light scattering and absorbing aerosols and gases. The radiative transfer characteristics which determine the visual range depend on time of day. Only local noon observations are used.

Haze Trend Summary

The U.S. haze patterns and trends from 1960 to 1992 were presented in the CD96 as 16 haze maps representing four time periods (5 year averages centered at 1960, 1970, 1980, and 1990) and the four climatological seasons (Quarter 1 is for December of prior year, January and February of indicated year, etc.) seasons. The average haze patterns, centered on 5 year averages for 1980 and 1990 are shown in Figure 4-11 and will be replaced by similar data for 1990 and 1995. Haze is indicated by the 75th percentile of the extinction coefficient which is calculated from the visual range, corrected to 60% relative humidity by the Koschmeider relationship.

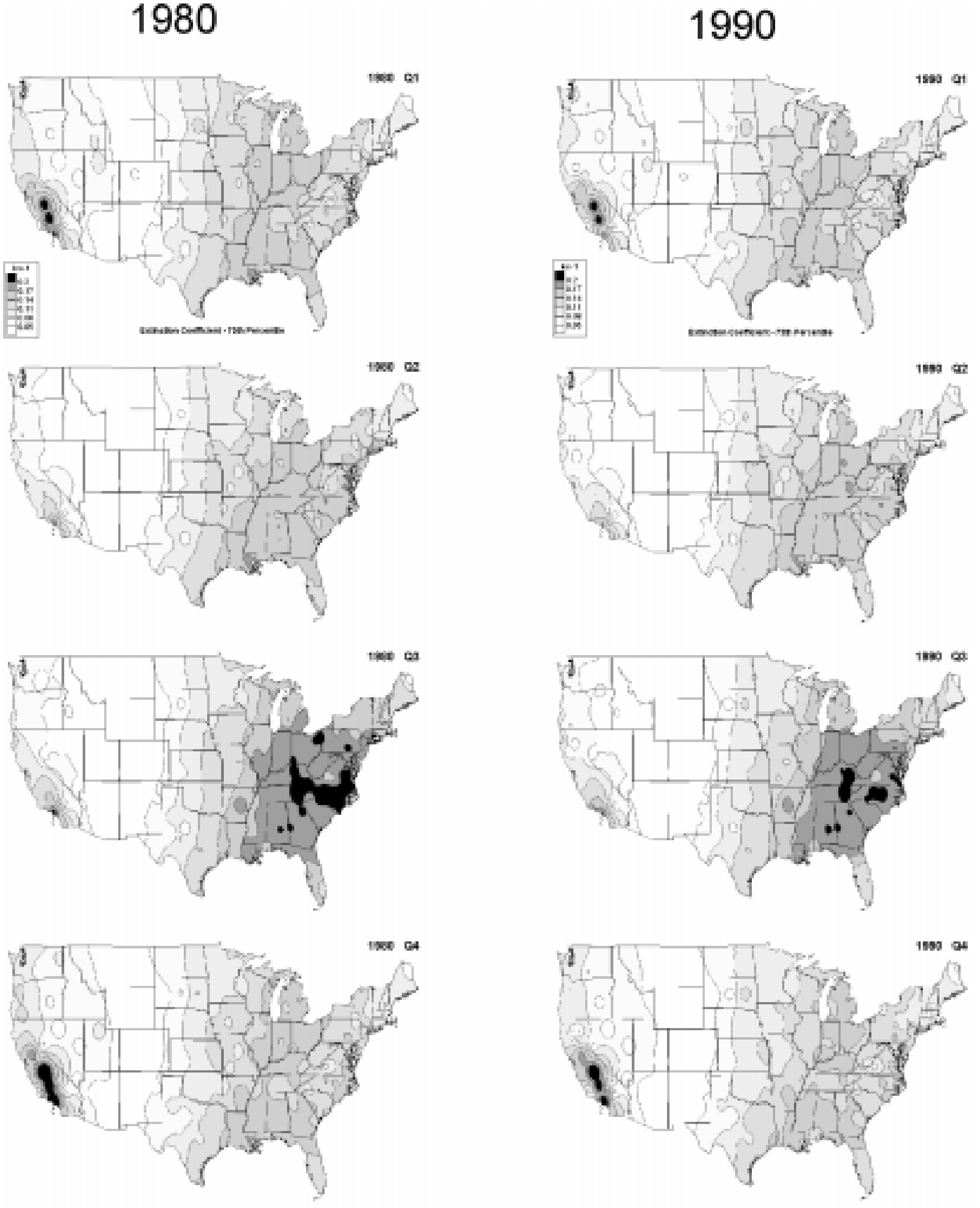


Figure 4-11. Five-year average haze patterns (75th percentile of the extinction coefficient) centered on 1980 and 1990 (to be replaced with patterns for 1990 and 1995). The relationship between haze, expressed as extinction coefficient (corrected to 60% relative humidity) is 1.9/extinction coefficient 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 = 11.2, 0.14 = 13.6, 0.11 = 17.3, 0.08 = 23.8, and 0.05 = 38.0. Q1 = Dec., Jan., Feb.; Q2 = March, April, May; Q3 = June, July, Aug.; Q4 = Sept., Oct., Nov.

Regional Pattern

Trends for specific regions in the eastern U.S. might be updated, from 1992 to 1998, and be presented in a manner similar to that shown in Figure 4-12 for 1940 to 1990 (CD96). The trend graphs represent the 75th percentile of B_{ext} for the stations located within the designated region. The trends are presented for Quarters 1 (winter) and 3 (summer) separately. The northwestern U.S. exhibits an increase of Quarter 3 haze between 1960 and 1970, and a steady decline between 1973 (0.22) and 1992 (0.12). In the winter quarter the haziness has steadily declined from 0.15 to 0.10 in the 30-year period. The Mid-Atlantic region that includes the Virginias and Carolinas shows a strong summer increase 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 (1960-1970). The upper Midwest (Figure 4-12) shows an opposing trend for summer and winter. While summer haze has increased, mostly 1960-1973, the winter haze has declined.

4.2.5.2 Urban Trends

$PM_{2.5}$ trends will be shown for those cities which have several years of $PM_{2.5}$ data as they become available. As an example, trend data from Stockton-Hazleton, CA are shown in Figure 4-13.

4.3 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 4-3 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, petrochemicals and wood products processing; mills and elevators used in agriculture; erosion

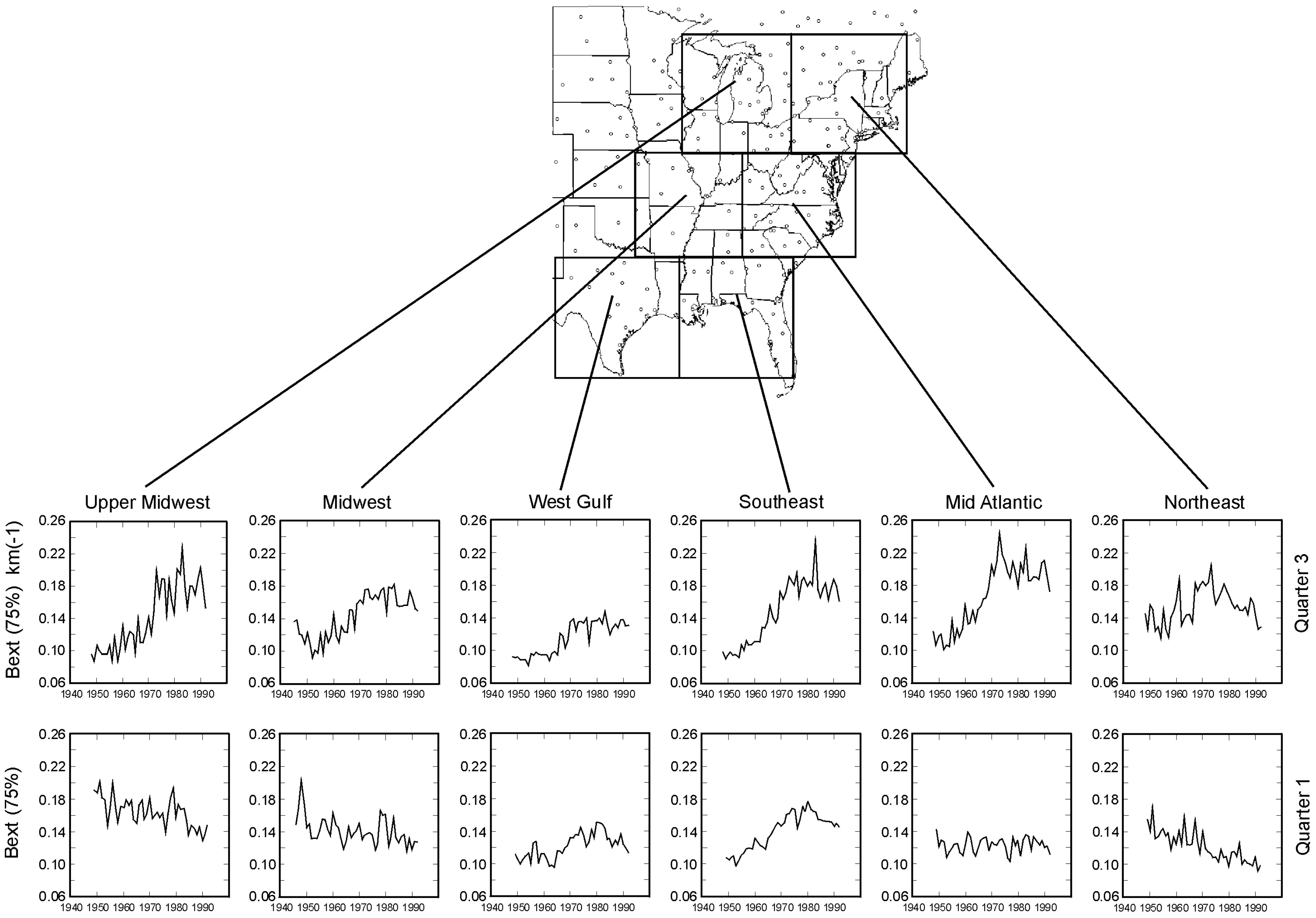


Figure 4-12. Secular haze trends (1940 to 1990) for six eastern U.S. regions, summer (Q1) and winter (Q2).

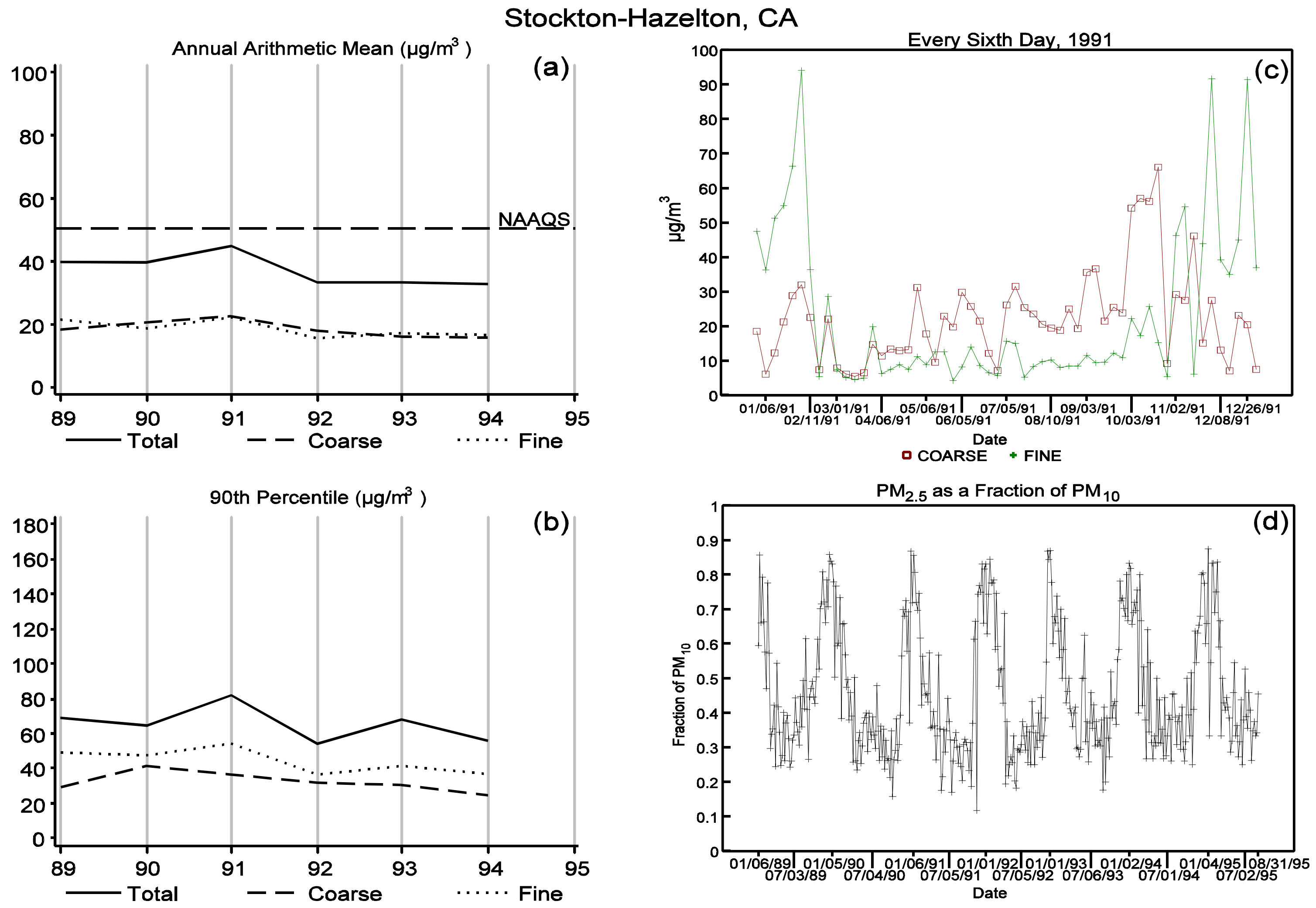


Figure 4-13. Trend data from Stockton-Hazelton from CARB: (a) fine, coarse, and total means; (b) fine, coarse, and total 90th percentiles; (c) every-sixth-day fine and coarse mass for 1991; and (d) fine and coarse mass as a fraction of PM_{10}.

TABLE 4-3. CONSTITUENTS OF ATMOSPHERIC PARTICLES AND THEIR MAJOR SOURCES

	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**[1]
NO_3^- Nitrate	—	Motor vehicle exhaust[2]	—	—	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, re-entrainment	Fugitive dust; paved, unpaved roads; agriculture and forestry	Erosion, re-entrainment	**Fugitive dust; paved, unpaved road dust, agriculture and forestry**	—	—
NH_4^+ Ammonium	—	Motor vehicle exhaust[2]	—	—	Emissions of NH_3 from wild animals, undisturbed soil	**Emissions of NH_3 from animal husbandry, sewage, fertilized land**
Organic carbon (OC)	Wild fires	**Open burning, wood burning, motor vehicle exhaust,** cooking	—	Tire and asphalt wear, paved road dust	Oxidation of hydrocarbons emitted by vegetation, (terpenes, waxes); wild fires	Oxidation of hydrocarbons emitted by motor vehicles, open burning, wood burning
Elemental carbon (EC)	Wild fires	**Motor vehicle exhaust, wood burning,** cooking	—	—	—	—
Metals	Volcanic activity	**Fossil fuel combustion, smelting,** brake wear	Erosion, re-entrainment, organic debris	—	—	—
Bioaerosols	Viruses, bacteria	—	Plant, insect fragments, pollen, fungal spores, bacterial agglomerates	—	—	—

[1] Major source of each component shown in boldface type.

[2] Relatively minor source of substance, included only for the sake of completeness.

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. 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. Since 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 4-3 are listed. Chemical characterizations of primary particulate emissions from a wide variety of natural and anthropogenic sources as shown in Table 4-3 were given in Chapter 5 of CD96. Summary tables of the composition of source emissions presented in CD96 and updates are given in Appendix A. 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, which 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 which are related to human activities (e.g., fertilized lands, domestic and farm animal waste). It is difficult to describe emissions from biomass burning as either natural or anthropogenic. Clearly, fuel wood burning is an anthropogenic source of PM, whereas wildfires would be a natural source. Forest fires have been included as a natural source, because of the lack of information on the amount of prescribed burning or accidental fires caused by humans. Similar considerations apply to the biogenic emissions of trace metals which may be remobilized from anthropogenic inputs.

Receptor models are perhaps the primary means used to estimate source category contributions to particulate matter at individual monitoring sites. Receptor models relate source category contributions to ambient concentrations based on composition analysis of ambient particulate and source emissions samples. In addition, receptor models have been developed for apportioning source categories of primary particulate matter and are not formulated to include the processes of secondary particulate matter formation. However, hybrid receptor models which use elements from a chemical transport model have been used to apportion source categories of gaseous precursors to secondary particulate matter (Stevens and Lewis, 1984).

A number of specialty conference proceedings, review articles, and books have been published to provide greater detail about source category apportionment receptor models (Cooper and Watson, 1980; Watson et al., 1981; Macias and Hopke, 1981; Dattner and Hopke, 1982; Pace, 1986; Watson et al., 1989; Gordon, 1980, 1988; Stevens and Pace, 1984; Hopke, 1985, 1991; Javitz et al., 1988). Watson et al. (1994a) present data analysis plans which include receptor models as an integral part of visibility and PM_{10} source apportionment and control strategy development. 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 CD96. The collection of the source category characterization profiles shown in Appendix 4A has been motivated in many cases by the need to use them in receptor modeling applications.

4.3.1 Source Contributions to Ambient PM

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 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 4-4. 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 4-5. 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

TABLE 4-4. 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
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]	—	—	

[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

TABLE 4-5. RECEPTOR MODEL SOURCE CONTRIBUTIONS TO PM_{10}

		% Contribution[3]										
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., 1994a)	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., 1994a)	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[j]	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., 1994a)	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., 1994a)	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., 1994a)	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 4-5 (cont'd). RECEPTOR MODEL SOURCE CONTRIBUTIONS TO PM$_{10}$

		% Contribution[3]										
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, steel haul road dust.
[w] Incineration.
[x] Unexplained mass.

to study. The results of the PM_{10} source apportionment studies were given in CD96 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 4-4 and 4-5. These differences reflect the nature of sources which are important for producing fine and coarse particulate matter shown in Table 4-3. They are also 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 only been recently that motor vehicle emissions can be 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 while 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 4-4 and 4-5 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 (Figure 4-1a). 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 4-4. The most notable difference in the relative importance of major source categories of $PM_{2.5}$ shown in Table 4-4 and PM_{10} shown in Table 4-5 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 4-5. 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 4-5, 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 has been virtually eliminated from vehicle fuels. However, recently organic species have replaced Pb as a source marker for motor vehicle emissions (e.g., Rogge et al., 1993a).

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 4-5, so average source contribution estimates are probably not representative of annual averages. Quoted uncertainties in the estimated contributions of the individual sources shown in Table 4-4 range from 10 to 50%. Uncertainties of source contribution estimates are not usually reported with the average values summarized in Table 4-5. 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.

4.4 EMISSIONS ESTIMATES AND THEIR UNCERTAINTIES

In principle, source contributions to ambient PM could also 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). A number of 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, apart from uncertainties in the inventories given above. 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 which 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.

4.4.1 Emissions Estimates for Primary Particulate Matter and SO_2, NO_x, and VOCs in the United States

Estimated emissions of primary $PM_{2.5}$ from different sources in the United States are summarized in Figure 4-14. The estimates are based on information presented in the U.S. EPA National Air Pollutant Emission Trends Report, 1997 (U.S. Environmental Protection Agency, 1998) to which the reader is referred for detailed tables showing trends in $PM_{2.5}$ emissions from a number of source categories from1990 to 1997; descriptions of the methodology used in the construction of these tables; and descriptions of the uncertainties 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 (VOCs), and ammonia (NH_3).

Estimated total nationwide emissions of primary $PM_{2.5}$ were 7.5 Tg yr^{-1} in 1997. The category of fossil fuel combustion referred to in Figure 4-14 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

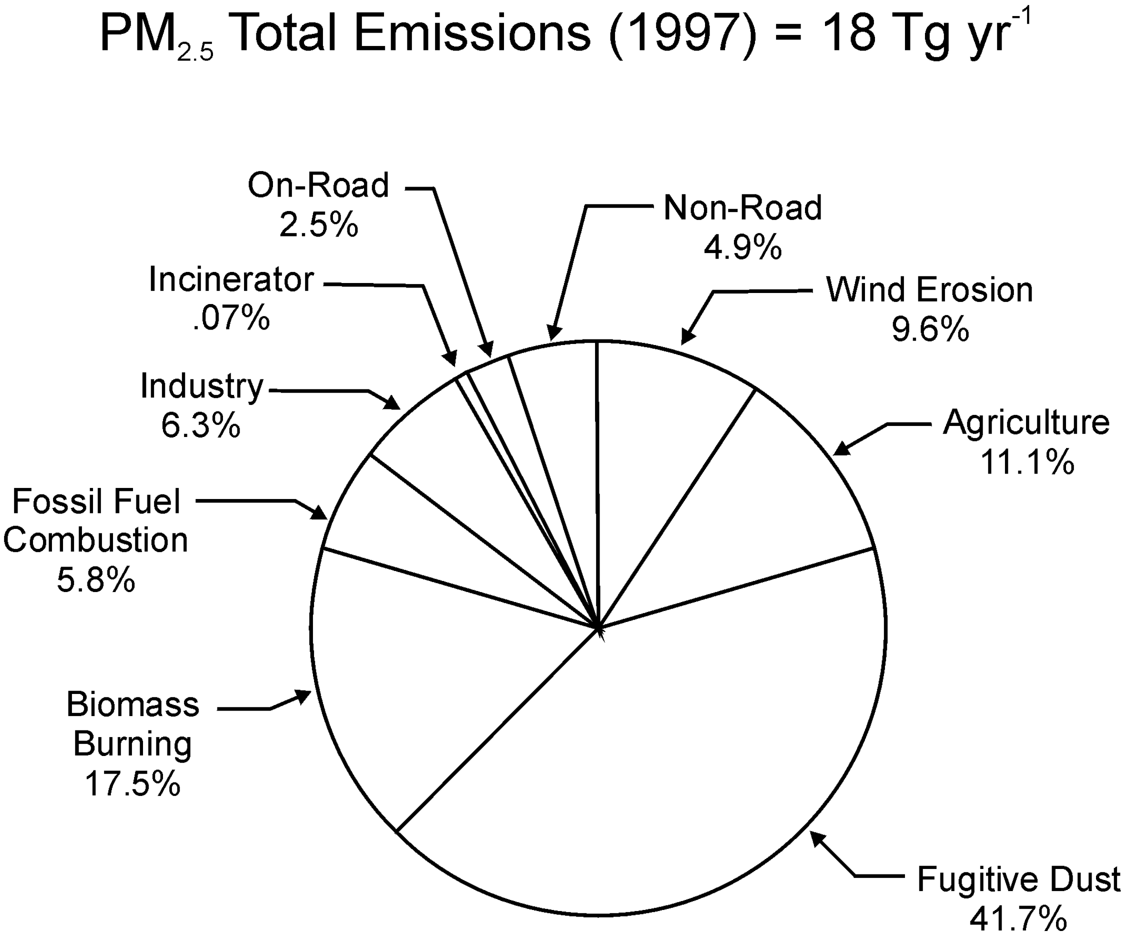


Figure 4-14. Nationwide emissions of PM$_{2.5}$ from various source categories.

Source: U.S. Environmental Protection Agency (1998).

and transport of industrial goods. Incineration refers to the burning of non-biomass waste by residences and municipalities. The on-road vehicles category includes contributions from gas and diesel powered vehicles. Non-road engines and vehicles include their emissions in transportation, construction, and other commercial, industrial and recreational activities. Wind erosion refers to the raising of mineral dust by the wind. The biomass burning category includes contributions from residential wood burning, open burning of vegetation, and forest fires. The agriculture category includes mainly emissions of soil dust related to the production of agricultural crops and livestock. Fugitive dust refers mainly to mineral dust raised by on-road and non-road vehicles during their operation. As can be seen from inspection of Figure 4-14, the raising of mineral dust by wind erosion, agriculture, and as fugitive dust constitutes the largest primary source (62.4%) of $PM_{2.5}$ on a nationwide basis. Biomass burning constitutes the second largest primary source (17.5%) of $PM_{2.5}$. The gross composition of emissions from most of these categories is summarized in Table 4-3. Total emissions of $PM_{2.5}$ as well as contributions from individual source categories were relatively constant over the period from 1990 to 1997 (U.S. Environmental Protection Agency, 1998). While crustal dust constitute over 60% of the total $PM_{2.5}$ inventory, they constitute less than about 10% of the source strengths inferred from the receptor modeling studies shown in Table 4-4. However, it should be remembered that secondary components often represent the major fraction of ambient samples. Dust sources constitute 88% of the annual average PM_{10} National Emissions Inventory (U.S. Environmental Protection Agency, 1994), but they average more than 50% of the contribution to average PM_{10} concentrations in only about 40% of the entries shown in Table 4-5. 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 widely dispersed and 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.

The geographic distribution of primary $PM_{2.5}$ emissions is shown in Figure 4-15 and the distribution of primary PM_{10} emissions is shown in Figure 4-16. As may be expected, high emissions of $PM_{2.5}$ are centered around many large urban areas. Although mineral dust sources account for most of the emissions, their contributions are distributed much more widely than are those from combustion sources. The nature of the distribution of mineral dust sources is shown more clearly in Figure 4-16 where high densities of PM_{10} emissions are also found in sparsely populated areas.

Estimated contributions from individual sources to emissions of gaseous precursors to secondary PM formation are summarized in Figure 4-16 for SO_2 , NO_x , VOCs, and NH_3. Information about the yield of particulate matter formed during the oxidation of VOCs is given in Section 3.4.

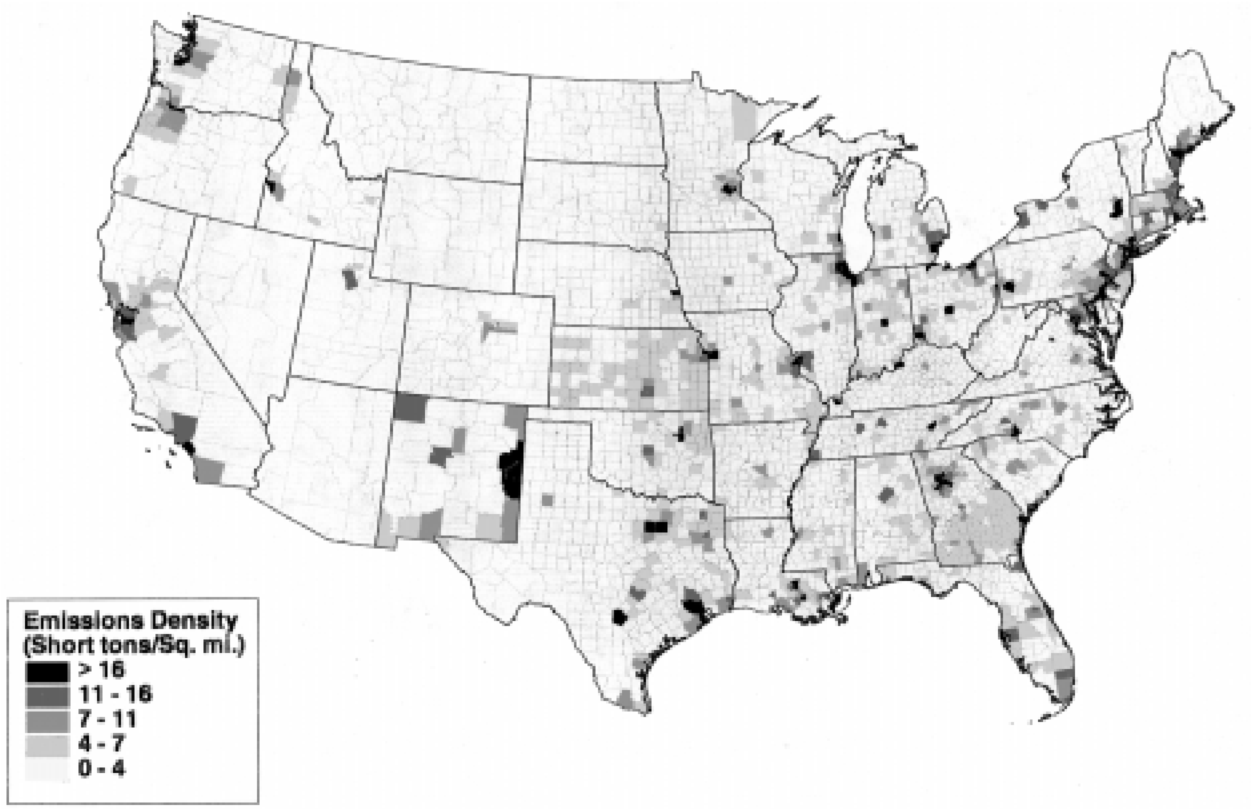


Figure 4-15. Distribution of primary $PM_{2.5}$ emissions across the United States.

Source: U.S. Environmental Protection Agency (1998).

Although total emissions of gaseous precursors (SO_2, NO_x, VOC's, and NH_3) are shown in Figure 4-17, it should be remembered that these values cannot be directly translated into production rates of particulate matter. Dry deposition and precipitation scavenging of some of these gases can occur before they are converted to particulate matter 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. While the chemical oxidation of SO_2 will lead quantitatively to the formation of $SO_4^=$, the yield of particulate matter from the oxidation of VOCs will be much less because only a small fraction of

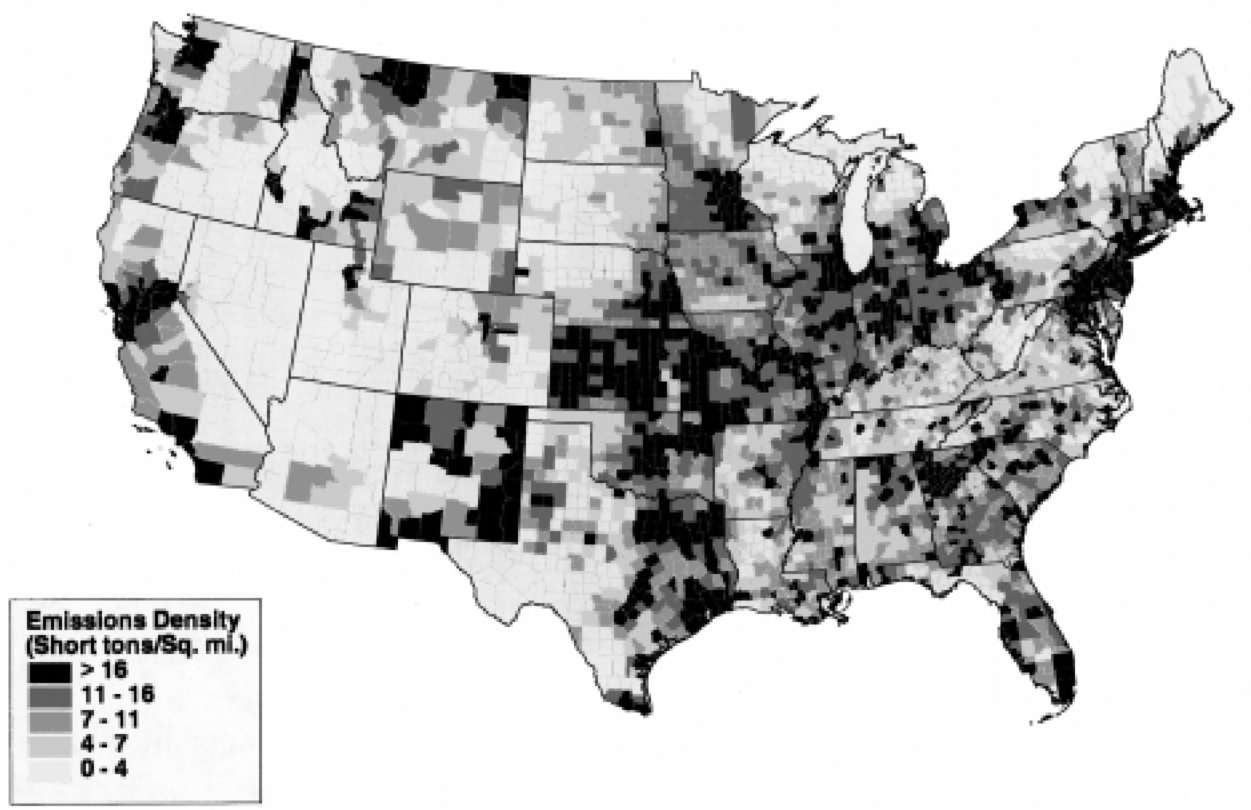


Figure 4-16. Distribution of primary PM_{10} emissions across the United States.

Source: U.S. Environmental Protection Agency (1998).

VOC's react to form particles, and those that do have efficiencies less than 10% (c.f. Section 3.4).

The values shown in this section are based on annually averaged quantities. 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 which reaches its peak during cold weather. Cold weather also affects motor vehicle exhaust particulate emissions, both in terms of chemical composition and emission rates (e.g., Watson et al., 1990a; 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, while the minimum occurs during the

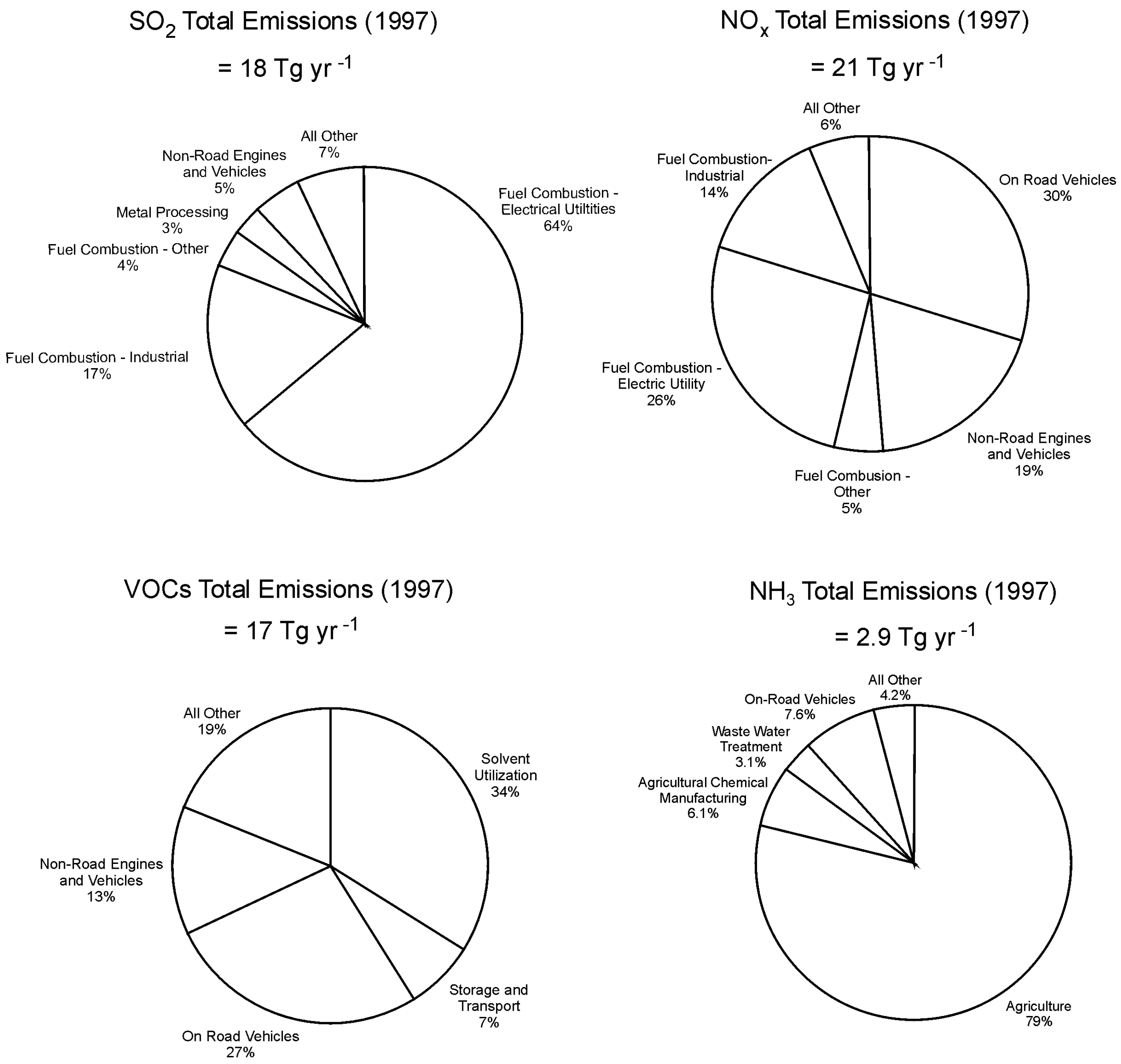


Figure 4-17. Nationwide emissions of SO_2, NO_x, VOCs, and NH_3 from various source categories.

Source: U.S. Environmental Protection Agency (1998).

summer (Gillette and Hanson, 1989). Effects are being made to account for the seasonal variations of emissions in the nationwide emissions inventories.

4.4.2 Uncertainties of Emissions Inventories

As described in CD96, 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, and control device efficiencies. Additional uncertainties arise during the compilation of an emissions inventory because of missing sources and computational errors. The variability of emissions can cause errors when annual average emissions are applied to applications involving shorter time scales.

Activity rates for well-defined point sources (e.g., power plants) should have the smallest uncertainty associated with their use, since accurate production records need to be kept. On the other hand, activity rates for a number of areally dispersed fugitive sources are extremely difficult to quantify. Emissions factors for easily measured fuel components which are released quantitatively during combustion (e.g., CO_2 and 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 age, their maintenance history, and operating conditions. It is virtually impossible to assign uncertainties in control device performance due to these factors. It should be noted that the largest uncertainties occur for those devices which 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, but becomes problematic for poorly characterized area sources of both primary PM and precursors to secondary PM formation. Further research is needed to better characterize the sources of pollutants in order 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 4-14 to 4-17) 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. As rough estimates, uncertainties in emissions estimates could be as low as 10% for the best characterized source categories, while 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 obtain cross-sections of pollutants upwind and downwind of major urban areas from aircraft. 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, non-steady wind flows, and general logistic difficulties.

4.5 LONG RANGE TRANSPORT OF PM 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, as evidenced by the transport of PM from uncontrolled biomass burning in Central America and southern Mexico which resulted in anomalously high PM levels observed in southern Texas and to a lesser extent, 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, 1995). Most dust storms in the deserts of China occur in the spring after the snow has melted and before vegetation has grown following the passage of strong cold fronts. Strong winds and unstable conditions result in the rapid transport of dust into the middle and upper troposphere (4-5 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.

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 ten days principally during the summer. As can be expected, the frequency of dust events is highest in the southeastern United States and about half are observed only within the state of Florida and these are associated with dense hazes in Miami during the summer (Prospero et al., 1987) such that African dust is the dominant aerosol constituent in south 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 m m^{-3} throughout the affected areas with mean maximum dust contributions of 19.7 ± 8.4 mg m^{-3} during these events, and a peak contribution of 32 mg m^{-3} to 24-h average $PM_{2.5}$ levels.

4.6 SUMMARY AND CONCLUSIONS

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. Secondary constituents are smaller but still important components of $PM_{2.5}$ in the central and western United States. Minerals constitute the largest fraction of $PM_{(10-2.5)}$ throughout the United States. Data collected in the Los Angeles Basin and Philadelphia 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.

Due to 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 4-3. The distinction between natural and anthropogenic sources is not always obvious. While 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. Most forest fires in the United States may ultimately be of human origin, either through prescribed burning or accident.

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. Compositional profiles developed for receptor modeling applications are perhaps the most accessible and reliable means of characterizing the composition of emissions. 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 which are typically measured in ambient monitoring-source receptor model studies, are needed to account for most of the observed mass of PM in these studies. Again, it should be emphasized that, because of limitations in receptor modeling methods in treating secondary components, these efforts are more likely to be successful for primary components, although it should be mentioned that methods are being developed to apportion secondary constituents by source categories.

Windblown dust from whatever source represents the largest single source of $PM_{2.5}$ in the U.S. emissions inventory. Although dust emissions (62% of total U.S. $PM_{2.5}$) are far in excess of any other source of primary or secondary $PM_{2.5}$ in any region of the country, measurements of soil constituents in ambient samples suggest that the overall contribution from this source could be less than 10%. 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 widely dispersed and 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 away from the sources of the dust.

As seen in Table 4-3, emissions of mineral dust, organic debris, and sea spray are concentrated mainly in the coarse fraction of PM_{10} (> 2.5 μm aero. diam.). A small fraction of this material is in the $PM_{2.5}$ size range (< 2.5 μm aero. diam.). Nevertheless, concentrations of crustal material can be appreciable especially during dust events. It should also be remembered that virtually all of the Saharan dust reaching the United States is in the $PM_{2.5}$ size range. Emissions from combustion sources (mobile and stationary sources, biomass burning) are 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_{10} emissions should be viewed with caution and emissions from specific source categories are best discussed on an individual basis.

Although most emphasis in this chapter has been on sources within the United States, it should also be remembered that sources outside the United States also contribute to ambient PM levels that can, at times, result in exceedances of the ambient NAAQS for PM. Saharan dust storms contribute routinely to PM loadings in areas east of the Mississippi River. The results of Perry et al. (1997) indicate that 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. Large scale dust storms in the deserts of central Asia have recently been found to contribute to PM levels in the Northwest on an episodic basis. Uncontrolled biomass burning in central America and Mexico resulted in exceedances of the daily NAAQS for PM in Texas.

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APPENDIX 4A

Composition of PM Source Emissions

This appendix includes figures and tables showing the elemental composition of emissions from various source categories discussed in Table 4A-3. The material is mainly derived from Chapter 5 of CD96, to which the reader is referred for further details. The primary emphasis in the figures and tables is on the source composition of $PM_{2.5}$ particles.

The compositions of soils and average crustal material are shown in Table 4A-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 4A-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 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 seiving 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

TABLE 4A-1. AVERAGE ABUNDANCES OF MAJOR ELEMENTS IN SOIL AND CRUSTAL ROCK

Elemental Abundances (ppmw)			
	Soil	Crustal Rock	
Element	(a)	(b)	(c)
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: (a) Vinogradov (1959); (b) Mason (1966); (c) Turekian (1971), Model A; as quoted in Warneck (1988).

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 4A-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 4A-3. The chemical composition of paved road dust consists of a complex mixture of particulate matter from a wide variety of sources. Hopke et al. (1980) found that the inorganic composition of urban roadway dust in samples from Urbana, IL could be described in terms of contributions from natural soil, automobile exhaust, rust, tire wear, and salt. Automobile contributions arose from exhaust emissions enriched in Pb;

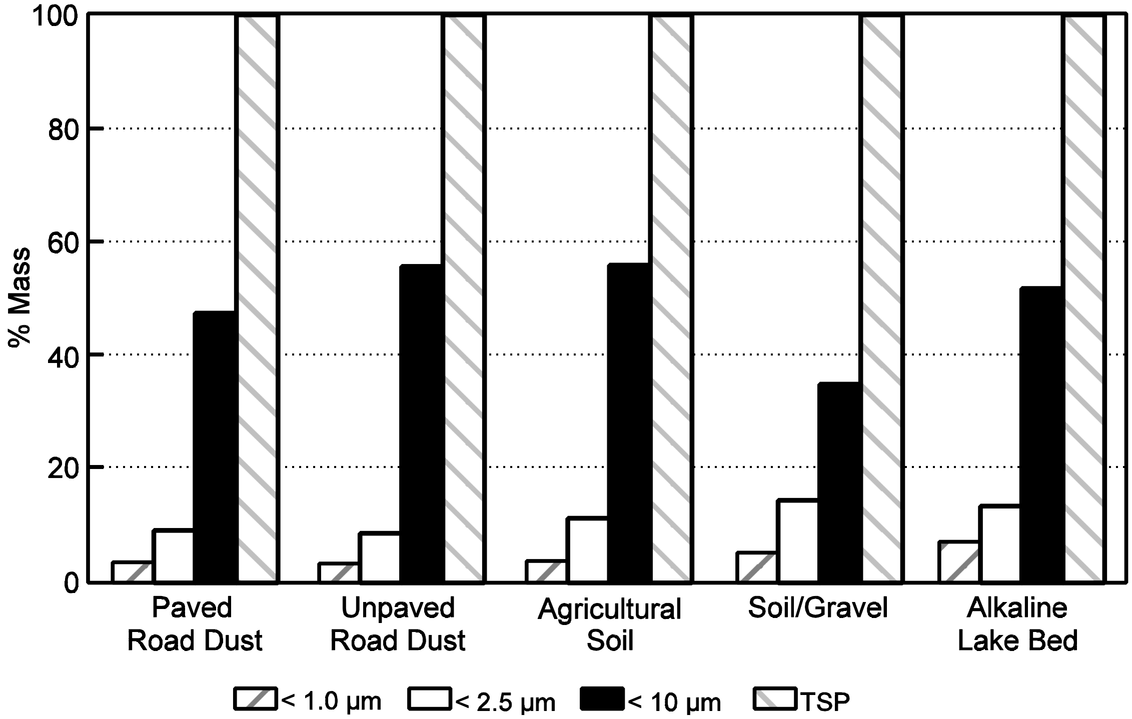

Figure 4A-1. Size distribution of particles generated in a laboratory resuspension chamber.

Source: Chow et al. (1994).

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.

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 4A-2 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, while 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,

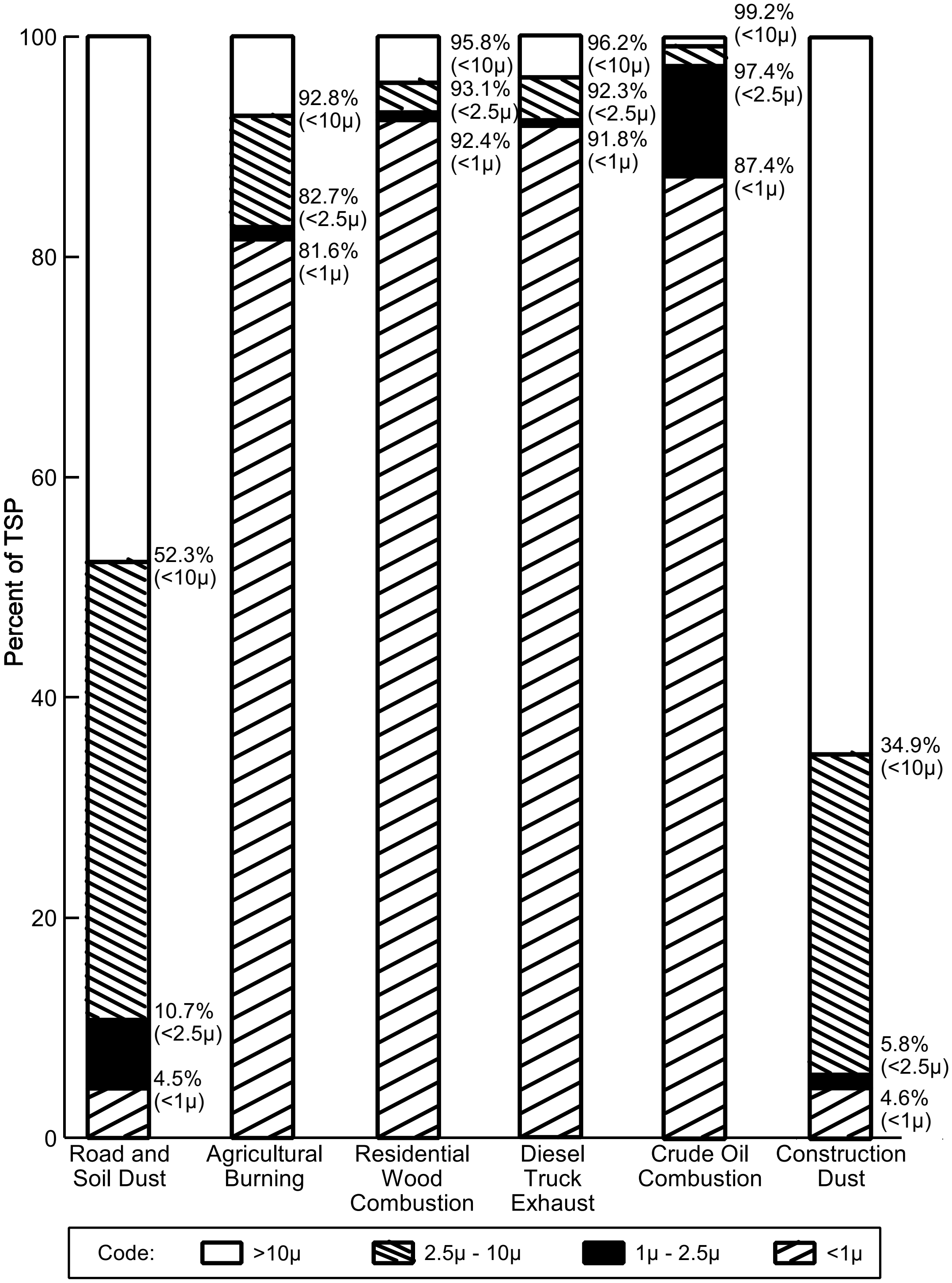

Figure 4A-2. Size distribution of California source emissions, 1986.

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

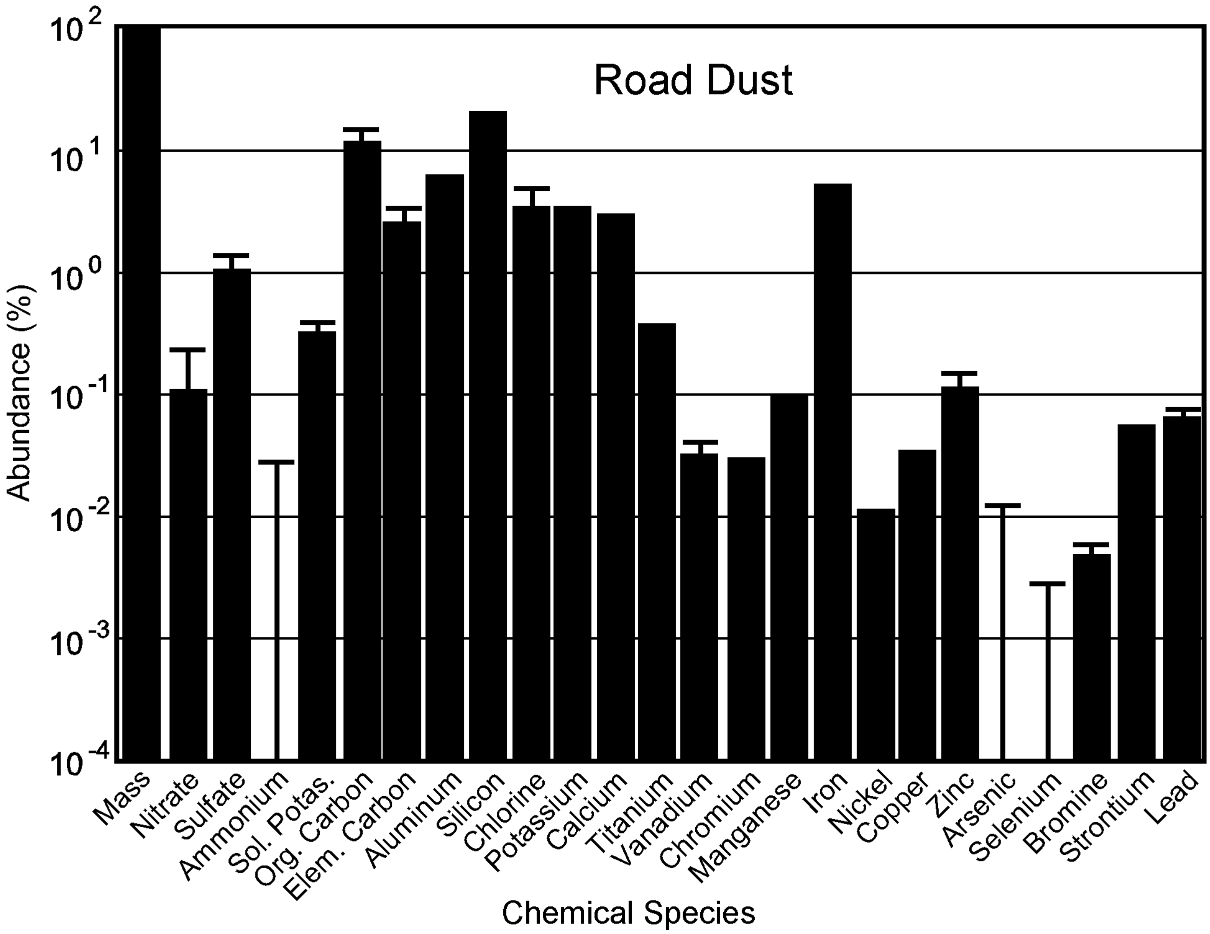

Figure 4A-3. Chemical abundances for $PM_{2.5}$ emissions from paved road dust in Denver, CO. Solid bars represent fractional abundances, and the error bars represent variability in species abundances. Error bars represent detection limits when there are no solid bars.

Source: Watson and Chow (1994).

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. A number of trace elements are greatly enriched over crustal abundances (in different fuels), such as Se in coal

TABLE 4A-2. 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	20000 ± 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 4A-2 (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 4A-2 (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

N = Number of samples.
ND = Not detected.
The “% mass” entries give the average percentage of the total emitted mass found in the fine fraction.
(a) Omitted because of sample contamination.

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

and V 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 since V at combustion temperatures is known to catalyze the oxidation of reduced sulfur species. Although Table 4A-2 only gives values of the fine particle composition, measurements of coarse particle composition were also reported by Olmez et al. (1988) which were qualitatively similar.

Apart from emissions in the combustion of fossil fuels, toxic trace elements are emitted as the result of various industrial processes such as steel and iron manufacturing and non-ferrous 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 4A-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 4A-2) with the composition of incinerator emissions in Washington D.C., and Chicago, IL, (Olmez et al., 1988) shows agreement for most constituents to better than a factor of two.

The principal components emitted by diesel and gasoline fueled vehicles are organic carbon (OC) and elemental carbon (EC) as shown in Table 4A-3. 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, while 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 one to two 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 /hr to the various load conditions specified in the Federal Test

TABLE 4A-3. FRACTIONAL ORGANIC AND ELEMENTAL CARBON ABUNDANCES IN MOTOR VEHICLE EMISSIONS

Fuel Type	Organic Carbon	Elemental Carbon	N[e]	Sources
Diesel				
Denver, CO[a]	23 ± 8%	74 ± 21%	3	1, 2
Los Angeles, CA[a]	36 ± 3%	52 ± 5%	2	3, 4, 5, 6
Bakersfield, CA[b]	49 ± 13%	43 ± 8%	3	7
Phoenix, AZ[b]	40 ± 7%	33 ± 8%	8	8
Unleaded gasoline				
Denver, CO[a]	76 ± 29%	18 ± 11%	8	1, 2
Los Angeles, CA[c]	93 ± 52%	5 ± 7%	11	3, 4, 5, 6
Los Angeles, CA[a]	49 ± 10%	39 ± %	11	3, 4, 5, 6
Phoenix, AZ[b]	30 ± 12%	14 ± 8%	9	8
Leaded gasoline				
Denver, CO[a]	67 ± 23%	16 ± 7%	3	1, 2
Los Angeles, CA[c]	52 ± 4%	13 ± 1%	3	3, 4, 5, 6
Los Angeles, CA[a]	31 ± 20%	15 ± 2%	3	3, 4, 5, 6
Mixed (tunnel and roadside)				
Denver, CO	50 ± 24%	28 ± 19%		1, 2
Los Angeles, CA[d]	38 ± 6%	38 ± 5%	3	3
Phoenix, AZ	39 ± 19%	36 ± 11%		8

Sources: (1) Watson et al. (1990b), (2) Watson et al. (1990a), (3) Cooper et al. (1987), (4) NEA, Inc. (1990), (5) Peltier et al. (1990a), (6) Peltier et al. (1990b), and (7) Houck et al. (1989), cited in (8) Watson et al. (1994b).

Notes: (a) Modified Federal Test Procedures followed in dynamometer tests; (b) Roof monitoring at inspection station; (c) 55 km/hr steady speed in dynamometer tests; (d) Rt. 1 tunnel at LA airport, (e) N = Number of samples.

Procedures (FTPs). Also shown are the results of sampling from mixed vehicle types along roadsides and in tunnels.

The results shown in Table 4A-3 were obtained during the late 1980's, and, so, may not be entirely representative of current vehicles. Examples of data for the trace element composition of motor vehicle emissions obtained in Phoenix, AZ are shown in Table 4A-4. SO_2 emissions are also shown in relation to the mass of fine particles emitted. As can be seen, small quantities of soluble ions such as $SO_4^=$ and NH_4^+ are emitted. The ammonium may be emitted as the result of an improperly functioning catalytic converter, or may simply be the result of contamination during sample handling and analysis. Four fractions are given for the organic carbon fraction and three for elemental carbon. These refer to abundances measured at different temperatures in a thermographic analysis. Temperatures for OC1, OC2, OC3, and OC4 are 120 °C, 250 °C, 450 °C, and 550 °C, respectively; and, for EC1, EC2, EC3, they are 550 °C, 700 °C, and 800 °C, respectively, in He/2% O_2. The abundances of trace elements are all quite low, with most being less than 1%. 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 since Pb has been removed from gasoline. However, it should also be remembered that restrictions in the use of leaded gasoline have resulted in a dramatic lowering of ambient Pb levels. 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 of 1997 in Colorado are shown in Table 4A-5. As can be seen from Table 4A-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. Emissions from “smokers”, i.e., light duty vehicles with visible smoke emitted from their tailpipes, 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 which are high emitters of hydrocarbons and carbon monoxide will also tend to be high emitters of PM (Sagebiel et al., 1997; Cadle et al., 1997). Particle emission rates are also correlated with vehicle acceleration and emissions occur predominantly during periods of heavy acceleration even in newer vehicles (Maricq et al., 1999).

TABLE 4A-4. PHOENIX PM$_{2.5}$ M0TOR VEHICLE EMISSIONS PROFILES (% MASS)

Chemical Species	Auto	Diesel
NO_3^-	3.9 ± 2.9	0.31 ± 0.40
SO_4^{2-}	2.3 ± 1.3	2.4 ± 1.0
NH_4^+	1.7 ± 1.0	0.87 ± 0.13
OC	30.1 ± 12.3	40.1 ± 6.6
OC1	11.3 ± 3.5	21.0 ± 6.3
OC2	9.2 ± 6.8	9.1 ± 1.9
OC3	4.6 ± 2.2	5.9 ± 1.3
OC4	3.5 ± 1.5	4.0 ± 1.5
EC	13.5 ± 8.0	32.9 ± 8.0
EC1	11.7 ± 7.2	4.4 ± 1.3
EC2	3.1 ± 1.6	27.9 ± 5.6
EC3	0.15 ± 0.30	0.69 ± 0.82
Al	0.41 ± 0.20	0.17 ± 0.12
Si	1.64 ± 0.88	0.46 ± 0.18
P	0.11 ± 0.07	0.06 ± 0.06
S	1.01 ± 0.48	1.24 ± 0.28
Cl	0.34 ± 0.32	0.03 ± 0.06
K	0.25 ± 0.14	0.04 ± 0.03
Ca	0.71 ± 0.41	0.16 ± 0.06
Ti	0.07 ± 0.13	0.00 ± 0.15
Cr	0.02 ± 0.01	0.00 ± 0.01
Mn	0.10 ± 0.04	0.01 ± 0.01
Fe	0.68 ± 0.42	0.16 ± 0.07
Cu	0.07 ± 0.06	0.01 ± 0.01
Zn	0.27 ± 0.22	0.07 ± 0.02
Sb	0.02 ± 0.13	0.01 ± 0.14
Ba	0.06 ± 0.40	0.14 ± 0.47
La	0.15 ± 0.51	0.18 ± 0.59
Pb	0.16 ± 0.07	0.01 ± 0.03
SO_2[a]	32.8 ± 13.9	66.9 ± 24.0

Source: Watson et al. (1994b).

Note: Elemental abundances ≤0.01% (V, Co, Ni, Ga, As, Se, Br, Rb, Sr. Y, Zr, Mo, Pd, Ag, Cd, In, Sn, Au, Hg, Tl, U) in XRF analyses excluded; OC = organic carbon; EC = elemental carbon.

[a] Relative to total PM$_{2.5}$.

TABLE 4A-5. EMISSION RATES (MG/MILE) FOR CONSTITUENTS OF PARTICULATE MATTER FROM GASOLINE AND DIESEL VEHICLES

	Gasoline Vehicles				Diesel Vehicles	
	Low	Medium	High	Smoker	LDD[a]	HDD[b]
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

[a] Light duty.
[b] Heavy duty.

Source: Lawson and Smith (1998).

In addition to fossil fuels, biomass in the form of wood may be burned in forest fires or as fuel for heating or cooking. At first glance these two broad categories might seem to serve to distinguish between natural and anthropogenic sources. However, many forest fires result from human intervention, either deliberately through prescribed burning in forest management or accidentally through the improper disposal of flammable material or fugitive sparks (e.g., Andreae, 1991). On the other hand, human intervention also suppresses lightning triggered fires and can also lead to the buildup of combustible fuel on the forest floor. Not enough data are available to assess the effects of humans on forest fires, except for land clearing for agriculture. 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 can also strongly 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 4A-4. These data were obtained in Denver during the winter of 1987-1988 (Watson and Chow, 1994). As was the case for motor vehicle emissions, organic and elemental carbon are the major components of particulate emissions from wood burning. It should be remembered that the relative amounts shown for organic carbon and elemental carbon vary with the type of stove, the stage of combustion and the type and condition of the fuelwood. Fine particles are dominant in 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).

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

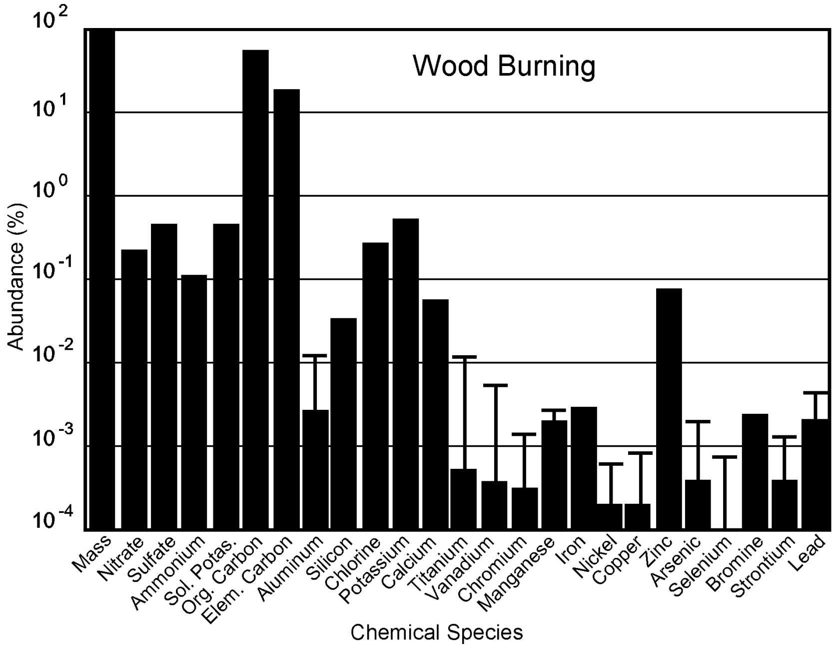

Figure 4A-4. Chemical abundances for $PM_{2.5}$ emissions from wood burning in Denver, CO. Solid bars represent fractional abundances, and the error bars represent variability in species abundances. Error bars represent detection limits when there are no solid bars.

Source: Watson and Chow (1994).

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, namely a nucleation mode, an accumulation mode, and 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 4A-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 4A-6. 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 4A-6 with those shown in Figure 4A-4, there are a number of similarities and differences (especially with regard to the heavy metal content) in the abundances of many species. The abundances of some crustal elements (e.g., Si, Fe) are higher in Table 4A-6 than in Figure 4A-4 perhaps reflecting additional contributions of entrained soil dust.

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 which 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.

Since 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

TABLE 4A-6. MEAN AEROSOL COMPOSITION AT TROPICAL SITE (SRIWIJAYA UNIVERSITY, SUMATRA, INDONESIA) AFFECTED HEAVILY BY BIOMASS BURNING EMISSIONS[1]

Component	Abundance (%)	Component	Abundance (%)
OC	76	Cr	bd[2]
EC	1.2	Mn	bd[2]
$SO_4^{=}$	11	Fe	3.9×10^{-2}
Al	bd[2]	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[2]	Pb	3.1×10^{-3}

[1] The mean $PM_{2.5}$ concentration during the sampling period (11/5-11/11/97) was 264 $\mu g/m^3$.
[2] beneath detection limit.

Source: Pinto et al. (1998).

displacement reactions which 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 MSA (methane sulfonic acid) 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. 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 are also to be found in ambient aerosol samples in this size range. While material from all the foregoing categories may exist as individual particles, bacteria are usually 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 as well characterized 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, wild fires and biotic sources (Nriagu, 1989). Biologically mediated volatilization processes (e.g., biomethylation) are estimated to account for 30-50% 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 which have uncertainty ranges of an order of magnitude.

The discussion above focused mainly on the elemental composition of emissions. Carbon was treated mainly as organic carbon and elemental carbon. However, there are literally hundreds of organic compounds which have been quantified in ambient and source samples which are lumped routinely into the category of organic carbon. These compounds, many of which have been used in source apportionment studies as signature (e.g., Schauer et al., 1996), consist of high molecular weight alkanes, hopanes and steranes, organic acids, aldehydes, polycyclic aromatic hydrocarbons and steroids. Profiles of organic compounds from meat cooking (Rogge et al., 1991); automobiles and heavy-duty diesel trucks (Rogge et al., 1993a); road dust, tire debris and brake linings (Rogge et al., 1993b); vegetative detritus (Rogge et al., 1993c); natural gas home appliances (Rogge et al., 1993d); cigarette smoke (Rogge et al., 1994); hot asphalt roofing tar pots (Rogge et al., 1997a); distillate fuel oil burning (Rogge et al., 1997b); and pine, oak, and synthetic log burning in residential fire places (Rogge et al., 1998) have been obtained. Many individual compounds are present in concentrations much less than 1 ng/m^3 in ambient PM samples. They have been used in only a limited number of studies (mainly in Los Angeles) by only a small number of groups. Measurement methods need to be standardized and made more cost-effective to take advantage of the opportunities they offer in studies throughout the United States.

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5. HUMAN EXPOSURE TO AMBIENT PARTICULATE MATTER: RELATIONS TO CONCENTRATIONS OF AMBIENT AND NON-AMBIENT PM AND OTHER AIR POLLUTANTS

5.1 INTRODUCTION AND BASIC CONCEPTS

This chapter examines ambient particulate matter (PM[1]) air quality and that portion of ambient PM which penetrates into indoor microenvironments. It also examines, to a lesser extent, the contributions of sources of non-ambient PM to total PM exposure. This is to aid in the interpretation of the acute and chronic epidemiology studies discussed in Chapter 6, in which ambient PM concentrations are assumed to be an indicator, or a surrogate, for the mean community exposure to PM of ambient origin, or an individual's exposure to ambient PM. Thus, this chapter has three objectives:

(a) To provide a review of pertinent studies of personal exposures to total PM (ambient PM plus non-ambient PM).

(b) To evaluate linkages of human exposure to PM of ambient origin estimated from concentrations of PM measured at a fixed-site monitor located at some central location in a community under study.

(c) To quantify the contribution of PM of ambient origin to total personal PM exposure.

The 1996 Particulate Matter Air Quality Criteria Document (PM AQCD) (U.S. Environmental Protection Agency, 1996) thoroughly reviewed the PM exposure literature through 1995 and early 1996. This chapter reviews the history of PM AQCD developments from 1969 to the present. It then thoroughly reviews key pre-1996 studies, the new PM exposure literature from 1995/6 through 1998 to date, and some literature accepted or submitted for publication later in 1999.

The U.S. Environmental Protection Agency regulatory authority for PM extends to the ambient air, defined in 40 CFR 50.1(e) as that portion of the atmosphere, external to buildings, to

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[1] In this chapter PM without a subscript refers to PM in general. PM_x refers to the mass of PM collected by a monitor with a penetration fraction of 0.5 for particles with an aerodynamic diameter of X microns (XμmAD).

which the general public has access (Code of Federal Regulations, 1994)[2]. Therefore, polluted air inside a building, or anywhere on private property owned or controlled by the source of pollution, is not regulated by the National Ambient Air Quality Standards (NAAQS). However, it is necessary to consider total personal exposure to ambient PM, both in regulated ambient air and within non-regulated indoor air. This is because ambient (outdoor) particles penetrate into non-ambient (indoor residential and occupational) microenvironments where, on average, people spend 87% of their time (Klepeis et al., 1999). Therefore, when people are indoors, they are exposed to a mixture of PM of ambient origin and particles generated indoors from sources not regulated by EPA (e.g., cigarette smoke or an occupational activity).

Particulate matter represents a generic class of pollutants which requires a different interpretation of exposure in contrast to that for the gaseous criteria pollutants, such as CO (Mage, 1985). Whereas a molecule of CO emitted from a motor vehicle is indistinguishable from a molecule of CO emitted from a cigarette, a 1-μm aerodynamic diameter (AD) particle emitted from a motor vehicle and a 1-μm AD particle emitted from a cigarette may have a different shape, mass, chemical composition, solubility and toxicity (Siegmann et al., 1999). In the atmosphere, a particle may be a single entity, or an agglomeration of particles, such as a particle from motor vehicle exhaust bound to a particle from cigarette ash. Furthermore, indoor sources of particles also produce a wide variety of particles of varying AD and composition that people are exposed to, as shown in Figure 5-1 (Owen et al., 1992). Most of these particles can be fragmented by mechanical activity and their detritus may exist at smaller ADs than shown.

A subject's personal exposure to PM is theoretically measured by sampling the concentration of PM in the inhaled air entering the nose or mouth. The inlet to a personal monitor is normally placed at the outer limit of the breathing zone to avoid a negative sampling bias that could be caused by dilution of the collected air by the exhaled breath which is depleted of PM. However, such placement does not allow sampling of directly inhaled cigarette smoke or the inhaled air that passes through a dust mask. Thus, personal monitoring of PM exposure of

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[2] In this chapter, the term "ambient air" means that portion of the ambient atmosphere that may be considered representative of a community and not unduly influenced by any specific identifiable source (e.g., not at the side of a highway, or next to a coke oven). "Outdoor air" is taken to mean that portion of the atmosphere, external to buildings, where a PM concentration measurement may be unduly influenced by an immediate source of PM (undiluted cigarette smoke, backyard barbecue, idling motor vehicle, etc.). Thus, all ambient air is outdoor air, but not all outdoor air is ambient air.

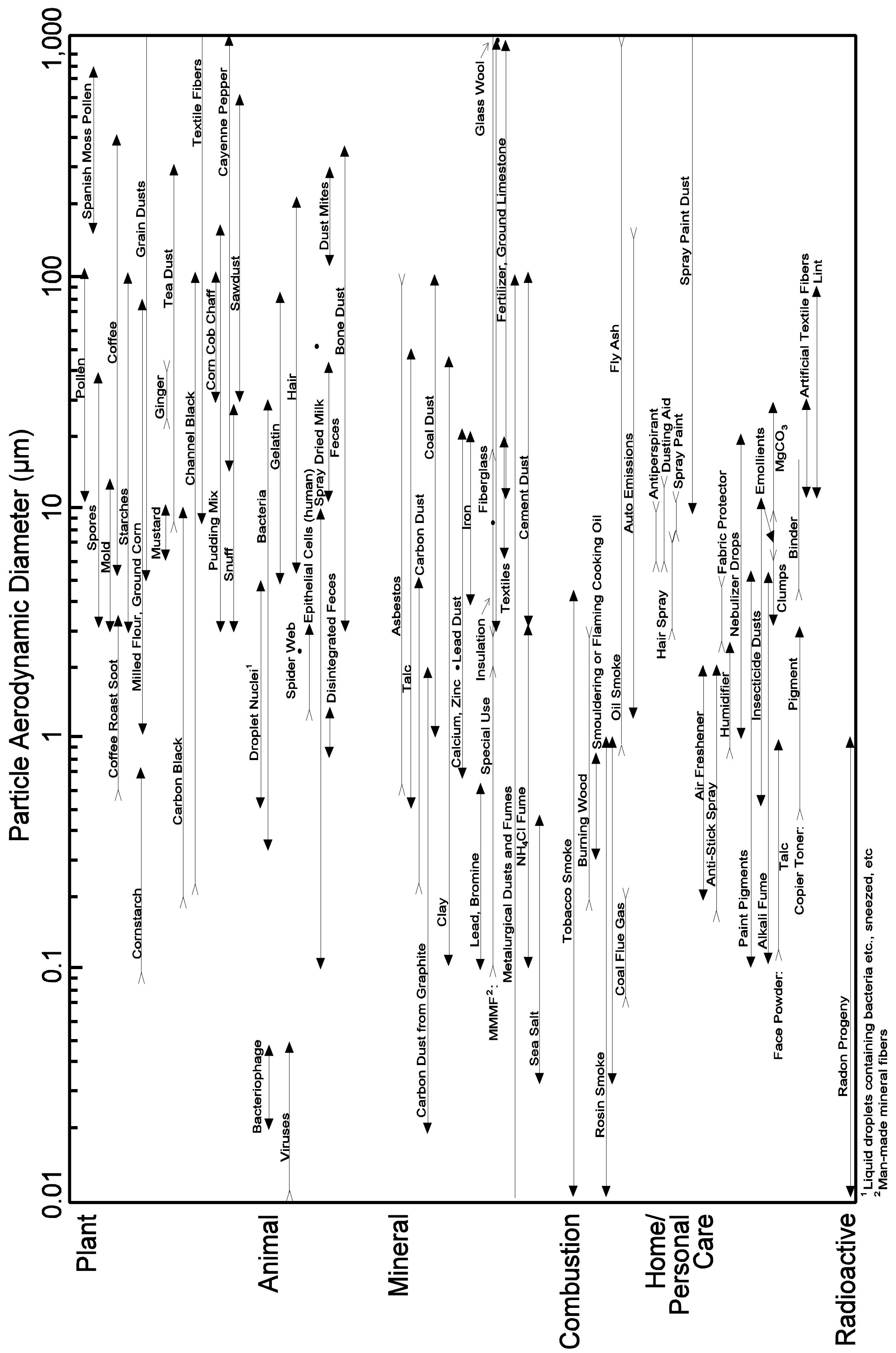

Figure 5-1. Sizes of various types of indoor particles.

Source: Owen et al. (1992).

non-smokers not using a dust mask can be adequately characterized by a personal monitor worn by the subject with the sampling inlet close to, but not in, the breathing zone.

The total PM exposure of an individual during a period of time is composed of exposure to many different particles from various sources while in different microenvironments. Duan (1982) defined a microenvironment as “a [portion] of air space with homogeneous pollutant concentration”; it has also been defined (Mage, 1985) as a volume in space, during a specific time interval, during which the variance of concentration within the volume is significantly less than the variance between that microenvironment and its surrounding microenvironments. For example, a kitchen with a wood stove can constitute a single microenvironment for total PM when the stove is off, and all people in the kitchen would have similar PM exposures. When the stove is on, the kitchen could have a significant vertical PM concentration gradient, and a child on the floor in a far corner and an adult standing at the stove could be exposed to significantly different PM concentrations. When a concentration gradient exists, such as from smoke from a lit cigarette, where the gradient goes from mg/m^3 to μg/m^3, the former definition of a microenvironment breaks down because there is no homogeneous concentration. Alternatively, the latter definition requires a rather impractical specification of a large number of transient microenvironments.

In a given microenvironment, such as one in the kitchen example above, the particles may originate from a wide variety of sources. PM may be generated from within (e.g., the stove, deep frying, burning toast), from without (ambient PM entering through an open window), from another indoor microenvironment (cigarette smoke from the living room), or from a personal activity that generates a heterogeneous mix of PM (e.g., sweeping the kitchen floor and resuspending a mixture of PM from both indoor and outdoor sources that had settled out).

In general, as a function of space and time, people pass through a series of microenvironments. Thus their average total daily exposure ($\mathbf{E}$ μg/m^3) to PM can be expressed as the sum of their exposures within the microenvironments they occupy. With appropriate averaging over sets of four classes of microenvironments (e.g., $\underline{\text{in}}$doors, ambient-$\underline{\text{out}}$doors, $\underline{\text{occ}}$upational, and in-$\underline{\text{tra}}$ffic), the average total exposure of a non-smoker can be expressed as follows (Mage, 1985):

$$\mathbf{E} = (E_{in}t_{in} + E_{out}t_{out} + E_{occ}t_{occ} + E_{tra}t_{tra}) / T \qquad (5\text{-}1)$$

where each value of E is the mean value of total PM concentration in the microenvironment class *while the subject is in it*, time (t) is the total time the subject is in that microenvironment during the study period, and T is equal to the sum of all times (usually 24-h). Note that E_m is not necessarily a 24-h time-weighted-average (TWA) of PM concentration in an indoor microenvironment. Thatcher and Layton (1995) report that "merely walking into a room increased the particle concentration by 100%". Consequently, an integrated measurement of air quality in an enclosed space that includes time when it is unoccupied, or not occupied by a specific subject, may not be a valid measure that can be used to estimate the exposure of that specific subject while in that microenvironment (Larssen et al., 1993). A measured microenvironmental concentration when the space is unoccupied will tend to be biased low as a measure of the exposure within it during periods of occupancy. For example it is incorrect, as it is for NO_2, to associate a PM exposure to a person, while cooking at a gas stove in a kitchen, with a 24-h kitchen PM concentration measurement that is influenced by periods when the stove was off (Smith et al., 1994).

5.1.1 The History of Understanding Human Exposure to Particulate Matter

The 1969 PM AQCD (National Air Pollution Control Administration, 1969) only discussed ambient PM concentrations as indices of a general exposure to PM, to the extent that the document index mentions neither *exposure* nor *indoor*. The introduction stated "Air quality criteria are descriptive; that is, they describe the effects that have been observed to occur when the ambient level of a pollutant has been reached or exceeded specific figures for a specific time period. . . .Epidemiologic studies [are presented that] analyze the effects of pollution from ambient exposure of groups of people living in the community." The indoor microenvironment was considered protective and no mention was made of sources of pollution indoors. For example, it was suggested that the decrease in mortality associated with reduction of PM pollution in London, after the 1952 Fog, may possibly have been related to the report that "a great deal of publicity has been given to the harmful effects of smog, and more susceptible individuals have been encouraged to use masks and filters, and to stay indoors."

In the context of protection from ambient PM afforded by staying indoors, the document caveats as follows: "There has, however, been a minimum of attention paid to indoor and domestic environments and their potential contribution. Measurement of such indoor exposures might be difficult, but omission of the information could well modify the appraisal of the importance of particulate pollution" [e.g., ambient PM as measured by a high volume sampler would now appear less potent because susceptible people would stay indoors on high pollution days].

The 1982 PM AQCD (U.S. Environmental Protection Agency, 1982) reported on indoor PM concentrations as follows: "Yocom et al. (1971) studied TSP in public buildings, offices and homes using a scaled down version of the hi-vol sampler. . .Indoor levels were about half outdoor levels on the average. . . Alzona et al. (1979) reported elemental analyses for calcium and iron, normally coarse-particle components, and for zinc, lead and bromine, components of fine particles. . . it appears that tracer components of coarse particles do not penetrate any of these structures as readily as the fine components."

However, early personal PM exposure monitoring studies indicated that some people's personal activities, along with PM generated by personal and indoor sources (e.g., cigarette smoking), could lead to PM indoors and personal exposures to total PM that exceeded the concentration of the PM found in the immediate outdoor air or in the local ambient air (Binder et al., 1976; Repace and Lowrey, 1980; Spengler et al., 1980). This was reported as follows: "It is apparent that, in the absence of smoking, indoor and outdoor levels of fine particulate mass are almost the same. However, smoking contributes very significantly to indoor level."

The section concluded: "Therefore, fine particles readily penetrate buildings and occur inside to about the same extent as outdoors. Indoor activity adds incrementally to outdoor levels and, frequently, somewhat higher levels of fine particles are observed indoors. Smoking adds very materially to indoor levels."

The 1982 document also summarized the situation as follows: "Because stationary ambient-air pollution monitors provide general statistics on composite population exposures, it would be extremely difficult (if not impossible) to predict an individual's actual exposure to PM on the basis of community air-monitoring data alone."

"Although outdoor concentrations of pollutants can be measured at particular sites, our highly mobile population can be exposed to either higher or lower values than community monitors show. Indoor particle levels can be high because of smoking, cleaning operations, or normal activities. Exposures of individuals to PM can vary more than community monitors show." (Volume II, page 5-138)

In the period between 1982 and 1996, many more studies on personal PM exposure and indoor PM were reported that documented the fact that, in most inhabited domestic environments, indoor PM concentrations, and personal PM exposures of the residents, were greater than the simultaneous ambient PM concentrations (e.g., Sexton et al., 1984; Spengler et al., 1985; Clayton et al., 1993). Clayton et al. (1993) referred to their finding of a 60% excess of daytime personal PM_{10} exposure in Riverside, CA, relative to a time-weighted-average of indoor and outdoor PM_{10} concentrations, as a "personal cloud" which is discussed later in this chapter.

In 1996 it was known, from personal monitoring and indoor monitoring, that some PM constituents, such as sulfates, are almost always lower indoors than outdoors because of the virtual absence of indoor sources and the presence of sinks for sulfates in indoor settings (exceptions can occur if high sulfur coal or kerosene are used as fuel in a poorly vented stove or space heater). However, this relationship does not hold for most other PM constituents, as the indoor and personal monitoring data show both higher- and lower-than ambient PM concentrations in indoor settings as a function of particle size and human activity patterns.

The largest coarse mode particles (>10 μm AD), which are generally of non-anthropogenic origin (e.g., wind blown dust), require turbulence to provide vertical velocity components greater than their settling velocity to allow them to be lifted and remain suspended in the air (Figure 5-1). Particles of ambient origin enter into an indoor setting either by bulk flow, as through an open window, in which all particles can enter at the inlet condition, or by pressure driven drafts and diffusional flows through cracks and fissures in the barriers of the building envelope when all windows are closed. In the latter mode of entry, velocities are relatively lower, thereby increasing the settling out of the largest coarse particles (>25μm AD) in the passage through the barriers (Larssen et al., 1993; Thatcher and Layton, 1995).

Indoor settings are usually quiescent (Matthews et al., 1989), unless fans or Heating-Ventilation-Air Conditioning (HVAC) systems are in use. Ambient particles that enter indoors quickly settle out by gravity or electrostatic forces, leading to familiar dust layers on horizontal surfaces and vertical TV screens that require constant cleaning (Raunemaa et al., 1989; Kildesø et al., 1999). However, human activity in indoor settings, such as smoking and cooking, does generate fine particles (<2.5 μm); cooking, dusting, vacuuming and general activity can generate coarser particles (>2.5 μm), or resuspend coarse particles that previously had settled out (Litzistorf et al., 1985; Thatcher and Layton, 1995; Abt et al., 1999a,b).

The National Research Council (1991) summarized the changing concept of concern for computing a person's total exposure to air pollutants, such as PM, instead of using an ambient concentration as a surrogate, as follows:

"Advances in indoor-air exposure studies have demonstrated the significant health effects from indoor emissions and exposures to contaminants that had been regulated only as outdoor pollutants. . .These demonstrations of high indoor contaminant levels showed the importance of accounting for incremental exposures from microenvironments when making risk assessments. . . These data have indicated the potential importance of indoor sources of contaminants."

However, from efforts to help resolve the apparently paradoxical situation that health effects were being associated with ambient PM concentrations, but personal exposures to total PM were found to be uncorrelated with ambient PM concentrations, a new realization began to emerge. The early works of Janssen et al. (1995) at Wageningen University, and Tamura et al. (1996a) at Tskuba University, revealed that longitudinal total PM exposures of an individual were highly correlated with ambient PM concentrations because the variance of non-ambient PM exposures (same home and work place from day to day) seemed to be small compared to the variance of ambient PM concentrations. Retrospective analyses of other data (Lioy et al., 1990; Clayton et al., 1993) by Mage and Buckley (1995) also showed that the mean community personal exposure on a given day was much more positively correlated with ambient PM concentrations than the cross-sectional correlation of all the subjects' exposures taken individually and analyzed together.

The non-peer-reviewed status of these publications (Tamura et al. [1996a] was in press at the time) led to a very conservative treatment of these findings in the 1996 PM AQCD (U.S. Environmental Protection Agency, 1996). Therefore, the 1996 PM AQCD, Chapter 7, represented a cautious transition away from the 1982 PM AQCD, and, for the first time, it made a distinction between exposure to PM of ambient origin and exposure to total PM of all origins. Consequently, the exposure chapter gave equal emphasis to the presentation and discussion of sources of PM in indoor domestic microenvironments and the infiltration of ambient PM into these indoor microenvironments. However, in summary, several suppositions and conclusions were cited, that, when woven together, could implicitly support the premise that exposures to PM of ambient origin are highly correlated with ambient PM concentrations and would make a correlation of ambient PM concentration with community health effects plausible. For example: "For the morbidity/mortality studies described in Chapter 12 that use SAM [stationary ambient monitoring] as the independent variable, that SAM can be interpreted to stand as a surrogate for the average community exposure to PM from sources that influence the SAM data." (Volume I, page 7-119).

"(4) Personal exposures to outdoor-generated PM of any size fraction $\leq$ PM_{10} can be estimated from the fraction of time spent indoors and an estimate of the air exchange rate and deposition rate associated with that size fraction.

(5) The relationship between ambient concentration and [total] personal exposure [to PM] is better for finer size fractions of ambient PM than for coarser PM. Higher correlations of ambient concentrations and personal exposures have been found for fine PM constituents (such as sulfates) without indoor sources.

(6) For a study population of nonsmokers for which there is a significant positive correlation between personal exposures and ambient concentrations, the ambient concentration can predict the mean personal exposure with much less uncertainty than it can predict the exposure of any given individual.

(22) Variations in personal exposure due to fluctuations produced by indoor sources of PM are independent of the variations in personal exposure produced by [fluctuations of] ambient PM." (Volume I, pages 7-163 and 7-165)

Since 1996, the work of Janssen and colleagues has been peer reviewed and published, and several other related articles discussing it have been published, or accepted for publication [Mage et al., 1999; Wallace, 1999a] - and are reported on later in this document. The net result is that the current literature appears to support the concepts that:

(1) ambient PM concentration is an index of exposure to PM of ambient origin, and that this index is currently the most appropriate quantity to relate to human health effects associated with the ambient PM concentrations within communities in epidemiologic studies;

(2) a measurements of an individual's personal exposure to total PM from all sources, indoors and outdoors, ambient and non-ambient, is the most appropriate index to use to relate that individual's health effects from that combined exposure to PM from all those different categories of sources.

5.1.1.1 Caveat

In virtually all the experimental studies of personal exposures to PM to be described in the rest of this document, with noteworthy exception of the U.S. Environmental Protection Agency Particle Total Exposure Assessment Methodology (PTEAM) study (Clayton et al., 1993), the Toronto, Ontario study of Pellizzari et al. (1999), and the Expolis exposure study (Jantunen et al., 1998), the studies were all conducted with subjects who were not chosen by a scientific probability-sampling schema (SPSS). Strictly speaking, without an SPSS, the results of all such studies apply only to the subjects sampled on the days that they were sampled, and no valid inference can be made to any other population or period of time. Although such studies may report significant differences, confidence intervals and *p* values, albeit they were peer reviewed, perhaps not by survey statisticians, they have no statistical meaning.

> "In many cases researchers are reluctant to face the problems that may be present in the survey. An 'ignorance is bliss' attitude and gratuitous assumptions are made about the quality of the data (the million nonrespondents are adequately represented by the ten respondents). For a one-time survey, conventional wisdom often dictates using methods that are believed to give good results for the funds available without adequate investigation of alternatives." (Lessler and Kalsbeek, 1992).

This chapter reports experimental results of such non-SPSS studies for what they are, without the authors' reports of statistical significance where such would not be valid, and it integrates the content of all these studies with the above *caveat* in mind.

5.1.2 Exposure to PM of Ambient Origin and Total PM

Personal exposure to the PM of ambient origin is important for several reasons:

(1) The U.S. EPA regulates PM emitted into the atmosphere from mobile sources and stationary industrial or commercial sources, but it does not control PM emissions in any private indoor location.

(2) The human body may react differently to PM of ambient origin and PM of non-ambient origin, because such particle mixtures have different chemical composition.

(3) Comparison of personal exposures to mixtures of PM of ambient origin and personal exposures to mixtures of PM of non-ambient origin, if possible to differentiate, may provide

clues as to the difference in their acute toxicity on a unit size and mass basis (Siegmann et al., 1999).

(4) Often in epidemiologic studies, the lagged daily mean ambient PM concentration level in a community is used as a surrogate to characterize a subject's exposure to ambient PM. Personal exposure to PM of non-ambient origin might act as a confounder or an effect modifier in such epidemiologic studies, if people's exposures to non-ambient PM are correlated with their exposures to ambient PM. This is true even if exposure to non-ambient PM may cause similar but independent health effects.

In general one can think of an individual's total exposure to PM as arising from several distinct categories: 1 - Ambient PM; 2 - Outdoor PM; 3- Indoor PM; 4- Personal activity PM; 5- Personal PM. Figure 5-2 shows how people can be exposed to combinations of these categories while outdoors as well as indoors. The following describes these categories in detail to clarify their differences and definitions as used in this chapter:

(1) Ambient PM: As defined in Section 5.1, PM of ambient origin is that PM that is formed in the ambient atmosphere and emitted into it. Ambient PM is well mixed in the outdoor air so that all people in the community are exposed to it, over time, at approximately the same mean concentration. This is true more so for fine mode PM than for coarse mode PM. The major sources of primary and secondary ambient PM species are industry, traffic, commerce, domestic emissions such as wood smoke, and natural wind blown dust or soil (see Chapter 3).

(2) Outdoor PM: PM of outdoor origin differs conceptually from PM of ambient origin. It is measured as the difference between the PM concentration at an outdoor location which is not in the ambient atmosphere (i.e., on private property or by a road side) and the simultaneous ambient PM concentration. Scaperdas and Colvile (1999) give an example of such non-representative air quality monitored outdoors 5-meters from an urban intersection.

(3) PM emitted or formed indoors: PM is emitted at home as house dust resuspended by human activity and cleaning procedures, environmental tobacco smoke (ETS), cooking fumes, pets, etc. PM emitted indoors at work varies with type of occupation. Aerosol formation occurs indoors from the dark (no sunlight) reaction of ozone with gaseous terpenes and other hydrocarbon species such as α-pinene and limonine, often found in household deodorizers. Kamens et al. (1999) reported " Some of the products have subcooled liquid vapor pressures

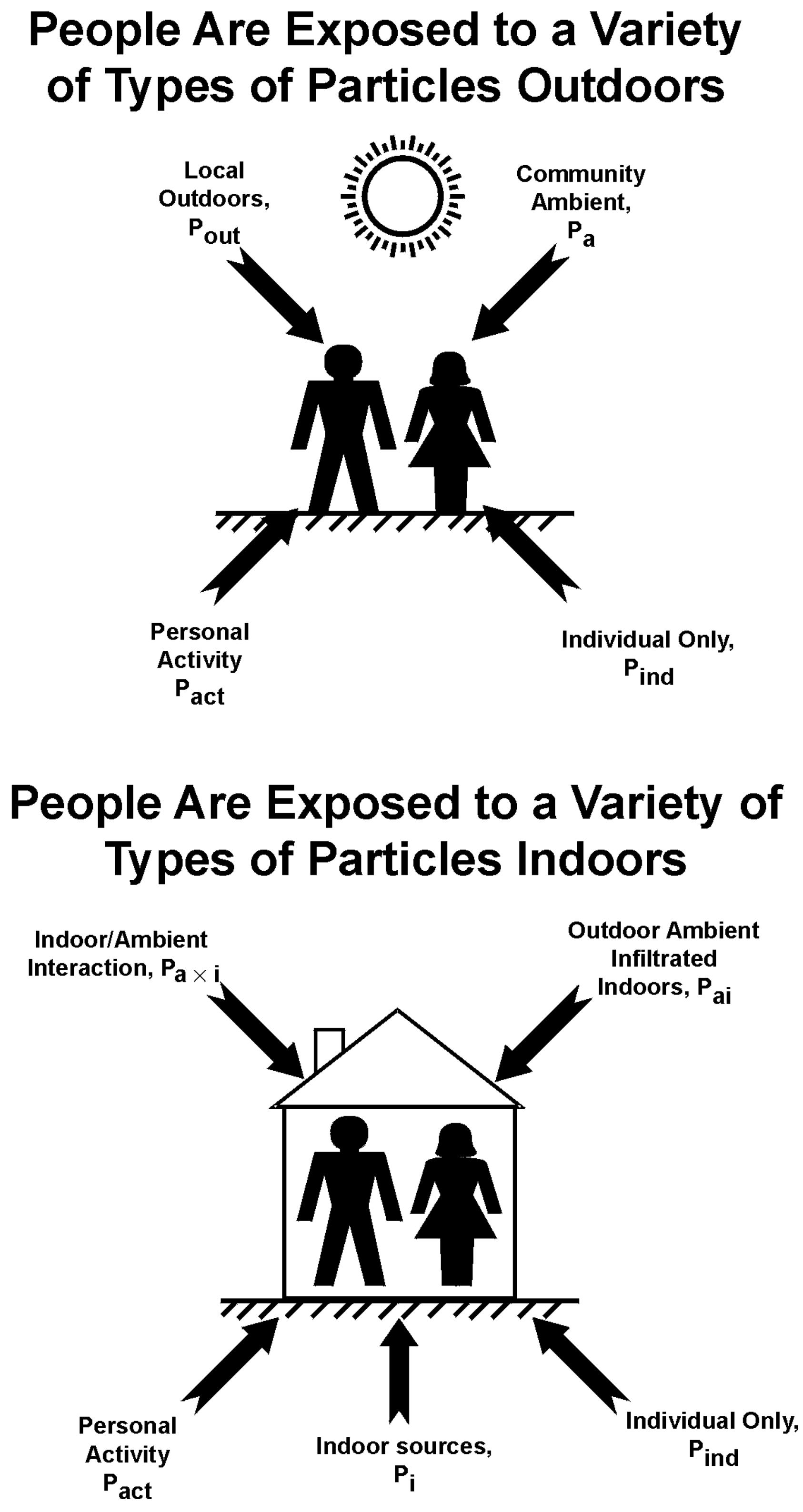

Figure 5-2. Categories of particle exposure outdoors and indoors.

Source: Wilson and Mage (1999).

which are low enough to initiate self-nucleation." Weschler and Shields (1999) report on a study of these dark ozone reactions, and report "The results demonstrate that ozone/terpene reactions can be a significant source of sub-micron particles in indoor settings", as high as 95 $\mu g/m^3$ under simulated conditions. Indoor generated PM is considered to be well mixed in an indoor microenvironment.

(4) Personal activity PM: Personal activity sources can exist either indoors or outdoors. These are microscale PM generating activities that primarily influence the exposure of the person performing the activity, from either a PM generating activity (hobby or occupation) or a physical activity that brings the subject into the undiluted PM plume from a local source (standing on a street corner or holding a lit cigarette between puffs). Thus personal activity PM exposure is only measured by a personal monitor carried by the subject, because a stationary monitor located nearby will not measure the high PM concentration generated by that activity. The difference between a personal monitor measurement and an area-representative measurement several meters away is sometimes called a "personal cloud" (Wallace, 1999a).

(5) Exposure to personal PM: This category pertains to all PM exposures that cannot be measured by a personal exposure monitor (PEM). i) Actively smoking creates a stream of smoke with a high PM concentration that is inhaled directly and it is not sampled by a personal monitor carried by the subject. This contribution to a daily exposure can be estimated from the Federal Trade Commission (FTC) ratings of mg delivered divided by the estimated total ventilation volume inhaled during a 24-h period by the smoker (Federal Trade Commission, 1994). For a smoker who breathes at an average rate of 10 Lpm over a day, each 1 mg of tar inhaled represents an exposure increment of 70$\mu g/m^3$ to their daily PM exposure as measured by a personal PM monitor. ii) Wearing a courtesy-mask for a respiratory infection, or a dust-mask or respirator for an occupation or hobby, removes an unknown fraction of the PM measured by a PEM in the inhaled air. The resulting contribution to daily PM exposure can only be estimated from the efficiency of the filter given by the manufacturer and the PEM data.

An important distinction that was developed in the 1996 PM AQCD between exposures to ambient $PM_{2.5}$ and non-ambient $PM_{2.5}$ (categories 2 to 5 above) is the relative homogeneity of the concentration of $PM_{2.5}$ of ambient origin compared to the heterogeneity of exposures to $PM_{2.5}$ of non-ambient origin. As discussed in the following section, virtually all people in a community are routinely exposed to a similar mixture of $PM_{2.5}$ of ambient origin when in the ambient atmosphere, with more heterogeneous exposures to coarse mode PM and semivolatile PM constituents in the western U.S. than the eastern U.S. See the discussion in Chapter 4 of the spatial and temporal variability of chemical composition of ambient PM in rural and urban communities in different regions of the U.S.

5.2 EXPOSURES TO PM CONCENTRATIONS IN THE COMMUNITY AMBIENT ATMOSPHERE

This section addresses the question, "How well does a concentration of PM measured at a community ambient monitoring station reflect the PM concentration in the outdoor air elsewhere in that area at both the local and regional levels?"

Spatial variation of PM at the local level. Kotchmar et al. (1987) measured TSP, and fine ($PM_{2.5}$) and coarse (PM_{10} - $PM_{2.5}$) using dichotomous samplers, in five cities across the U.S., at Bakersfield, CA; Riverside, CA; Granite City, IL; Owensboro, KY; Tampa, FL. In each city three identical PM monitors of each type were sited in accord with EPA guidelines at separations ranging from 1.6 km to 10 km. The monitors were run simultaneously for periods ranging from two weeks to two months. The means of the $PM_{2.5}$ monitoring data within each city were found to be highly uniform but the coarse PM data had a major variability. The authors concluded "Only fine particles were found to have equivalent mean concentrations, suggesting that only one monitoring site in each community is required to provide an adequate exposure estimate of the outdoor component. However, variable concentrations of total inhalable and/or coarse particles were found, which implies a requirement for multiple monitoring sites [for sampling ambient coarse mode particles]".

Quackenboss et al. (1991) studied exposure to PM_{10} and related health effects in Tuscon, AZ. The ambient PM_{10} data measured by the Pima County Department of Environmental Quality (PCDEQ), method unspecified, were compared to the outdoor PM_{0} measured at the homes of the subjects in the study, using a Harvard indoor aerosol sampler (Marple et al., 1987). The distances between the homes and the PCDEQ monitors ranged up to 20 km. The Harvard-indoor-sampler data measured outdoors had a statistically significant slope of 0.63 ± 0.03 when fit through the origin [intercept ≡ 0] versus the ambient PM_{10} values reported by PCDEQ. The authors do not report any collocated inter-comparison between these two different monitors to document whether the 0.63 factor was more due to differences in instrumental inlet penetration curves, than to higher PM at the ambient monitoring sites. The spread of the daily outdoor PM_{10} about the ambient values was quite large ($R^2 = 0.185$), but no data are provided to show whether this variance is predominantly in either the coarse mode or the fine mode of the PM_{10}.

Lillquist et al. (1998) measured outdoor PM_{10} at three hospitals in Salt Lake City and compared the measurements from November 29, 1994 through April 29, 1995 with the simultaneous measurements at the Utah Department of Air Quality (DAQ) ambient monitoring station nearby. The three hospitals were 3.4, 5.6 and 12.5 km from the DAQ site, and the mean PM_{10} values measured were quite different, leading to the conclusions that "Under conditions of high atmospheric PM_{10} concentrations...Salt Lake City, UT requires more than one monitor. When ambient PM_{10} concentration data are used as a predictor of individual exposure, more than one centralized monitor is absolutely necessary."

These results for the Salt Lake City, UT area are in direct contrast to those reported by Pope et al. (1999) at a similar scale of separation, in the same season and general area (Provo, UT in the Utah Valley) one year later (November 18, 1995 - March 15, 1996). In this period the Utah Valley PM_{10} data monitored at three sites (at separations of 4 to 12 km) were virtually identical, with Pearson correlations of 0.92 and 0.96. The greater degree of variability in the PM_{10} of the Salt Lake City, UT area, relative to the Provo, UT area, may be related to the higher presence of wind-blown crustal material in the Salt Lake City area. Pope et al. (1999) reported that increased health effects in the Utah Valley were associated with stagnation and thermal inversions leading to a buildup of anthropogenic PM_{10}, whereas the similarly high concentrations of PM_{10} created by high winds picking up crustal materials were not associated with increased health effects in that same community. Thus, this is an indication that it may be important to differentiate exposure to PM of ambient anthropogenic origin from locally-variable high concentrations of wind blown dust, as in Salt Lake City, which may not be as important for health effect prediction as anthropogenic ambient PM.

Buzorius et al. (1999) measured short-term aerosol number concentrations by using a condensation particle counter at several locations in metropolitan Helsinki, Finland. They report that number concentration can vary in magnitude with the local traffic intensity, and that "during the working days concentration averages of 10 min - 1 h are good representatives of concentration variation in relatively large areas of the city." They conclude, "Therefore, by sampling at one point in the [urban] space one can describe changes in relatively large area of the city with correlation coefficient > 0.7".

Dubowski et al. (1999) point out that although the relationship of small variation of $PM_{2.5}$ mass concentration may hold for a community, 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; urban and semi-urban 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 1000 times lower than the total mass concentration, so that such a gradient of 0.03 to 0.01μg/m^3 for these components would not be noticeable for total $PM_{2.5}$ mass measurements of order 25 μg/m^3.

Jedrychowski and Flak (1998) report on the spatial variation of suspended particulate matter (SPM) measured as "black smoke" (BS) in Cracow, Poland during the years 1991 - 1995. The authors report that, for both winter and summer, the city could be divided into a central "high pollution zone" and regions of lower pollution concentrations decreasing with distance from the city center. The authors do not report the size fraction of the PM collected or the calibration procedure used to convert the BS reading into SPMμg/m^3. Thus, their results may emphasize the effect of the black carbon content related to local traffic density variations which could produce a gradient signal imposed on a more uniform background of well mixed emissions of PM.

Väkevä et al. (1999) measured the vertical gradient of submicron particles in an urban street canyon of Lahti, Finland. They monitored number concentration by using a TSI screen diffusion battery and a condensation particle counter at 1.5 m and 25 m above the street at rooftop level. "It was concluded that dilution and dispersion decreases the concentrations of pollutants emitted at street level by a factor of roughly 5 between the two sampling heights." The presence of such a local vertical gradient of concentrations for people living in high-rise buildings may need to be considered in studies of exposures to PM of urban populations.

Spatial variation of ambient PM on a regional scale. Burton et al. (1996) report on the spatial variability of sulfates and PM in metropolitan Philadelphia, PA and their data, also discussed by Wilson and Suh (1997), show very little variance in spatial mass concentrations. They showed that there was a gradient of ammonium sulfate across the city, with a maximum in the urban area center, indicative of ammonia generation by human activities, leading to a composition variation of that component of urban PM.

Keywood et al. (1999) reported their analysis of PM variability measured in six Australian cities using a MOUDI sampler. They reported that PM_{10} was more highly correlated with $PM_{2.5}$ than with coarse PM (PM_{10} - $PM_{2.5}$), suggesting that "variability in PM_{10} is dominated by variability in $PM_{2.5}$". Although the authors found that mass of $PM_{2.5}$ was highly correlated with mass of PM_1 ($r^2 = 0.98$), the mass of the ultrafines (nuclei mode), reported both as $PM_{0.15}$ and by integration under a fitted curve, had weak correlations with $PM_{2.5}$ of $r^2 = 0.50$ and 0.01, respectively. This suggests that although a single monitoring station may be adequate for characterizing fine mode ambient PM in a community, the ultrafine mode mass of ambient PM, like the coarse mode mass, may require additional monitoring.

Leaderer et al. (1999a) 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, VA 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, VA 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 the coarse mode PM, estimated as PM_{10} - $PM_{2.5}$, no significant correlation among these sites was found (n = 30, r = -0.20).

Jantunen et al. (1998) and Koistinen et al. (1999) report on the protocol and quality assurance procedures of the EXPOLIS exposure monitoring study that included measurements of ambient and microenvironmental concentrations of $PM_{2.5}$, and personal exposures to $PM_{2.5}$. A planned article (Jantunen et al., 2000) is expected to report the final results of their exposure analyses on these measurements. Their preliminary results show that: (1) in Basel and Helsinki, a single ambient monitoring station was sufficient to characterize the ambient $PM_{2.5}$

concentration in each city - only a few simultaneous measurements of ambient $PM_{2.5}$ were made in the four other EXPOLIS cities (Athens, Grenoble, Milan and Prague) so no other intra-city comparisons are available at this time; and (2) by using microenvironmental concentration data collected while the subjects were at home, at work, and outdoors, the time-weighted-averages of these data 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.

In summary, a $PM_{2.5}$ measurement at a properly cited ambient monitoring location can represent the mixed mean concentration of ambient $PM_{2.5}$ that exists in the ambient atmosphere of that local area. Coarse mode PM is apparently influenced more by local sources than $PM_{2.5}$ so this finding of a single monitoring site as being sufficient for $PM_{2.5}$ is not generally applicable to the coarse fraction of PM.

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., 1999a). When $PM_{2.5}$ and PM_{10} are collected independently, and the coarse fraction is obtained by difference, as $PM_{10-2.5} = PM_{10} - PM_{2.5}$, 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 $PM_{10-2.5}$ on two separate filters, the coarse fraction also is expected to have a larger error than the fine fraction. There is a possible error due to loss of mass below the cut-point size and a gain of mass above the cut-point size which 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.

Carrothers and Evans (1999) also discuss the effect of relative measurement errors (both instrumental error and Berkson-type error) when analyzing the relative toxicity of ambient $PM_{2.5}$ to that of the coarser mode ($PM_{10} - PM_{2.5}$). They present a model that allows an estimate of the relative bias in the regression coefficients of coarse and fine PM on daily mortality, and conclude that “if one pollutant is truly more harmful than the other, then it must be measured more precisely than the other, in order not to bias the ratio of the fine and coarse regression coefficients”. The authors note “the need for spatial variability data, i.e., several ambient monitors situated across a metropolitan area for a period of many months" so that "definitive conclusions can be made regarding the possibility of bias due to differences in measurement [Berkson-type] error among correlated pollutants".

Wilson and Suh (1997) review the difference between the chemistry, sources and factors influencing exposures to generic fine and coarse ambient PM (see Chapter 3). They point out "The infiltration factor, which gives the fraction of outdoor particles found indoors, . . . is greater for the fine particles than for coarse particles, largely because of the lower indoor lifetimes of coarse particles relative to fine particles." Wilson and Suh (1997) hypothesize that because the ambient monitoring data for $PM_{2.5}$ are more constant across an urban area than the corresponding concentration data for coarse mode PM, represented by (PM_{10} - $PM_{2.5}$), and PM_{10} is more highly correlated with $PM_{2.5}$ than with (PM_{10} - $PM_{2.5}$), the health effects associated with total PM_{10} are more likely to be related to the variations of the fine mode portion of the $PM_{2.5}$ than the variations of the (PM_{10} - $PM_{2.5}$) measure of the coarse fraction.

The authors note that $PM_{2.5}$ is most often a mixture of fine mode PM and coarse mode PM because the lower tail of the coarse mode extends below 2.5μm AD, and since 2.5 μm is a 50% cut point, not a 100% cut point, a $PM_{2.5}$ sampler collects some PM > 2.5 μm. They conclude that "Fine and coarse particles are separate classes of pollutants and should be measured separately in research and epidemiologic studies. PM_{10} and $PM_{(10 - 2.5)}$ are indicators or surrogates, but not measurements, of fine and coarse particles." Janssen et al. (1999a) report "A method to estimate the distributions of various fractions of PM_{10} in ambient air in the Netherlands". However, their method estimates the $PM_{2.5}$ fraction, but not the fraction of PM_{10} that is exclusively in the fine mode aerosol, as recommended by Wilson and Suh (1997).

5.3 EXPOSURES TO AMBIENT PM IN INDOOR MICROENVIRONMENTS

Besides the exposure to ambient PM while outdoors, people are also exposed to PM of ambient origin in the non-ambient indoor-type microenvironments of the residence, workplace, school, motor vehicle, etc. Ambient PM enters indoors from the outdoors by both forced and free convection. An equal quantity of indoor air must also leave through the same type of passages to maintain the pressure equal between the indoors and outdoors. Figure 5-3 shows an idealized indoor microenvironment exchanging air with the ambient surroundings.

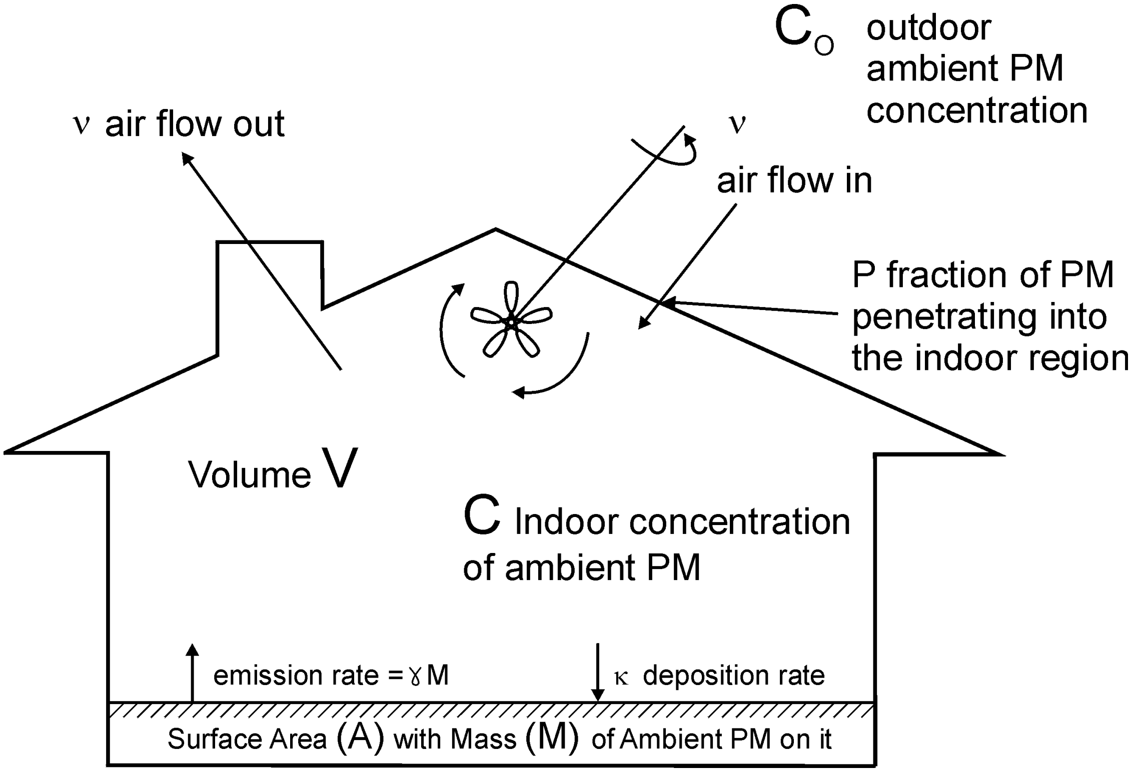

Figure 5-3. Two compartment model for PM deposition and resuspension by human activity in a residential microenvironment.

As described by Alzona et al. (1979), Tung et al. (1999) and Kulmala et al. (1999) the ambient PM intrusion process can be modeled for a well mixed indoor volume (*V*) by a mass balance equation between start time t = 0, and stop time t = T, with initial condition C = C(0), @ t = 0. Here C(0) is the concentration of PM that originated from the ambient air that is found in the indoor air while the adjacent outdoor air has a PM concentration of Co = Co(0), @ t = 0:

$$V\,\mathrm{dC}/\mathrm{dt} = v\,P\,\mathrm{Co} - v\,\mathrm{C} - k\,V\,\mathrm{C} + \mathrm{Q}_{\mathrm{a}} \qquad (5\text{-}2)$$

where V = volume of the well mixed indoor air, m^3 ;

v = volumetric air exchange rate between the indoor and outdoor condition, m^3/hr;

P = fraction of ambient PM that is not deposited on the inlet surfaces during the entry into the indoor volume from the ambient condition, a function of v, $0 < P < 1$;

Co = concentration of ambient PM in the outdoor air that enters into indoor volume V, $\mu g / m^3$;

C = concentration of the ambient PM in the indoor volume V, $\mu g / m^3$;

k = deposition parameter for the ambient PM upon the interior surfaces within volume V, 1/hr; a function of the distribution of PM aerodynamic diameter (AD), presence of air cleaners or in-line filters in air circulation systems, etc.

Q_a = A discontinuous rate of resuspension of some of the ambient PM that had entered volume V at time t > 0 and had been deposited on interior surfaces, μg/hr; $Q_a \geq 0$.

All the parameters, save for V, are assumed to be functions of time and PM AD. For example, the deposition parameter (k) can increase as a step function if an air cleaner is turned on. Anuszewski et al. (1998) showed that in-line filters in heating systems may remove PM of optical diameters less than 1 μm. The volumetric air exchange rate (v) is always finite, but it varies with wind speed, indoor to outdoor temperature difference, and as windows are opened or closed. For particles larger than 1 μm AD, which can settle by gravity, the penetration factor P is expected to decrease with decreasing air exchange flow rate (v) because the time that is available, for gravitational deposition in passage through cracks and fissures, increases as the flow rate decreases. Suh et al. (1993) showed that operation of an air conditioning system leads to usage of a lower air exchange rate, resulting in lower PM concentrations of ambient constituents, such as sulfates. The resuspension parameter (Q_a) can be zero when the volume V is unoccupied, or while occupied but people are sleeping or sedentary and $Q_a > 0$ when people are active within V.

It is important to note that the Koutrakis et al. (1992) reformulation of Equation 5-2, presented as Equation (7-3) in U.S. Environmental Protection Agency (1996), was used to compute average values of deposition rate (k) independent of any resuspension of deposited material. This deposition parameter (k) will vary widely for PM_{10} as its relative amounts of fine mode and coarse mode PM vary. Therefore, the term Q_s (emission factor of indoor sources, in units of μg/hr) in Equation (7-3) *op. cit.*, contains within it the resuspension of PM from ambient sources that was deposited on previous days or earlier on the very day of the measurement.

If C(0) is of the order of Co(0) and we assume an average value for Q_a, we can estimate the average steady state value of C. This is done by setting dC/dt = 0 in Equation 5-2 and solving for C as follows:

$$C \approx (\mathrm{Co}\, P\, a + Q_a / V) \;/\; (a + k), \tag{5-3}$$

where $a = v / V$, the number of air exchanges per hour.

The outdoor PM (Co) at the location of the air inlet to indoor volume V may not be exactly equal to the ambient PM concentration (Ca) measured at the neighborhood air monitoring station that can be several kilometers away. Let us assume that there are no major sources of PM between the monitoring station where Ca is measured and the location where Co is measured, and that the surrounding urban area is relatively homogeneous in terms of traffic, residential communities and commercial activities including light industry. With this frame of reference, we can model the measured outdoor concentration (Co) as equal to the measured ambient monitoring station concentration (Ca) plus a small random component (ϵ) that has a mean of order zero and a finite variance.

This parameter (ϵ) covers the true spatial variation of ambient PM resulting from micro-scale weather variations and local sources. For example, on some days there is a wind vector component from the monitoring station to the modeled indoor location and on other days the vector will be from the indoor location to the monitoring station. Sophisticated methods that account for presence of sources and the topography between ambient monitoring stations are available for estimating ϵ by interpolating ambient pollutant concentrations between monitoring stations (Beyea and Hatch, 1999). The parameter ϵ also allows for random measurement errors from the weighing of the filters and the measurement of the flow rate. This leads to the relationship for the concentration of ambient PM in the indoor microenvironment (C), in terms of the measured ambient concentration (Ca) as:

$$C \approx \mathrm{Ca}\, Pa / (a + k) + [\in Pa + Q_a / V] / (a + k) \tag{5-4}$$

Equation 5-4 indicates that an indoor microenvironment will tend to equilibrate with the ambient PM at a fractional value of the ambient PM concentration.

Clayton et al. (1993), Özkaynak et al. (1996a) and U.S. Environmental Protection Agency (1996) report the results of the Particle Total Exposure Assessment Methodology (PTEAM) Study carried out in Riverside, CA in 1990. 178 subjects carried personal PM_{10} monitors for one day each, while PM_{10} was being monitored in their home, outside their home (Co) and in their community (Ca). At each home, an air exchange rate was measured using a continuously emitting source of a perfluorocarbon tracer (PFT). Using the procedure of Koutrakis et al. (1992), Özkaynak et al. (1996a) determined average values of P and k for PM_{10} of 1 and 0.65/hr respectively, and 1 and 0.39/hr for $PM_{2.5}$. For the 178 homes, 174 values of a were successfully obtained during the daytime period from approximately 7am to 7pm. The histograms of the values of $P\,a\,/\,(a+k)$ for the 174 monitored homes are shown for PM_{10} and $PM_{2.5}$ as Figure 5-4. These values represent an estimate of the average fraction of the outdoor PM that was found inside the home. Because of the positive resuspension term (Q) the actual values will be expected to be higher than the values shown. However, there is minimal resuspension of submicron particles and very little $PM_{2.5}$ is resuspended (U.S. Environmental Protection Agency, 1996) so the reported values of k and Q_{is} in the PTEAM study for $PM_{2.5}$ are unlikely to have been appreciably affected by ambient PM resuspension. Exposure to the ambient accumulation mode PM ($\sim 0.1\ \mu m < AD < \sim 1\ \mu m$) is inferred by the relations of exposure to sulfur and sulfates which are predominantly in this size range (Leaderer et al., 1999a). PM in this size range has a deposition parameter of order 0.2/hr (Özkaynak et al., 1996b).

In summary, the indoor microenvironment will have an appreciable amount of the ambient $PM_{2.5}$ equilibrated within it. In the case of the PTEAM homes during the fall season in Riverside, CA, where temperatures were moderate and homes had an air exchange rate of approximately a = 1/hr, the fraction of the ambient PM_{10} to be found within the indoor residences was approximately $1/(1+0.65) \approx 0.6$. For $PM_{2.5}$ the fraction $1/(1+0.39) \approx 0.7$. For sulfate the fraction $1/(1+0.16) = 0.85$. The combined exposure to PM of ambient origin both indoors and outdoors is analyzed in Section 5-7.

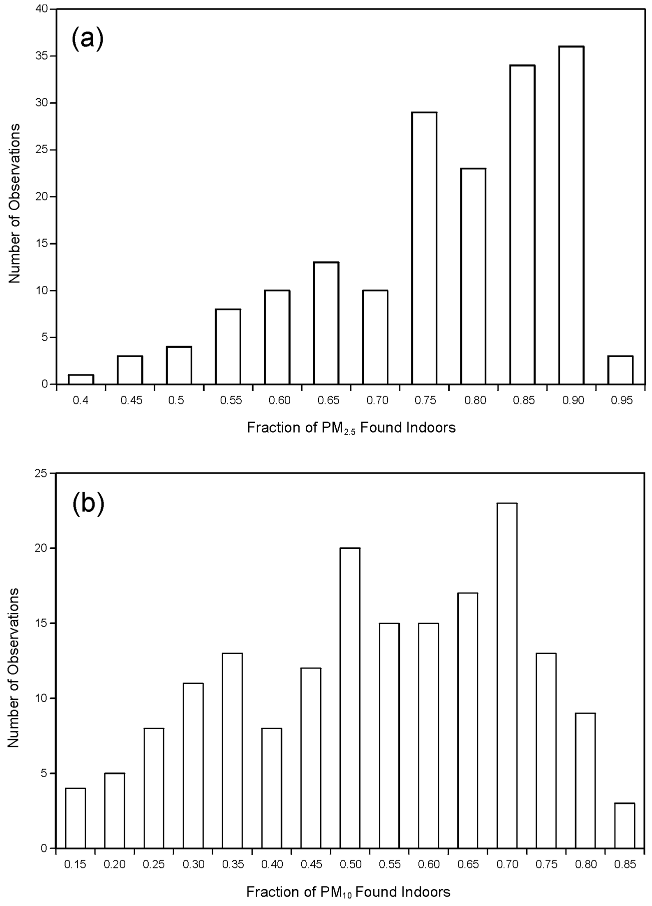

Figure 5-4. Histograms of the estimated fractions of outdoor $PM_{2.5}$ (a) and outdoor PM_{10} (b) found indoors during the PTEAM study in Riverside, CA (Computed from data of Özkaynak et al., 1996a).

5.4 EXPOSURES TO PM OF INDOOR ORIGIN

U.S. Environmental Protection Agency (1996), Wallace (1996), and Ott and Roberts (1998) review and discuss the pre-1996 literature on PM as found indoors from indoor sources. Most particles generated indoors by human activities have different chemical and physical properties than those generated by anthropogenic ambient sources (Siegmann et al., 1999). In the U.S., in general, combustion product PM from ambient sources is from the burning of fossil fuels (e.g., coal, gasoline, fuel oil) and wood, and combustion product PM from indoor sources is from biomass burning (e.g., tobacco, wood, foods, etc.). However, some indoor sources of PM, such as cigarette smoking, meat cooking and coal burning (in China), occur both indoors and outdoors and may constitute an identifiable portion of the measured ambient PM by use of source apportionment techniques (Cha et al., 1996; Kleeman and Cass, 1998). During the PTEAM study (Özkaynak et al., 1996a) some non-ambient particles that appeared on personal monitoring filters were identified as skin flakes, fibers and carpet debris. These PM species are considered as "inert or nuisance dusts" by the U.S. Department of Labor (Code of Federal Regulations, 1998), which has established an 8-hour $PM_{3.5}$ time-weighted-average (TWA) occupational standard of 5,000 $\mu g/m^3$ for controlling them. Some other non-inert PM species of indoor or occupational origin may be carcinogenic (e.g., cigarette tars, radon progeny) or produce chronic effects (e.g., silica, asbestos). However, there is no evidence that day-to-day fluctuations of personal exposures to PM species such as these that are not known to produce acute effects at lower concentrations, could cause the day-to-day fluctuations of the acute health effects (mortality and morbidity) that are associated with the day-to-day fluctuations of ambient PM concentrations in epidemiologic studies (Schwartz et al., 1999).

The major sources of indoor PM in the residence include cigarette smoking, cooking, and unvented or poorly vented combustion devices such as stoves and kerosine heaters. Human and pet activities also lead to PM detritus production from track-in soil, fabrics, skin and hair, home furnishings, etc., which can all be found in the ubiquitous house dust found on floors and in the lint trapped by the filter of a clothes dryer. This generic house dust and lint is suspended in the indoor air by air movements and, after deposition, it can be resuspended by cleaning activities of sweeping, dusting and vacuuming. Other sources of PM in the home may arise from hobby activity, and from para-occupational materials brought into the home by workers on their persons (Sterling et al., 1995). Biological aerosols commonly found indoors are discussed in Chapter 7 of U.S. Environmental Protection Agency (1996).

Abt et al. (1999a) studied the PM size distribution and sources of PM in four non-smoking households in the Boston metropolitan area, and confirm previous findings that the major indoor emission sources of PM are cooking, cleaning and human activity. They discuss the size characteristics of these ubiquitous sources and report "The size of the particles generated by these activities reflected their formation processes, with combustion processes (oven cooking, toasting and barbecuing) producing fine particles, and mechanical processes (sauteing, frying, cleaning, and movement of people) creating coarse particles." The authors suggest that at air exchange rates of less than 1/hr the indoor sources of PM predominate in the indoor microenvironment and at air exchange rates above 2/hr, the outdoor sources of PM predominate.

The smoking of cigarettes is the major contributor to PM concentrations from indoor sources in the homes where people smoke. Neas et al. (1994) report from the Harvard 6-City Study that the between 1983 and 1986, annual average $PM_{2.5}$ was $31\mu g/m^3$ higher in the homes of consistent smokers than in the homes of consistent non-smokers. An extensive investigation has been recently performed on environmental tobacco smoke (ETS) exposures of non-smokers in homes and workplaces in Europe by Phillips et al. (1994, 1996, 1997a,b, 1998a,b,c, 1999). For example, Phillips et al. (1999) sampled non-smokers homes and workplaces in Basel, Switzerland and computed annual total ETS exposures as the mean “Potential inhaled quantity” in mg of RSP. They found that the median exposures of non-workers in smoking households were 15% higher than in smoking households, and at the 90th percentile that smoking households were 100% higher than the non-smoking households.

Jenkins et al. (1996a,b) made similar measurements in the U.S. and report that smoker’s homes in 1993 and 1993/1994 averaged 17 and 20 ug/m^3 above the mean values in non-smoker’s homes, respectively. The higher effect of smoking (31 ug/m^3) reported by Neas et al. (1994) in 1983 - 1986 may have been related to changes in smoking habits in the decade between these studies, such as smoking reduced tar cigarettes and smoking less cigarettes in the home in the more recent Jenkins study.

Klepeis et al. (1996) measured $PM_{3.5}$ due to environmental tobacco smoke (ETS) using a TSI 8510 piezobalance. They measured air exchange rates in two airport glass-enclosed smoking lounges and estimated a rate of emission of 1.43 mg/min per cigarette smoked by means of a box model for a well-ventilated lounge volume. The $PM_{3.5}$ coefficient of variation (σ/μ) in the room was 0.12 indicating that the lounge was indeed well-mixed. The authors concluded that personal exposures to ETS can be satisfactorily modeled in such microenvironments. Such a model may be useful for calculating the non-ETS PM found in indoor microenvironments where smokers are present, which is often mostly of ambient origin.

For smoker’s homes in Riverside, CA, the PTEAM study (Özkaynak et al., 1996a) reported that ETS constituted about 75% of the $PM_{2.5}$ generated by indoor sources and 55% of the PM_{10} generated by indoor sources, which corresponds to approximately 35% of the coarse PM

(PM_{10}-$PM_{2.5}$) generated by indoor sources. For those homes (smoking and non-smoking) in which cooking took place, cooking fumes were responsible for 66% of the $PM_{2.5}$ indoor emissions.

Occupational exposures to PM generated indoors are a major source of PM exposure for "blue collar" workers involved in the "dusty trades". OHSA standards for PM are both specific, for industries such as coal mining and textile manufacturing which have significantly different toxicities of their PM (e.g., coal dust vs cotton dust), and generic, for all "inert and nuisance dusts" not specifically mentioned (Code of Federal Regulations, 1998). An 8-h time-weighted-average (TWA) $PM_{3.5}$ generic standard of 5 mg/m^3 has been established, in part, to maintain visibility in work places for personal safety, as well as for respiratory health protection. It is interesting to note that the American Conference of Governmental Industrial Hygienists (1996) has established similar guidelines for generic PM, not specific to an industry ("containing no asbestos and < 1% crystalline silica"), as "Particulates Not Otherwise Classified (PNOC)". Their recommended 8-h TWA for such PNOC as "inhalable particulate" (PM_{100}) and "respirable particulate" (PM_4) are 10 mg/m^3 and 3 mg/m^3, respectively.

5.5 PERSONAL EXPOSURES TO PM OF ONE'S OWN PERSONAL ACTIVITIES

Personal activities, such as body motion, cigarette smoking, hobbies and occupational tasks may generate a plume of particles that abruptly decreases in concentration with distance from the person generating the particles. This is especially important in certain occupational settings. Average concentrations of inhalable dust [~PM_{50}, American Conference of Governmental Industrial Hygienists (1996)] over 50 mg/m^3 have been measured by personal monitoring of agricultural activities, with an average respirable fraction (PM_4) of 4.5 mg/m^3 (Nieuwenhuijsen et al., 1999).

Teschke et al. (1999) report on personal total PM exposure data (~PM_{50}) from workers in industry involving wood-production, wood-finishing and wood-construction, as collected by the U.S. Occupational Safety and Health Administration Integrated Management Information System (Stewart and Rice, 1990). The data set consisted of 1632 observations over the period from 1979

-1997. The arithmetic mean exposure was 7.93 mg/m^3, the geometric mean was 1.86 mg/m^3, 12 values exceeded 100 mg/m^3, and the maximum reported value was 604 mg/m^3.

During the time of the existence of the activity plume, a subject will be exposed to a much higher PM concentration than would be measured by a stationary PM monitor several meters away. Mage and Ott (1996) analyzed this situation for a cigar being smoked in a large tavern. During the period while the cigar is burning (called theα period) and during the period immediately after the cigar is extinguished, during which the plume is mixing into the rest of the indoor air (the β period), the person generating that plume will be exposed to a higher concentration of PM than an indoor monitor located in the same room. Then, after the plume is mixed (the γ period), the subject and a monitor anywhere in that microenvironment will experience the same concentration of that material.

The difference between the reading of a personal monitor and an indoor monitor during the α and β periods represents the PM exposure due to a person's own personal activities. This incremental exposure above the surrounding microenvironmental concentration is unique to the subject, save for the case where someone else is immediately next to the monitored person (e.g., a helper holding parts together to be welded by a monitored welder).

5.6 PERSONAL PM EXPOSURE

This is PM exposure that occurs from direct inhalation of tobacco smoke by a smoker. By placing the item (pipe, cigar, cigarette) to the mouth, the smoker inhales the concentrated fumes directly into the lung and completely bypasses the inlet of a personal PM monitor worn by the smoker. This exposure category is distinct from the personal smoking-activity exposure described in the previous section, which can be captured by a personal monitor in the breathing zone of the subject.

The magnitude of this source is appreciable and dominates all other categories of exposure when computing the total exposure to PM of a smoker from all sources of ambient and non-ambient PM. The nominal amount of PM (tars) delivered by each brand and type of cigarette smoked are reported by the Federal Trade Commission (1994). The concentration (mg/m^3) delivered by each puff is not reported. However, for a person breathing at an average of 10 Lpm over a day, or 14.4 m^3/day, each 1 mg delivered adds approximately 70μg/m^3 to the 24-h average PM exposure of the smoker. Consequently, a subject smoking 20 cigarettes (one pack) per day, rated by FTC at 10 mg tar each, would have an average daily PM exposure of 14 mg/m^3.

Siegmann et al. (1999) point out a major difference between cigarette smoke particles and other combustion source particles derived from candles, paper, and motor vehicles. "The particles of cigarette smoke are much larger than the other ones, and grow with time to even larger ones" and "particles generated when a cigarette is smoked are known to contain liquid matter which will contract the particles to denser material due to the surface tension of the liquid". The latter effect would also increase the Stokes' Law settling velocity of the particle, which would increase the effective aerodynamic diameter (AD) of the particle.

5.7 EXPOSURE TO PM OF AMBIENT ORIGIN IN BOTH INDOOR AND OUTDOOR MICROENVIRONMENTS

Let a subject living in the residence of volume V, at the location where the outdoor PM concentration is Co, spend some fraction of time outdoors (y), and the remaining fraction of time (1 - y) in the residence where Equation 5-4 applies. For simplicity, let us also assume that while outdoors the subject is close to home and exposed to the local outdoor PM concentration Co [Co = Ca + ϵ, where Ca is the ambient monitoring station value and ϵ is a random increment of order zero with a finite variance]. The subject's total exposure to PM of ambient origin (Ea) during a complete day will be as follows:

$$\mathrm{Ea} \approx \mathrm{y}(\mathrm{Ca} + \epsilon) + (1 - \mathrm{y})[\mathrm{Ca}\ Pa + \epsilon\ Pa + \mathrm{Q_a} / V] / (a + k), \tag{5-5}$$

$$\text{or Ea} \approx \alpha\ \mathrm{Ca} + \beta \tag{5-6}$$

where $\alpha = \mathrm{y} + (1\text{-y})\, P\, a / (a + k)$

$\beta = \epsilon\, [\mathrm{y} + (1 - \mathrm{y})\, P\, a / (a + k)] + (1\text{-y})\, \mathrm{Q_a} / V\, (a + k)$

Equation 5-6 means that a person's daily exposure to the ambient PM is proportional to the concentration Ca at the monitoring station (α Ca) plus a random variable (β). The variable β has a term with mean zero and finite variance representing the effect of the spatial variation in the ambient air (ϵ), plus another positive term with a finite variance representing resuspension of that day's settled ambient PM by mechanical activity in volume V (walking on carpets, sitting on stuffed furniture, dusting or vacuuming, etc.).

From Equation 5-6 we expect that someone living in a style such that they are not exposed to any appreciable additional occupational PM or indoor generated PM to have a measured personal exposure to total PM (E) that is highly correlated with the ambient PM concentration. However, should someone live in a style in which they are exposed to additional PM generated at work and at home, as from passive cigarette smoke, cooking, fireplace emissions, etc., then this increment to the exposure would appear mathematically as if it were a gross enlargement of the random term β. Because the strengths of these indoor sources are independent of both the ambient concentration Ca and the outdoor concentration Co, the resulting correlation of total personal exposure (to ambient PM plus non-ambient PM) with the ambient PM concentration would be decreased, and approach zero. These are the relationships that have been observed in the PM exposure literature, as discussed in the following section.

People are exposed to PM of ambient origin while indoors (C, defined as the concentration of PM of ambient origin in the indoor microenvironment) and outdoors (Co, where $\mathrm{Co} \approx \mathrm{Ca}$ due to possible spatial variation of PM from the monitoring station concentration Ca). Consequently one must include the exposure to ambient PM indoors in any analysis of the total exposure to PM of ambient origin. The analysis below follows the formulation of Mage (1998) and Kulmala et al. (1999).

During any given period T, the exposure to PM of ambient origin (Ea) is defined by Equation 5-7.

$$\mathrm{Ea} = 1/\mathrm{T}\,[\int_0^{\mathrm{T}} \delta_{oi}\mathrm{Co}\,\mathrm{dt} + \int_0^{\mathrm{T}} \delta_{io}\,\mathrm{C}\,\mathrm{dt}] \tag{5-7}$$

where $\delta_{oi} = 1$ if outdoors and $= 0$ if indoors; $\delta_{io} = 1$ if indoors and $= 0$ if outdoors.

Because of the current inability to monitor the quantity of ambient PM inside the indoor locations where people spend their time, Equation 5-7 is often modified to estimate Ea by assuming either $\delta_{io} = 0$ or $\mathrm{C} = \mathrm{Co}$ at all times, resulting in Equation 5-8 as follows:

$$Ea \approx 1/T \int_0^T Co\, dt \qquad (5\text{-}8)$$

Equations 5-7 and 5-8 are both attempts at addressing the question, “How much of the ambient PM that existed in the ambient atmosphere during the previous T = 24-h period are people exposed to during that period?” However, in practice, a calculation complication exists. A portion of the coarse mode ambient PM that enters the home and then is deposited in the home during the interval $0 < t < T$ is resuspended by human activity during the 24-h measurement period (Kildesø et al., 1999). There is expected only minimal resuspension of fine PM directly, but any fine PM that settled out and adhered to a coarse particle could also be resuspended. It is difficult, if not impossible, to distinguish the resuspended ambient PM from the PM of non-ambient origin that is also resuspended by the same human activities.

Figure 5-3 shows the two compartment model that is used for this analysis. The first compartment is the indoor air of volume *V* and the second compartment is the surface area (A) within volume *V* where ambient PM mass is deposited. The other parameters are as defined previously. The PTEAM study (Özkaynak et al., 1996a,b) reports widely variable values of *k* for night and day conditions which may be influenced by diurnal patterns of resuspension. The fraction of the mass (*M*) of freshly deposited ambient PM on surface *A* that is resuspended per unit time is a function of human activity, such as walking on a surface and creating vibrations and air currents sufficient to levitate a particle. The differential equations that describe the daily accumulation of ambient PM on interior surfaces (*M*) and the time variation of ambient PM in volume V are as follows:

$$V\, dC/dt = P\, \nu\, Co - \nu\, C - k\, V\, C + \gamma\, M \qquad (5\text{-}9)$$

$$dM/dt = k\, V\, C - \gamma\, M \qquad (5\text{-}10)$$

where γM is the resuspension rate (mass/time) of that day’s previously deposited ambient PM that is assumed to be proportional to the mass (*M*) deposited on the surface, $\gamma \geq 0$.

The solutions to equations 5-9 and 5-10 are coupled, and C and *M* must be solved for numerically using the randomly varying values of Co, *P, k, v,* and γ due to weather and human activity in the indoor location. The initial conditions for the integration are as follows: $M = M(0)$ @ t = 0; C = C(0) at t = 0.

At the start of the integration at t = 0, the ambient PM inside an indoor microenvironment (C) is some unknown fraction of the outdoor PM that developed from air exchange over the previous 24-hrs; if some of that material may already be deposited on the indoor surfaces then $M(0) \geq 0$. In the following analysis, the mass of ambient PM on the surfaces that had deposited from the previous weeks' depositions (since the last house cleaning) is assumed to be uncorrelated with the concentration of ambient PM on the measurement day so it does not enter into the equation.

Except for the trivial conditions where γ is equal to zero, the solutions to coupled Equations 5-9 and 5-10 are beyond the scope of this chapter, because several parameters and initial conditions are unknown. For example, γ is close to zero when the indoor occupants are all asleep and/or sedentary; it is larger while the occupants are moving about; it is maximal while an occupant is dusting, sweeping or vacuuming. The value of the air exchange parameter *v* varies with the wind speed and varying window and door openings, and *k* varies with the size distribution of the mixture of PM in the ambient air that penetrates into the home. Consequently, the approach chosen here is not to solve them simultaneously because of the unknown parameters. Rather, Equation 5-9 is solved with $\gamma = 0$, and the result is reported as an inequality because the exposure to PM of ambient origin with resuspension ($\gamma > 0$) must be greater than the exposure without resuspension ($\gamma = 0$).

Table 5-1 summarizes some of the parameters necessary for creating a solution to Equations 5-7 and 5-9. The air exchange rate (*a*) is the ratio v / V, and it was measured in the PTEAM study by collection of a continually emitted tracer gas inside the subject homes. These data for *a* contain two important artifacts that lead to a negative bias (an underestimation) of the average value of *a.* First: When the air exchange rate was too high, the collected tracer was below the minimum detectable level (MDL) of the analytical procedure. Özkaynak et al., (1996a,b) used the MDL values of *a* as alternative default values for computing *k* and *P* in order to maximize the amount of data available for the analysis using a non-linear optimization procedure (Koutrakis et al., 1992). Second: The concentration of tracer gas, and therefore the

TABLE 5-1. SUMMARY OF THE MEAN VALUES OF PM VARIABLES FROM THE PTEAM STUDY

Parameter	$PM_{2.5}$ 7am-7pm Day	$PM_{2.5}$ 7pm-7am Night	$PM_{2.5}$ 7am-7am Combined	PM_{10} 7am-7pm Day	PM_{10} 7pm-7am Night	PM_{10} 7am-7am Combined
k (1/ hour)	0.27	0.39	0.39	0.91	0.43	0.65
a* (1/ hour)	1.144	0.98	0.97	1.144	0.98	0.97
P**	1	0.89	1	1	0.88	1
Co (μg/m3)	48.9	50.5	49.7	94.9	86.3	90.6
Q_{other} (mg/hr)***	1.46	0.784	1.08	14.3	2.82	5.64

Source of Data: Özkaynak et al. (1996a).
* Values of air exchange above the maximum level of detection (LOD) were assumed equal to the LOD.
**P was constrained to the range $0 \leq P \leq 1$.
***Emission rate other than from cooking and smoking. This may include some resuspended ambient PM.

amount of the tracer collected, is inversely proportional to the air exchange rate. Therefore, the reported air exchange rate (a) is the reciprocal of the average reciprocal of the instantaneous air exchange rates. The negative bias arises from the fact that $1 / [(1/a + 1/a^*) /2]$ is always less than $(a + a^*)/2$. Examination of these PTEAM data in Table 5-1 leads to the following observations:

1. PM penetration in Riverside, CA was lower at night than during the day. At night, where homes are closed tighter than during the day, and wind velocities are lower, PM entry velocities are slower which allows more time for PM deposition during the transit through the building cracks and fissures. This is shown by lower nighttime values of the air exchange rates (a) and penetrations (P) in Table 5-1. The non-linear optimization procedure (op. cit.) found a solution with the 12-h daytime penetration fraction as $P \approx 1.15$ (Wallace, 1999b). Given that the penetration fraction must always be equal to or less than 1, Özkaynak et al. (1996a) constrained the solution by setting $P = 1$ and the other parameter values were recomputed accordingly. The combined 24-h (daytime + nighttime) values also had to be constrained by setting $P = 1$. Thus the unconstrained PTEAM data analysis indicates that the average nighttime penetrations were approximately 80% of the average daytime values (0.89/1.15). This observation of higher daytime penetration of PM may not hold in other

locations, or for all homes in a given location. For example, where it is hot during the day and cool at night, people with an HVAC system may keep windows closed during the day and open them at night to cool off.

2. Indoor emissions (including resuspended ambient PM) are much greater for coarse PM (PM_{10} - $PM_{2.5}$) than for $PM_{2.5}$, which is consistent with the literature findings that fine PM is held more tightly to surfaces than coarse PM. Resuspension of previously settled PM is expected to be greatest during the day when people are most active (Roorda-Knape et al., 1998). For example, Larssen et al. (1993) report a study of three days in an unoccupied apartment in Oslo on a busy street, showing that the indoor fraction of ambient coarse PM in their study is of order 0.2. In the PTEAM study the PM collected during the second 12-h day period contained some of the PM deposited during the first 12-h night period that was resuspended by daytime activity. This increased the amount of the nighttime PM that the subject was exposed to during the 24-h period, but the analysis treated it as a component of Q_{other}.
3. There is an opposite and counter-intuitive relation with the *k* values. The computed *k* for $PM_{2.5}$ is higher at night than during the day (0.39/hour vs 0.27/hour), which is expected since turbulence (which provides upward velocity components to counter Stoke's Law settling) is less when homes are closed and people are resting and sleeping. Turbulence reduces gravitational settling but also decreases the boundary layer thickness through which PM must diffuse to reach surfaces for deposition which may increase deposition rates for the ultra-fine PM (< 1 μm AD). For PM_{10} the opposite variation of k is observed. The PM_{10} *k* value decreases from a day time value of 0.91/hour to a nighttime value of 0.43/hour which is counter to the $PM_{2.5}$ behavior, and also counter to the deposition increase from day to night during passage of PM_{10} into the indoor environments. There are several possible explanations for these phenomena:

a) There are experimental errors in all measured values, such as air exchange rate (*a*) and concentrations (Co and C). Such experimental errors can inadvertently cause artifacts to appear like values of $P > 1$ as cited earlier (Özkaynak et al., 1996a). The air exchange rate data set $\{a\}$ contains two artifacts as previously discussed. The minimum detectable level (MDL) of perfluorocarbon tracer (PFT) mass collected corresponds to a maximum detectable air exchange rate because an increase in air exchange rate lowers the amount of tracer collected. The <MDL PFT data for *a* were reported in two ways: as the maximum level of detection (LOD) for the air exchange rate corresponding to the PFT MDL, and at twice that LOD corresponding to half the PFT MDL. The authors then chose the LOD values of *a* for the computation of the parameters *k* and *P* shown in Table 5-1. The usage of the set of these estimated air exchange rates as LOD introduces an unknown variance component into these analyses because the authors weighted the LOD air exchange values derived from below MDL values equally with the air exchange values derived from above MDL data.

b) There are some counter-intuitive results from the procedures used. From first principles, the mean value of *a, k* and *P* for both night and day should be between their respective daytime and nighttime values. However, as shown in the last column, this is not true except for the *k* value for PM_{10} which is close to the mean of the day and night values. Other parameters in the report, not cited above, also do not display this conservation type property (i.e., $PM_{2.5}$ cooking emissions were rated at 1.56 mg/min during the day and 0.69 mg/min during the night, but for the 24-h average they come out at 1.66 mg/min)

c) The fundamental equation used for computing *k* and *P* is derived from a steady state solution to the mass balance equation shown above, by setting dC/dt = 0 in Equation 5-2. However, a steady state does not exist because all parameters except house volume (*V*) are functions of time. Furthermore, as time increases the mass of PM deposited on surfaces increases. If no intermediate cleaning takes place, the same movement will raise more dust at the end of the sampling day than at the beginning of the sampling day. Although one can put in mean values for these parameters there is a correlation between them because air exchange rate is higher during the day when ambient PM_{10} is higher (Özkaynak et al., 1996a). Thus, the steady state equation for 24-hrs may underestimate the contribution to the exposure to the daytime PM.

d) Özkaynak et al. (1996a) pooled 149 daytime observations and 144 nighttime observations into a data set of 293 day and night observations. This is a valid procedure if the parameters to be estimated have an identical expectation for the nighttime and daytime values, and the only difference between them during the night and day is a combined random fluctuation about their mean value with a random experimental error in their measurement. However, on a theoretical basis, one expects the values of *k* and *P* to be different between night and day because of the gross difference in air exchange rates (*a*) between night and day, and the fact that indoor human activity at night is usually much less than daytime activity. In the absence of the influence of human activity the indoor value of *k* only has a constant expectation if the relative size distribution, the proportion of $PM_{2.5}$ to (PM_{10} - $PM_{2.5}$), is constant. In PTEAM the day time $PM_{2.5}$ and (PM_{10} - $PM_{2.5}$) were approximately equal and at night there was approximately 50% more $PM_{2.5}$ than (PM_{10} - $PM_{2.5}$) (Özkaynak et al., 1996a).

e) Penetration (*P*) and decay rate (*k*) may both depend on air exchange rate (*a*) and, thus, may be correlated to each other. This may lead to unstable or inaccurate analyses.

f) The results are real and there is some mechanism operating that is not completely understood causing the opposite behavior of the *k* values for fine PM ($PM_{2.5}$) and coarse PM (PM_{10} - $PM_{2.5}$).

An alternative procedure to estimate mean values, and to conserve the property that mean 24-h values must be approximately intermediate between their constituent 12-h day and 12-h night values, would be to use only the complete data set that constitutes a nominal 24-h average by discarding all daytime sets without a matching nighttime set and *vice versa*. Then the 24-h mean value of indoor and outdoor concentrations could be used with the 24-h mean value of air exchange and reported in two ways: 1) from averaging the mass of PFT collected using only those data where it was greater than the MDL for both night and day; 2) from averaging the mass of PFT collected using <u>all</u> data, but giving lower weights to the default values of *a* computed with the arbitrarily set MDL PFT values. The unknowns in the equation would be the corresponding values of *P, k* and emission strengths (e.g., Q_{other}) averaged over 24-hrs. Such procedures should then give mean values of *P, k*, and emission strengths approximately intermediate to their day and night values.

Abt et al. (1999b) also model their PM size and number density data (Abt et al., 1999a) from four homes in the Boston area using the same Koutrakis et al. (1992) model described above, as used in the PTEAM study. The authors define the "effective penetration efficiency of outdoor air" for PM of various size ranges by the term $P\,a\,/\,(a + k)$ which represents the fraction of the outdoor PM found indoors at equilibrium. They report effective penetration efficiencies ranged from 0.38 to 0.94 for 0.02 - 0.5 μm particles with a maximum between 0.1 and 0.2 microns.

For 0.7 - 10 μm particles the efficiency values ranged from 0.53 to 0.12, decreasing with increasing particle size. Whereas the PTEAM study (Özkaynak et al., 1996a) only reported mean values of penetration (*P*) and deposition (*k*) values for their 178 subjects, these Abt et al. (1999b) data indicate that "estimated decay rates varied considerably both within and between homes, with variability attributed to factors including differences in air flow rates, house volumes and surface materials." This suggests that the variances of the distributions of $P\,a/(a + k)$ shown in Figure 5-4a and 5-4b, are underestimated because they were derived using the two PTEAM mean values of *k* as a constant.

5.7.1 Estimation of the Daily Exposure to PM of Ambient Origin

Let each person spend a fraction x of their time outdoors during the day and a fraction w outdoors during the nighttime periods during which PM is monitored [y≈ (x + w)/2]. While outdoors, people are exposed to 100% of the ambient concentration and while indoors, they are exposed to a lower fraction of the ambient PM as estimated by setting the derivative equal to zero in Equation 5-2 that resulted in Equation 5-3.

The resulting equation for the fraction (z) of the daily ambient PM one is exposed to, assuming 12-h daytime and 12-h nighttime sampling, is as follows:

$$z = \frac{[x + (1 - x)P\,a/(a + k)](Co)day + [w + (1 - w)P\,a/(a + k)](Co)\,night + F(M)}{(Co)day\ +\ (Co)night} \qquad (5\text{-}11)$$

where the function of deposited mass of ambient PM that is resuspended [F(*M*)] is ≥ 0. Because of the difficulty in computing *M* by solving Equation 5-11, as discussed previously, the assumption that [F(*M*)] is equal to zero for all time t > 0 allows a rewriting of Equation 5-11 as an inequality:

$$z \geq \frac{[x + (1 - x)P\,a/(a + k)](Co)\,day + [w + (1 - w)\,P\,a/(a + k)]\,(Co)\,night}{(Co)\,day\ +\ (Co)\,night} \qquad (5\text{-}12)$$

The estimation of z can be made using parameters from the PTEAM data set shown in Table 5-1 and the fractions of time spent outdoors (x and w) shown in Table 5-2. In this analysis

TABLE 5-2. AVERAGE FRACTIONS OF TIME SPENT OUTDOORS OR IN A VEHICLE IN THE PTEAM(DAY) STUDY AND NHAPS STUDY (NIGHT) [PTEAM NIGHTTIME DATA NOT AVAILABLE]

Location Outdoors	Daytime Fraction (8am-8pm)	Nighttime Fraction (8pm-8am)
Outdoors at home location	0.040	(See below)
Outdoors at other location	0.087	0.020 (Both locations)
Outdoors in vehicle	0.092	0.032
Total Outdoor Fraction	x = 0.219 (PTEAM)	w = 0.052 (NHAPS)

* Sources of data: Özkaynak et al. (1996a) and Klepeis et al. (1999).

it is assumed that the ambient PM (away from traffic) is relatively uniform throughout the community. The air exchange rate while driving a closed vehicle is very large (> 13/hour at 20 mph) so the subject in a vehicle would be exposed to ~ 100% of the ambient PM measured at the central site plus the PM generated by the surrounding traffic (Ott et al., 1992; Park et al., 1998).

A recent study (California Environmental Protection Agency, 1998) reports that $PM_{2.5}$ in motor vehicles is intermediate between the roadside concentration and the concentration measured immediately outside the vehicle. The inside/outside ratio for the vehicles in commuting traffic was approximately 2/3. Note that the locally generated PM from the traffic surrounding the vehicle does not directly influence the monitoring station measurement (Ca) or the outside air at the home (Co). Alm et al. (1999) monitored the particle count (by Climet-500 laser particle counter) in a commute vehicle in Kuopio, Finland and compared the results with the background values, estimated as the mean count at the start and finish of the trip at an off-road location. The authors found that the excess (vehicle - background) counts of fine PM (optical equivalent diameter < 1 micron OD) increased as the average vehicle and wind speeds decreased, and that the excess counts of coarser PM (> 1 micron OD) increased as wind speed and vehicle speed increased.

Substituting the corresponding parameters from Tables 5-1 and 5-2 in Equation 5-12, the mean values for the daily total fraction of the ambient PM that people are exposed to (z) are estimated to be $z \geq 0.75$ for $PM_{2.5}$ and $z \geq 0.64$ for PM_{10}. The bounds for the PTEAM study can be estimated from the daytime minimum (0) and maximum (0.976) values of x reported in PTEAM, and assuming that the nighttime minimum exposed subject is indoors (w = 0) and the maximum exposed subject at night is outdoors or in a vehicle for 4 of the 12 hours (w = 0.33). The estimates of the population range then becomes as follows:

For $PM_{2.5}$: z maximum ≥ 0.88; z mean ≥ 0.75; z minimum ≥ 0.72

For PM_{10}: z maximum ≥ 0.87; z mean ≥ 0.64; z minimum ≥ 0.58

The mean values, the caveats cited above not withstanding, are consistent with the PTEAM findings that approximately 3/4 of the indoor $PM_{2.5}$ and 2/3 of the indoor PM_{10} were of ambient origin (Özkaynak et al., 1996a). The minimum and maximum values are conservative because identical daytime and nighttime values of Cout,a, k and P are implicitly assumed for all homes in the study. A Monte Carlo analysis, allowing all parameters to vary randomly about their mean values, would increase the estimated variance of z so the maximum would increase and the minimum decrease.

Abbey et al. (1999) evaluated the effect of time spent indoors as a surrogate for exposure to PM from indoor sources. They compared the relative risk (RR) of mortality by nonmalignant respiratory disease with ambient PM_{10} concentration, for different amounts of time spent outdoors, in the 7th Day Adventist Health Study on Smog (ASHMOG). They assumed that the indoor concentration of PM_{10} of ambient origin was 70% of the outdoor PM_{10} concentration to allow for a protective effect of staying indoors. They found that RR for a $50\mu g/m^3$ increase of ambient PM_{10} increased when the number of hours spent outdoors increased (and the number of hours indoors decreased) during the week, as shown in Table 5-3. Thus, the authors reasoned that increased exposure to indoor generated PM and decreased exposure to PM of ambient origin did not appear to be a confounder in their analysis of the effects of ambient PM. This increasing RR trend with time outdoors is consistent with a higher exposure to particles of ambient origin with more time outdoors.

Further in regard to time spent outdoors, Abbey et al. (1999) explain their observed gender difference in health effects in which males appear to be more affected by ambient PM than females, as being related to the males' greater percentage of time outdoors than females of similar ages. However, Brunekreef (1999) points out that this is not a likely explanation: "As the authors (Abbey et al., 1999) note, fine particles readily penetrate indoors, and if it is the fine particles that matter, small differences in time spent outdoors cannot matter all that much."

TABLE 5-3. RELATIVE RISK (RR) OF NONMALIGNANT RESPIRATORY MORTALITY FROM INCREASING TIME SPENT OUTDOORS

Hours outdoors per week	RR per increase of 50 μg/m^3 PM$_{10}$	95% Confidence Interval
$t \leq 4$	1.07	0.85 - 1.34
$4 < t \leq 16$	1.18	0.90 - 1.55
$t > 16$	1.32	1.02 - 1.68

Source: Abbey et al. (1999).

The presence of appreciable amounts of PM generated indoors would add to the mass of the ambient PM collected by a personal PM monitor and cause the high correlations of personal exposure to PM of ambient origin with ambient PM concentrations to degrade and approach zero (U.S. Environmental Protection Agency, 1996; Monn et al., 1997; Monn and Junker, 1999). For example, Monn et al. (1997), (with clarification by personal communication [Monn, 1999]), reported that human activity increased the median Indoor/Outdoor ratio by 20% for PM$_{2.5}$ and 50% for PM$_{10}$. As a result, some authors (e.g., Gamble, 1998) have misinterpreted an absence of a significant correlation of ambient PM concentration with personal exposure to *total PM* as implying an absence of a significant correlation between ambient PM concentration and personal exposure to *PM of ambient origin*. [See Künzli and Tager (1999) comments on Gamble (1998), and the response by Gamble (1999).]

All people in a community, when outdoors, are exposed to a heterogeneous mixture of ambient PM$_{2.5}$ with small variations of composition and concentration from the ambient PM$_{2.5}$ measured at a central location. Therefore, no great ecological fallacy is produced and no large Berkson-type error is involved, in the use of community ambient PM$_{2.5}$ concentration as a surrogate for exposure to particles of ambient origin. This is because the mean exposure of a random sample of people in a community to PM$_{2.5}$ of ambient origin, while both outdoors and indoors (via PM$_{2.5}$ infiltration from outdoors), is an excellent predictor for the simultaneous exposure to PM$_{2.5}$ of ambient origin of virtually everyone in that community - exceptions for unusual circumstances such as home use of high performance air cleaners not withstanding. In stark contrast, the mean of the personal exposure to PM$_{2.5}$ or PM$_{10}$ of non-ambient origin (from residential and occupational emissions) of the same randomly chosen subjects would have virtually zero predictive power for estimating the exposure to $PM_{2.5}$ or PM_{10} of non-ambient origin of any person in the community not residing in the home of a sampled person.

Exposure to an arbitrary PM fraction (PM_x) from non-ambient sources is not of relevance to the question of personal exposure to PM_x of ambient origin, and an ambient PM_x concentration is not expected to be a surrogate for any arbitrary person's total exposure to PM_x as measured by a personal PM_x monitor that collects PM_x of both ambient and non-ambient origin. In the absence of appreciable indoor sources of PM_x, a personal exposure to total PM_x while indoors is primarily to the PM_x of ambient origin that infiltrates indoors. Under such conditions a measurement of personal exposures to PM_x that is mostly of ambient origin is expected to be highly correlated with ambient PM_x concentration as described in later sections.

People in a community are routinely exposed to widely different mixtures of PM of non-ambient origin with a large variance of composition and concentration. This wide variance arises from each individual's unique combination of occupation, personal habits (e.g., cigarette smoking), social contacts (e.g., living with a smoker) and non-occupational/residential activities (e.g., cooking, cleaning and dusting). A subject's exposure to PM of ambient origin and its chemical composition can be estimated from knowledge of the ambient PM concentration, its composition, the air exchange rate between ambient and indoor locations where the subject spends time, the deposition rate of the PM and the subject's time-activity patterns. In contrast, a subject's exposure to PM of non-ambient origin and its composition cannot be predicted accurately from measurements of other peoples' exposures to non-ambient PM concentration and its composition. Knowing the distributions of ambient PM concentrations (uninfluenced by an immediate source such as a barbecue) in all other backyards *does* allow the accurate prediction of the ambient PM concentration in the subject's own backyard; knowing the distribution of non-ambient PM concentrations in all other homes *does not* allow the accurate prediction of the non-ambient PM concentration in the subject's own home.

When people are members of a cohort whose individual health outcomes are hypothesized as due to ambient PM exposure (and other possibly co-occurring), and they are being tracked from day to day, it is important to determine each individual's daily total personal exposure to PM of ambient origin (Beyea and Hatch, 1999). However, additional information is needed for such epidemiologic studies to be able to separate the total PM exposure, if measured, into its two general components of exposure to ambient PM and the exposure to non-ambient PM (e.g., from residential or occupational sources). With this information it will be possible to improve the estimation of the health outcomes related to ambient PM exposure and separate them from those related to non-ambient PM exposure.

This chapter examines ambient PM air quality and that portion of ambient PM which penetrates into indoor microenvironments. It also examines, to a lesser extent, the contribution of sources of non-ambient PM to total PM exposure. This is to aid in interpretation of acute and chronic epidemiology studies assessed in Chapter 6, in which ambient PM concentrations are assumed to be an indicator or a surrogate for mean community exposure to PM of ambient origin or an individual's exposure to ambient PM. Thus, this chapter has three objectives:

(a) Provide a review of pertinent studies of personal exposures to total PM of various size fractions.

(b) Evaluate linkages of human exposures to PM of ambient origin estimated from concentrations of PM measured at a fixed-site monitor located at some central site in a community under study.

(c) Quantify the contributions of PM of ambient origin and non-ambient origin to total personal PM exposure.

At the present time, little published data are available for time scales of less than 12-h to compare short-term personal PM exposures, short-term peak ambient PM concentrations and short-term indoor PM concentrations found in different locations within a community, all for the same time interval. It has been hypothesized (Michaels, 1997, 1998) that some health effects may be better correlated with short-term 1-h peak PM concentrations than the 12-h or 24-h concentration averages containing the peak value. This has been supported by Delfino et al. (1998) with a finding of "1-h and 8-h maximum PM_{10} having larger effects than the 24-h mean" in relating asthma symptoms. Hourly PM data and even 1/2-h PM data (Keary et al., 1998) obtained by use of the TEOM® sampler (see Chapter 4 and Ayers et al. [1999] for a description of loss of semivolatile components) are beginning to become available in the literature. Such data may allow for more study of health in relation to the lagged effect of peak ambient PM concentrations.

The PM-mortality literature, to date, is based upon the general linearized model (GLM) assumption that there is a virtually linear relationship between health effects and ambient PM exposure characterized by ambient PM concentration in the concentration range below the existing PM_{10} NAAQS (Liang and Zeger, 1986). The relative risk has generally been modeled as a proportional or percentage increase in non-trauma mortality per unit increase in ambient PM concentration, such as 0.1% per 1 μg/m^3 of $PM_{2.5}$. For a strictly linear relation with PM of ambient origin, going from 10 μg/m^3 of $PM_{2.5}$ to 110 μg/m^3 of $PM_{2.5}$ would increase the base mortality rate by 10%. However, the actual 'compounding interest' effect of an increased rate of 0.1% with each additional 1 μg/m^3 of $PM_{2.5}$ would only increase the rate by $(1.001)^{100} = 10.5\%$ which closely approximates the linear increase. In the realistic range of ambient PM concentrations, the linear approximation is generally acceptable.

By the principal of superposition for a linear system, the health effect from exposure to a mixture of ambient PM and non-ambient PM is the sum of the health effect of the ambient PM exposure plus the health effect of the non-ambient PM exposure. This assumed linear-relation implies that the health effects of the PM of ambient origin are independent of the health effects of the PM of non-ambient origin in the current range of ambient and non-ambient PM concentrations in modern society. This is complementary with the finding that sources of indoor PM appear to operate independently of the ambient PM concentration.

Given this framework of linear analysis, if PM of non-ambient origin produced health effects similar to those produced by ambient PM, the fluctuations in the health effects of PM from non-ambient sources would be independent of the fluctuations in the health effects produced by PM of ambient origin - and therefore would not act as a confounder. Rather, they would appear as a source of random error in the linear epidemiologic analyses of human health and exposure to PM of ambient origin. Until nonlinear effects of PM exposures are demonstrated in clinical and epidemiologic studies, the sources of non-ambient PM, and the effects they produce on total personal exposure to PM, are treated as errors in the estimate of human exposure to PM of ambient origin. Thus PM of non-ambient origin (e.g., from personal activity and occupational or residential sources) is considered, at the present time, to play a minor role, if any, in the study of human health and its relationship to acute exposure to PM of ambient origin in community time-series studies.

5.8 AMBIENT PARTICULATE MATTER CONCENTRATION AS A SURROGATE FOR EXPOSURE TO PARTICULATE MATTER OF AMBIENT ORIGIN

The health effects due to ambient PM may depend upon an individual's genetic makeup, lung anatomy, and previous health history, and the mass, size and composition of those inhaled particles that can be deposited within various regions of the respiratory tract. The amount of this dose per unit lung area (mg/cm^2-day) will depend on the concentration of ambient PM inhaled (e.g., the instantaneous personal exposure to ambient PM); the ventilation rate and respiration frequency (a function of physical activity and basal metabolism); and the fractional PM deposition, which is a function of ventilation rate and respiration frequency, mode of breathing (e.g., oral or nasal), and any alteration of normal pulmonary flows due to lung dysfunction. If all people had identical ventilation rates (L/min - kg body weight), respiration frequency, and deposition patterns, then the potential-dosage distribution (mg/cm^2-day) could be linearly scaled to the personal ambient PM exposure distribution which would serve as a suitable primary surrogate. The usage of ambient PM concentration in health studies as a surrogate for personal exposure to PM of ambient origin, and thereby a secondary surrogate for the ambient PM dosage, would be suitable if ambient PM concentration is linearly related to the personal exposure to PM of ambient origin and the dose-response relationship is linear (Mage, 1983).

Adult ventilation rates are lowest (mean $\approx$ 6 L/min) during the night while asleep, highest (mean $\approx$ 12 L/min; peak $\approx$ 60 L/min) during the day while awake (Adams, 1993), and in phase with ambient PM concentration, which is also usually lower at night than during the day (Clayton et al., 1993). Consequently, the product of the 24-h average ambient PM concentration, the 24-h average ventilation rate, and the average deposition parameter for the average ventilation could seriously under-predict the amount of ambient PM deposited in the respiratory tract (Mage, 1980).

In practice, when relating human health to ambient PM pollution variables (as in Chapter 6), one is forced to use time-weighted-average (TWA) ambient PM concentration as a surrogate for ambient PM exposure and ambient PM dosage because typically only fragmentary data are available on personal exposures to PM of ambient origin in populations. Data are also limited on ventilation rates as a function of basal metabolism and physical activities (Adams, 1993), and on the pulmonary deposition rates of particles people are inhaling. The size distribution of PM in the ambient air is usually unknown, and its pulmonary deposition is affected by unmeasured individual physiological parameters.

In the sections that follow, the experimentally observed relationships between ambient PM concentration, indoor concentrations of ambient PM and non-ambient PM, total personal exposures to PM, and personal exposures to PM of ambient origin are discussed in detail. The following four caveats, developed in more detail in Chapter 7 of U.S. Environmental Protection Agency (1996), should be kept in mind:

1. Ambient PM concentration (times volume inhaled) is a surrogate for the dosage of ambient PM inhaled and deposited in peoples' respiratory tracts.
2. The daily dosage of total ambient PM deposited per unit surface area of the sensitive portion(s) of the respiratory tract is in turn a surrogate for the mass of the true (but unknown) species and/or size fraction of the ambient PM that is the specific aetiologic toxic agent(s) that act by a presently unknown mechanism.
3. Virtually all analyses and discussions of personal PM exposure presented here are based on personal exposure to PM of self-declared non-smokers.
4. A total TWA personal exposure to total PM (ambient PM plus non-ambient PM) is expected to be a poor surrogate for the personal exposure to PM of ambient origin. This will be particularly true for those people whose personal exposures to total PM are dominated by residential and occupational indoor sources, or personal sources such as a hobby activity or active smoking of tobacco.

5.9 CONCENTRATIONS OF AMBIENT PM FOUND INDOORS AND IN OTHER NON-AMBIENT ENVIRONMENTS

In the absence of appreciable indoor sources, there is an excellent correlation between ambient PM concentration (ambient PM is virtually all of ambient origin) and the concentration of PM found indoors. Figure 5-5 (Tamura et al., 1996a; U.S. Environmental Protection Agency, 1996) shows how the indoor PM_{10} correlated with the outdoor PM_{10} for a set of seven elderly non-smoke exposed individuals living in traditional Japanese homes. These Tokyo homes (Itabashi ward), where people routinely took their shoes off prior to entering, had *tatami* reed mat or carpeting on tatami or wooden flooring, and had gas for cooking. The study was designed to

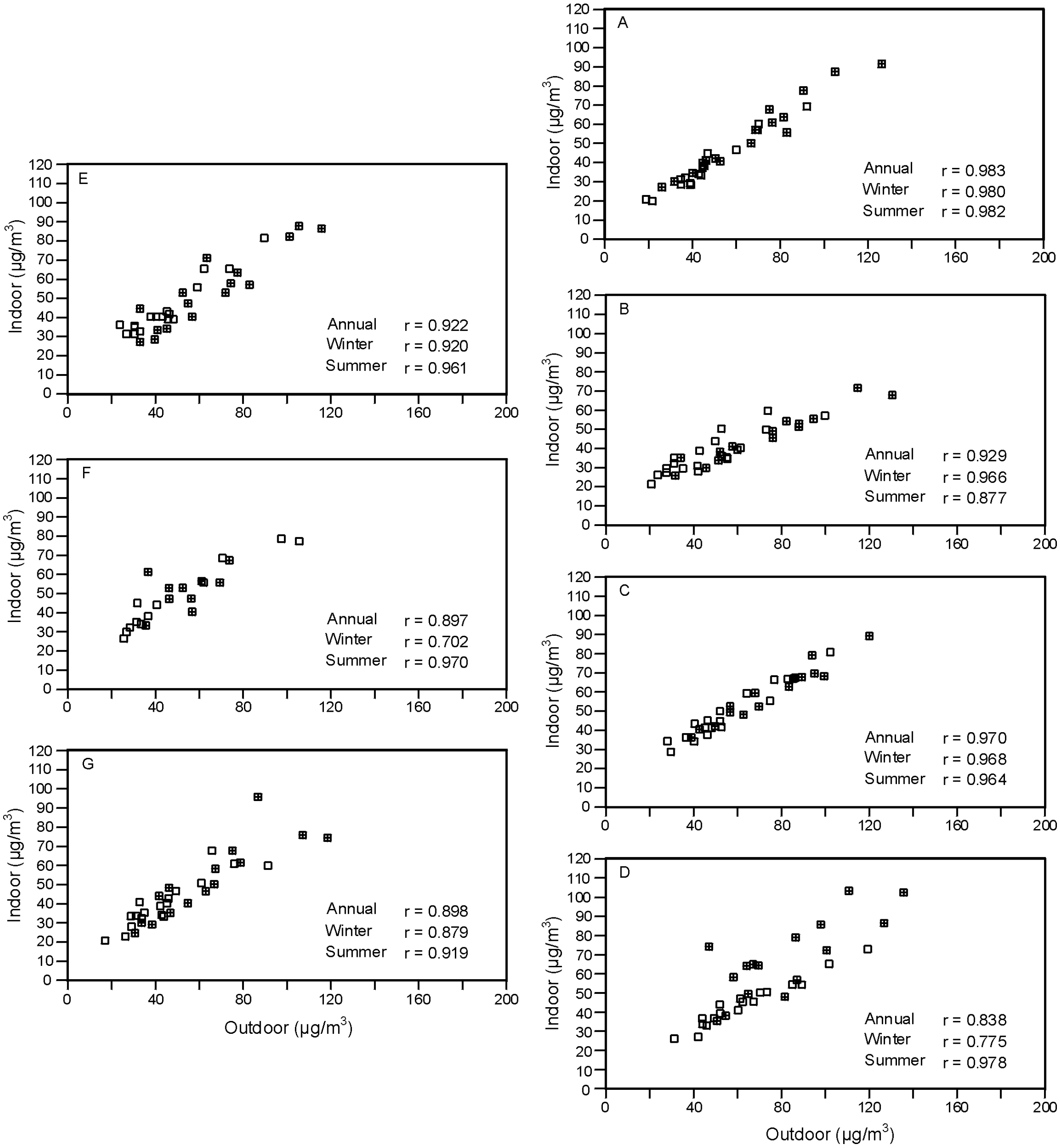

Figure 5-5. Individual indoor versus outdoor relationships of PM_{10} in Tokyo for the seven subjects (A-G) reported on by Tamura et al. (1996a). ⊠ Winter, □ Summer

monitor the exposures of people to ambient PM so the subjects were purposefully chosen in a non-random manner to eliminate indoor combustion sources of PM. Consequently, these results apply strictly to these seven people and cannot be used to infer a similar relationship in other

Tokyo homes. Table 5-4 provides the correlation coefficients reported and the designations A - G are the identifiers of the subjects with the indoor/outdoor relationships shown in Figure 5-5.

TABLE 5-4. SUMMARY OF CORRELATIONS BETWEEN PM $_{10}$ PERSONAL EXPOSURES OF SEVEN TOKYO RESIDENTS AND THE PM $_{10}$ MEASURED OUTDOORS UNDER THE EAVES OF THEIR HOMES, AND THE PM MEASURED AT THE ITABASHI MONITORING STATION

Subject ID	Number of Samples 48-h PM_{10}	Correlation between Personal and Outdoor at home (r)	Correlation between Personal and Itabashi Station (r)
A	9	0.958	0.876
B	9	0.874	0.747
C	11	0.846	0.848
D	9	0.922	0.964
E	10	0.960	0.925
F	7	0.776	0.801
G	9	0.961	0.952
A - G	64	0.834	0.830

Source: Tamura et al. (1996a).

Tamura et al. (1996a) did not report duplicate measurements of the indoor/outdoor monitors so it is not possible to correct these data for the variance component due to experimental errors of filter weighing and flowrate measurement. Such errors prevent two collocated measurements of PM from approaching a perfect correlation of r = 1, and are expected to decrease correlations, such as those shown on Figure 5-5. These data show that in the absence of major sources of indoor PM_{10} generation there is a high correlation relationship between indoor and outdoor PM_{10}.

Tamura et al. (1996b) performed another study in Osaka, Japan similar in design to their Tokyo study (Tamura et al., 1996a). The authors measured indoor and outdoor PM simultaneously at 26 homes (not chosen randomly) during the autumn seasons from 1990 through 1995. A dichotomous sampler was used with cut points at 2 and 10μm AD, and a greased impactor plate to collect PM > 10μm AD. There were 146 days when indoor PM and outdoor PM concentrations were successfully collected simultaneously in all three size ranges. The authors pooled all 146 pairs of observations and reported the group correlation coefficient between PM_{10} concentration measured immediately outdoors at the eaves of the home and the concentration of PM_{10} in the home. The regression line had a slope of 0.645, an intercept of 9.5 $\mu g/m^3$, and a correlation coefficient r = 0.865. It is interesting to note that when the authors pooled the data for only the 24 homes where 4 or more samples were collected (total number of data points not given) the correlation of r = 0.958 was almost identical to the summer correlation (Tamura et al., 1996a) of r = 0.950. The authors concluded "In the present study [Tamura et al., 1996b], similar relationships [to Tamura et al., 1996a] were confirmed with 18 houses even [though] the measurement period was limited in season and number of times [sampled].

Anuszewski et al. (1998) measured simultaneous indoor and outdoor hourly PM by light scattering using a portable nephelometer for 18 days at nine homes of non-smokers in Seattle, WA. Although light scattering does not provide a quantitative measure of concentration, the light scattering occurs from particles of optical diameters (not aerodynamic diameters) approximately centered about the wave length of the light source of the instrument. Therefore, the particles that scatter light using this instrument are primarily in the accumulation mode ($0.2 < AD < 1$ μm). An example was given in the article of how sweeping a patio (which raises primarily coarse PM) next to a kitchen only caused 25% of the increase in light scattering measured in the kitchen created by smoking a cigarette on the same patio.

The authors report that the mean indoor to outdoor ratio of hourly light scattering values was 0.98, and that correlations of indoor with outdoor were in the range $0.58 < R^2 < 0.99$. The minimum of 0.58 occurred in a home with an electrostatic precipitator (Figure 5-6) and the maximum of 0.99 occurred in a home with a standard in-line filter in the heating system (Figure 5-7). Tung et al. (1999) discuss the PM removal by a standard in-line air filter in a heating-ventilation-air conditioning (HVAC) system used in their study. "In the filtering process, particles with diameters less than 0.1μm were removed by diffusion removal mechanism. Particles with the size greater than 1μm were removed by interception and impaction." Therefore, operation of the in-line filter in the house B-1 may not have made any appreciable impact on the indoor PM concentration in the range of PM optical diameters (0.2μm < AD < 1)

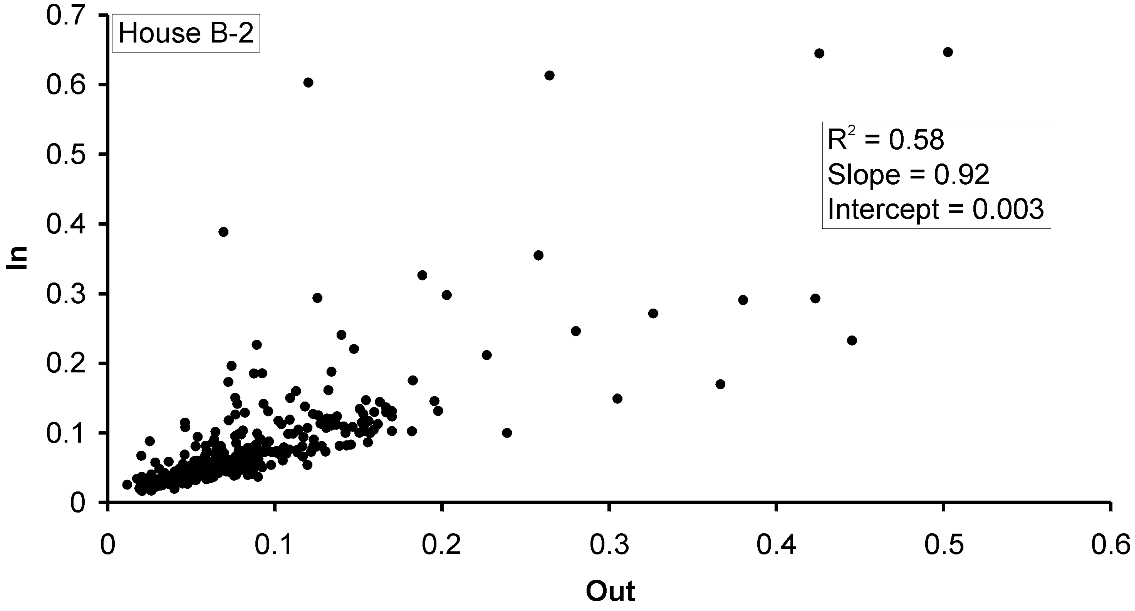

Figure 5-6. Comparison of light scattering coefficient (km^{-1}) by PM indoors and outdoors at a home with an electrostatic precipitator in operation.

Source: Anuszewski et al. (1998).

measured by the nephelometer. The absence of sources of PM in this size range in the home B-1 would then explain the almost perfect correlation between the indoor and outdoor PM shown in Figure 5-7. They report no source of PM in House B-2 that can explain the higher values indoors compared with outdoors as opposed to House B-1 where indoor and outdoor were virtually equal. House B-2 had “Some” activities in the studied room and “Medium” in/out traffic, whereas House B-1 had “Many” activities in the studied room and “Light” in/out traffic.

The average air exchange rates in both houses, B-1 and B-2, were equal (1.7/hr), which is much higher than the average in the U.S. reported by Murray and Burmaster (1995).

The electrostatic charging of PM in the size range monitored by the nephelometer in House B-2, and that PM subsequent precipitation, could explain a portion of the decrease in the indoor/outdoor PM ratio shown in Figure 5-6. The two homes with no in-line filters in the heating system had the highest minimum slopes [1.0, 0.95] and the six homes with in-line filters had intermediate minimum slopes [0.72 - 0.90]. The authors concluded that “For these nine

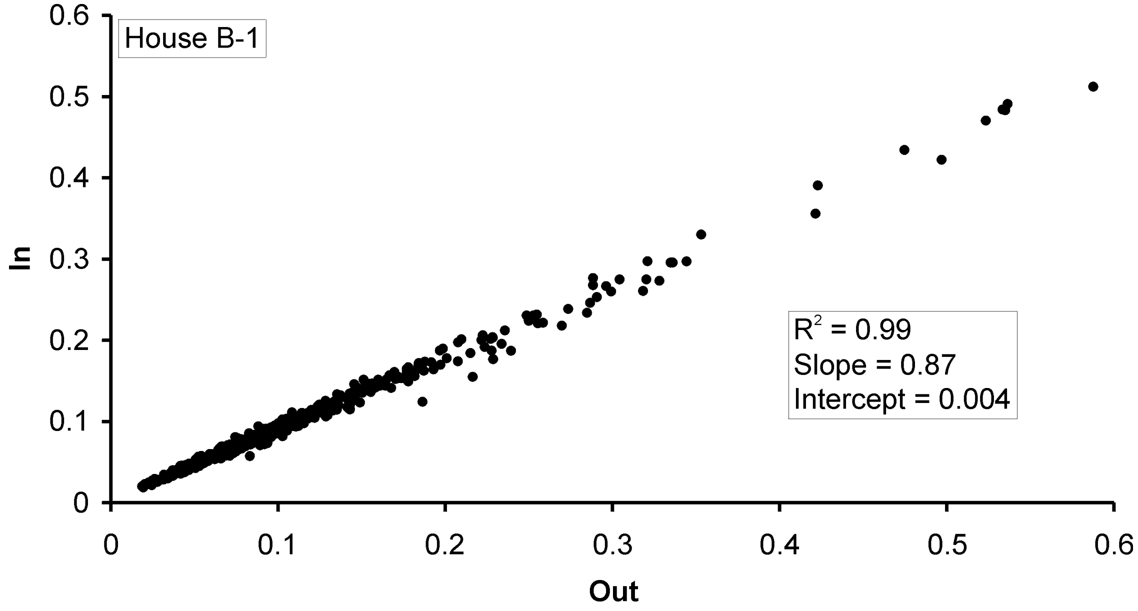

Figure 5-7. Comparison of light scattering coefficients (km^{-1}) by PM indoor and outdoors at a home with a standard in-line filter in the air recirculating system.

Source: Anuszewski et al. (1998).

homes, the dominant source of indoor fine particles, as indicated by [light scattering coefficient], appears to be the outside air."

Leaderer et al. (1999a) reported on an indoor/outdoor study of PM_{10}, $PM_{2.5}$ and related species (sulfate, nitrate, H^+, NH_4^+) at 58 residences in southwest Virginia, measured during the summer periods from 1995 to 1997. The residents were all non-smoker families participating in an epidemiologic study of maternal and infant health with respect to indoor air pollution (Leaderer et al., 1999b). Forty nine of the 58 homes were air conditioned (A/C) and 21 of the homes used gas for cooking.[3]

Table 5-5 summarizes these summer data collected in the area surrounding a central monitoring site located at Vinton, VA (6 km east of Roanoke, VA). Because of happenstance,

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[3] The residence locations were not chosen randomly to represent all residences in the area surrounding Vinton, VA so the standard statistical tests used by the authors may not apply to the sampled mean as representing the mean at any other locations in the southwest Virginia region.

TABLE 5-5. SUMMARY OF PM DATA DURING THE SUMMER IN AN INDOOR/OUTDOOR STUDY IN SOUTHWEST VIRGINIA

Pollutant	Sampling Site	n	Mean (Std Dev)
PM_{10} (μg/m^3)	Regional	47	26.0 (11.5)
	Outside all homes	43	28.0 (17.7)
	Inside A/C* homes	49	28.9 (18.7)
	Inside non-A/C homes	8	33.3 (14.2)
$PM_{2.5}$ (μg/m^3)	Regional	50	20.2 (9.9)
	Outside all homes	43	21.8 (14.8)
	Inside A/C homes	49	18.7 (13.2)
	Inside non-A/C homes	9	21.1 (7.5)
Coarse Mode (μg/m^3)	Regional	47	6.3 (2.7)
	Outside all homes	42	7.7 (6.2)
	Inside A/C homes	48	10.4 (8.5)
	Inside non-A/C homes	8	11.4 (9.7)
Sulfate ($SO_4^{=}$, nmol/m^3)	Regional	45	88.4 (51.6)
	Outside all homes	42	83.7 (53.7)
	Inside A/C homes	47	47.8 (36.3)
	Inside non-A/C homes	9	63.0 (37.3)
Acidity (H^+, nmol/m^3)	Regional	47	41.0 (28.5)
	Outside all homes	45	33.0 (36.9)
	Inside A/C homes	49	12.4 (15.3)
	Inside non-A/C homes	9	16.7 (9.4)
Ammonium (NH_4^+, nmol/m^3)	Regional	43	124.6 (59.0)
	Outside all homes	45	129.4 (87.8)
	Inside A/C homes	49	78.3 (77.2)
	Inside non-A/C homes	9	96.7 (68.9)
Nitrate (NO_3^-, nmol/m^3)	Regional	42	10.2 (5.0)
	Outside all homes	42	8.0 (5.4)
	Inside A/C homes	49	5.5 (8.9)
	Inside non-A/C homes	9	6.8 (4.6)

* A/C = Air conditoned

Source: Leaderer et al. (1999a).

some data were missing so the total numbers of samples for each category are not equal. The main findings of the summer study were that -

(1) there were no significant differences between the mean concentrations of all seven PM categories outside the homes and the same quantities at the regional site in Vinton, VA which was at an average distance of 96 km away from the residences.

(2) the cross-sectional correlations of Vinton, VA ambient PM with the outdoor residential PM on paired days were r = 0.5 for fine mode ($PM_{2.5}$, n = 34) and r = -0.2 for the coarse mode (PM_{10} - $PM_{2.5}$, n = 30).

(3) the indoor mean PM concentrations of the six independently measured quantities listed in Table 5-4 (PM coarse is not an independent measure) were all lower in the A/C homes than in the non A/C homes, which is significant at $p = (½)^6 = 1/64$.[4]

Leaderer et al. (1999a) also reported on PM sampling during the winter periods of 1995/96, 1996/97 and 1997/98, at 20 residences in Connecticut and 223 residences in the southwestern and central Virginia areas, similar to the summer PM sampling study described above. However, no central site PM data were collected during these winter periods in either state. The residents were all non-smoker families participating in an epidemiologic study of respiratory health with respect to indoor air pollution (Leaderer et al., 1999c). Kerosene heaters were used in 74 homes, and 52 of the homes with no kerosene heaters had gas stoves. Because the subjects were not chosen randomly the home characteristics and corresponding results of the study may not necessarily apply to any other residences and locations within the sampled area.

One important difference between the reported results for the winter and summer periods is that during the summer, fluctuations in ambient PM_{10} were more driven by the fluctuations of the ambient fine mode PM mass and during the winter the fluctuations in outdoor PM_{10} were more driven by the fluctuations of the outdoor coarse mass. Table 5-6 shows the regression coefficients (R^2) for these comparisons.

The authors assumed no generation of indoor sulfates for the homes without kerosene heaters in operation, and no enhanced deposition of sulfates for the homes with no A/C during

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[4] Because these are not random samples from a larger domain than N = 58, the measured means only represent the means at the 58 locations on the 58 days they were sampled, so there is a smaller sampling error than those predicted by the SD values in Table 5-4. The analytical measurement errors had an SD of 1.2 $\mu g/m^3$ for the $PM_{2.5}$, 1.1 $\mu g/m^3$ for the PM_{10}, 2 $nmol/m^3$ for the sulfate, and 1.3 $nmol/m^3$ for the H^+ ions.

TABLE 5-6. SEASONAL VARIATION OF REGRESSION COEFFICIENTS FOR PM_{10} WITH FINE AND COARSE MODE FRACTIONS

Season	Outdoor Location	n	R^2, PM_{10} vs Fine	R^2, PM_{10} vs Coarse
Summer	Vinton, VA	50	0.96	0.40
Summer	Southwest VA	45	0.21	0.12
Winter	Southwest VA and CT	53	0.07	0.90

Source: Leaderer et al. (1999a)

the summer. Then using the assumption that ambient sulfates characterized the fine mode component of ambient PM, and the measured ratios of sulfate indoors to outdoors, the authors estimated that ~75% of the ambient fine mode PM was found indoors during the summer in the homes sampled in southwest Virginia, and ~70% of the ambient fine mode PM was found indoors during the winter in the homes sampled in southwest Virginia and Connecticut.

5.10 PERSONAL PM MONITORING STUDIES AND FACTORS THAT INFLUENCE THEIR ABILITY TO ESTIMATE RELATIONSHIPS TO EXPOSURE TO PM OF AMBIENT ORIGIN

The science aspects of personal exposure monitor (PEM) usage for monitoring exposure to PM were reviewed in Chapter 7 of U.S. Environmental Protection Agency (1996). A PEM strictly measures the total exposure of the person carrying it and it applies to no other person (see the discussion of Figure 5-2 for possible exceptions from actively smoking and wearing of dust masks). A person stirs up PM instantaneously by the very act of arm waving (Bohne and Cohen, 1985; Cohen and Positano, 1986; Wallace et al., 1997) and Thatcher and Layton (1995) demonstrated that the effect of simply walking into a room creates a rapid rise of suspended PM, primarily >10 μm AD. These PM increases are created by the air currents of body movement, particles and fibers dislodged from clothes, and the vibrations and mechanical action of stepping or sitting on fabric surfaces.

Because of the PM gradients created by such movements and air currents, there is a microscale variation of PM surrounding a subject and this may contribute to what is known as a 'personal cloud'. Özkaynak et al. (1996a) defined 'personal cloud' as "a local increase in particles due to unknown sources", as evidenced by people in the PTEAM study who stayed home all day having higher personal PM exposure than the fixed indoor sampler recorded. This personal cloud may lead to a much higher personal PEM concentration of a different chemical composition than that of the PM collected by an area monitor located several meters away from the subject or in another connecting room in the same indoor environment. This phenomenon was recognized by Ogden et al. (1993) who noted that, when comparing static to personal sampling for occupational cotton dust exposure, "a mean background level of 0.5 mg/m^3 would correspond to a median personal exposure of about 2.2 mg/m^3."

McBride et al. (1999) documented the magnitude of the proximity effect by measuring, in a room of a home, the microscale variations in concentrations surrounding local sources of sulfur hexafluoride (SF_6), CO, polyaromatic hydrocarbons, and PM generated by burning an incense stick and by human activity of two-or-more people walking about the carpeted room [by Met-One laser particle counter]. Ratios of particle counts at distances of 1.0 m and 5.7 m from the sources of combustion and the center of activity were obtained at a constant height of 1.53 m above floor level. When only walking was performed, the ratio of closer mean to further mean was of order 1.5 for PM between 2.5 and 10 microns, and 1 for the PM less than 2.5 microns; When only combustion occurred, and no one was in the room, the ratio was of order 3 for PM less than 5 microns and more than 0.5 microns, and 1.5 for PM larger than 5 microns. They conclude that the proximity effect may help explain the existence of the personal cloud denoted by the difference between a personal monitor and an area monitor.

The 1996 PM AQCD Chapter 7 provided extensive coverage of many published studies, available as of 1996, that compared measurements of personal exposures to total PM and its constituents with the simultaneous PM and its constituents measured in the ambient air. It is shown below that these studies can be divided into two mutually exclusive categories:

Type 1. Longitudinal or time-series studies: A group of people are followed simultaneously for a long enough time (to provide statistical power) to determine the correlation in time of each person's personal exposure to PM with ambient PM concentration.

Type 2. Cross-sectional studies: A group of people are followed sequentially for a period of time, with each person's personal PM exposure sampled for only a few days during that period. A single correlation of the group's personal PM exposures with ambient PM concentration is computed from the subjects' pooled exposure data.

Because of their importance, two key Type-1 studies (Lioy et al., 1990; Tamura et al., 1996a) that were discussed in U.S. Environmental Protection Agency (1996) are discussed again in this new light (Mage et al., 1999) along with Janssen et al. (1999b). These three studies are unique in that each subject in the study cohort was followed for virtually the same chronological period of time as all the other subjects. This is in contrast to the Type-2 studies in the literature, such as PTEAM (Clayton et al., 1993), Spengler et al. (1985), and Pellizzari et al. (1999), in which different subjects were sampled on different days.

The important difference between these two study designs arises from the fact that each subject may have major residential indoor sources of PM that are highly correlated from day to day (the same stove and cooking fuel, the same rugs and furniture as reservoirs for resuspending PM, the same co-occupants of the home with day-to-day similar smoking or non-smoking habits, etc.) Given that these sources may provide a relatively constant increment of PM exposure to the subjects from non-ambient sources, the day-to-day variation of the study subject's total exposure may be driven by the variation of their exposures to PM of ambient origin. This coherence is lost when different subjects, each with different indoor sources, are sampled on different days and then grouped together for the data analysis, as described below.

As an example of such a Type-2 study, Pellizzari et al. (1999) monitored personal exposure to $PM_{2.5}$ of a random sample of several hundred people in Toronto, Canada, either once or twice for 3-day periods over the year from September, 1995 through August, 1996. The outdoor $PM_{2.5}$ was monitored simultaneously at the participants residences. The mean outdoor $PM_{2.5}$ during the measurement periods was 24.3 $\mu g/m^3$ and the mean personal exposure $PM_{2.5}$ was 67.9 $\mu g/m^3$. The reported correlation between the logarithms of personal exposure and outdoor concentration is 0.23, statistically significant at a level of 0.01. The authors concluded "These results, while statistically significant, indicate that none of the outdoor concentration data types can adequately predict personal exposure to particulate matter."

Lioy et al. (1990) measured 24-h personal PM_{10} exposures of 14 non-smoking individuals in Phillipsburg, NJ who were not otherwise exposed to cigarette smoke at home, for 14 consecutive days. Phillipsburg, NJ is a small city with a major industrial activity (cast iron pipe production). Lioy et al. installed four non-personal PM_{10} monitors at outdoor locations distributed throughout the city to monitor the ambient PM_{10}. These ambient PM_{10} monitors, included the Anderson Hi-Volume sampler and the 10 L/min Harvard impactor. Although they are designed to collect the same nominal PM_{10} fraction as the personal PM_{10} monitors, different monitors have slightly different penetration curves and slightly different cut-points than the personal PM_{10} monitors. Consequently, it is expected that this variation would increase the variance between the PM measured by a collocated personal PM_{10} monitor and a different type of ambient PM_{10} monitor.

The matrices of daily personal PM exposure and ambient PM data were reported by U.S. Environmental Protection Agency (1996). The matrices contain several estimated values computed by the E-M algorithm to correct for missing data and three obvious outlier values, as described in U.S. Environmental Protection Agency (1996) and by Mage et al. (1999). Figure 5-8 is the average daily personal PM_{10} exposure of the 14 subjects vs the average ambient PM concentration from the four ambient monitors. The regression R^2 value is 0.91, which assumes that the mean of the ambient PM values is the true mean ambient PM average on a given day. If the three personal exposure outliers (453, 809, 971 $\mu g/m^3$) replace their E-M estimated values, the regression would have a value of $R^2 = 0.34$ instead of 0.91. However, the average is an estimate with sampling error, so an orthogonal regression was also made to find the line that minimizes the sum of the squares of the prediction errors in both exposure and ambient concentration. With this framework, 98.4%of the variation of the mean exposure is predicted by the variation of the mean of the ambient concentrations. U.S. Environmental Protection Agency (1996) concluded that if additional subjects with similar non-smoke exposure lifestyles had been sampled on those 14 days in Phillipsburg, NJ and if additional air quality monitors had been placed in the community to more precisely estimate the mean ambient PM in the community, then the correlation coefficient between mean personal PM exposure and mean ambient PM would approach a limit of one with increasing sample size.

Tamura et al. (1996a) measured personal PM_{10} exposure of a set of seven elderly non-smoke-exposed individuals living in traditional Japanese homes, and this study was discussed in detail within U.S. Environmental Protection Agency (1996). The study was designed to monitor the exposures of people to ambient PM so they were purposefully chosen to minimize indoor sources of PM. Figure 5-5 shows how well the indoor PM_{10} correlated with the outdoor PM_{10} for these seven homes, indicating the minimal effect of indoor sources of PM.

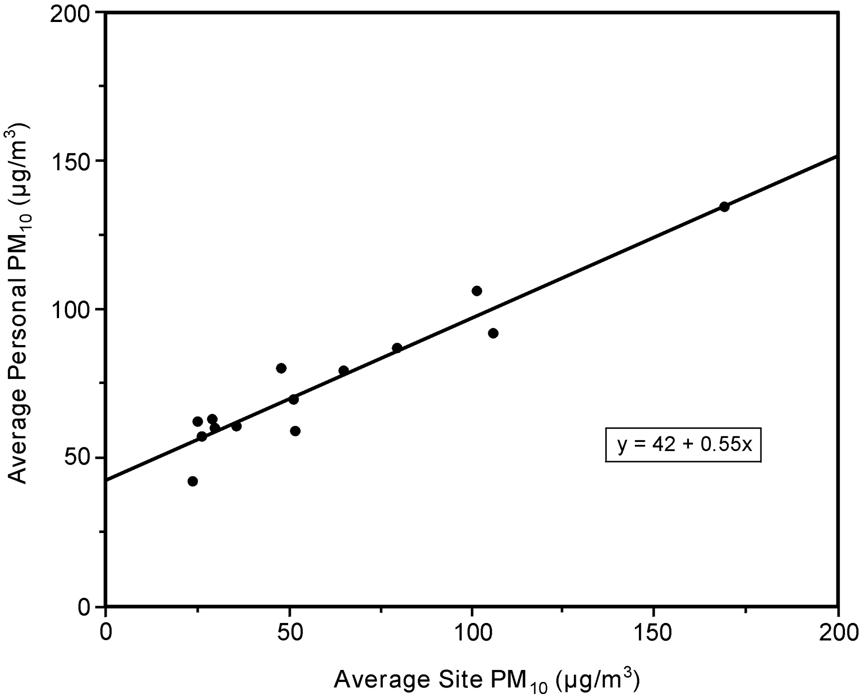

Figure 5-8. Plot of relationship between average personal PM_{10} exposure versus ambient PM_{10} monitoring data from Phillipsburg, NJ, and regression line calculated by U.S. EPA.

Source: Lioy et al. (1990).

Each subject carried the personal exposure monitor (PEM) for 48-hours, for up to 11 periods total over four seasons of the year 1992. Some data were missing due to random equipment failure, and the collected data set was screened to remove any observations which were contaminated by identifiable indoor sources of PM, such as cigarette smoking of visitors, or operation of an indoor combustion source such as a mosquito coil or an incense burner. The ambient data, the remaining exposure data, and the E-M algorithm used to estimate missing exposure data were reported in U.S. Environmental Protection Agency (1996). The individual personal exposure correlations with the ambient PM ranged from 0.77 to 0.96. Figure 5-9 shows the completed means of the eleven 48-hr average values versus the simultaneous 48-hr local Itabashi monitoring station values. The reported statistical analysis in U.S. Environmental

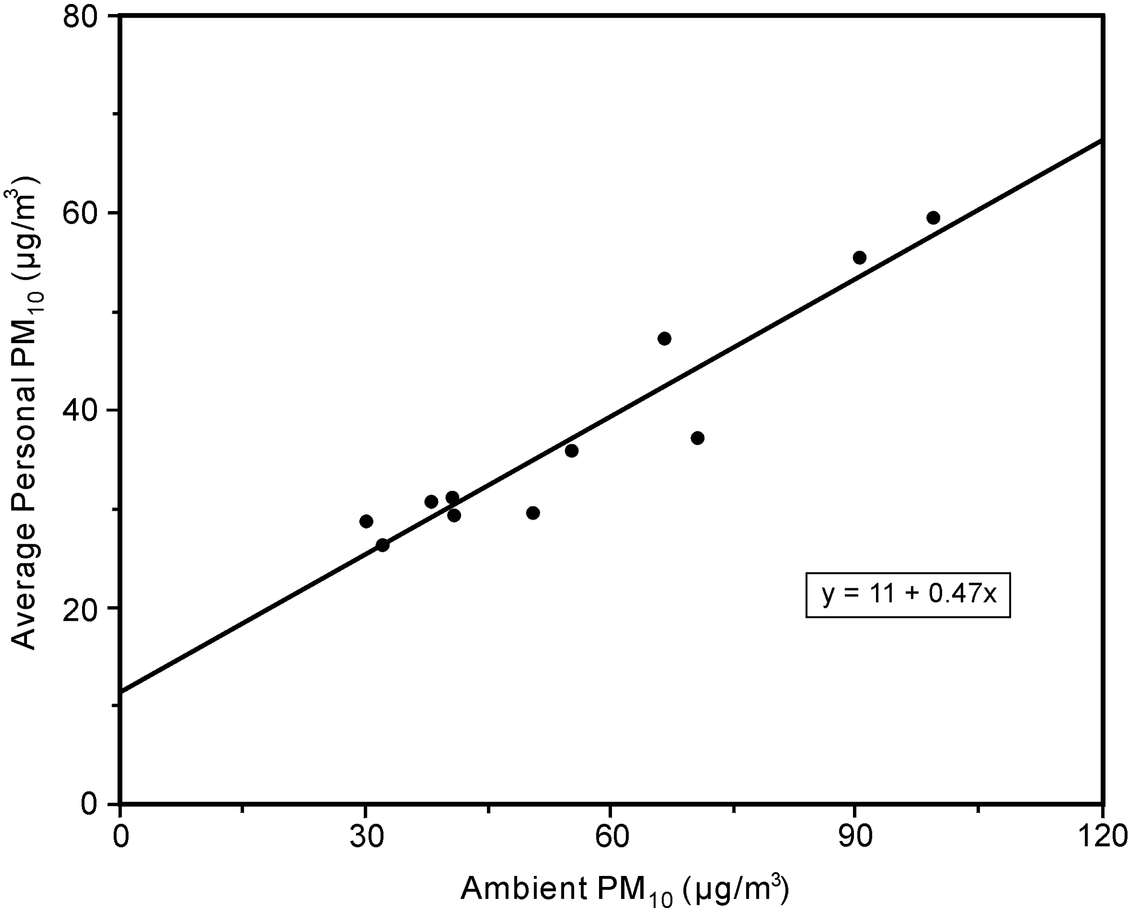

Figure 5-9. Plot of 48-h average personal PM_{10} exposure and ambient PM_{10} data from Japan—linear regression.

Source: U.S. Environmental Protection Agency reanalyses of data from Tamura et al. (1996a).

Protection Agency (1996) led to the fitted line that has an intercept of 11.3μg/m^3, a slope of 0.47, and a regression R^2 value of 0.91.

Tamura et al. (1996b) performed another study in Osaka, Japan similar in design to their Tokyo study (Tamura et al., 1996a). More than 24 subjects, all housewife non-smokers who were not exposed to smokers living at home, were sampled in a non-random manner during the autumn seasons between 1990 and 1995. A dichotomous sampler was used with cut points at 2 and 10 μm AD, and a greased impactor plate to collect PM > 10μm AD. There were 77 days when outdoor PM concentrations and personal exposures were successfully collected simultaneously in all three size ranges. The authors pooled all 77 pairs of observations and reported the group correlation coefficient between PM measured immediately outdoors at the eaves of the home and the personal exposure to PM of the housewife resident. The personal versus outdoor correlation results were for PM_2, r = 0.741; for PM_{10}, r = 0.672; for coarse mode PM_{10-2}, r = 0.343; and for the PM > 10 μm AD, r = 0.05. Because these data do not constitute a random sample, no statistical inferences can be made to other households.

Janssen (1998) reports the work of Janssen et al. (1995, 1997, 1998a,b, 1999b,c) on a study of personal monitoring of children and adults in the Netherlands. Janssen (1998) found that in longitudinal studies "Personal PM_{10} exposures of both adults (aged 50 to 70 years) and children(aged 10 to 12 years) were reasonably well correlated in time with ambient PM_{10} concentrations. Personal fine particle (FP) exposures were highly correlated with ambient FP concentrations" as shown in (Table 5-7). These cohorts were not random samples from a defined population so these results apply strictly to only the adults and children sampled.

TABLE 5-7. AVERAGE LEVELS OF PERSONAL EXPOSURES AND OUTDOOR CONCENTRATIONS AND THE CORRELATION (*r*) BETWEEN THEM IN LONGITUDINAL EXPOSURE STUDIES

Population	Size fraction	Number of subjects	Mean* personal $\mu g/m^3$	Mean* ambient $\mu g/m^3$	Median individual correlation *r*	Cross-sectional correlation *r***
All subjects	-	-	-	-	-	-
Adults	PM_{10}	37	62	42	0.50	0.34
Children	PM_{10}	45	105	39	0.63	0.28
Children	$PM_{2.5}$	13	28	17	0.86	0.41
Non-ETS exposed	-	-	-	-	-	-
Adults	PM_{10}	23	51	41	0.71	0.50
Children	PM_{10}	25	89	40	0.73	0.49
Children	$PM_{2.5}$	9	23	18	0.92	0.84

*Mean of individual averages.
**Mean value. Estimated by randomly selecting one measurement per subject, 1000 times.

Source of Data: Janssen (1998).

These data show that by excluding subjects with environmental tobacco smoke (ETS) exposure, correlation coefficients increased in all cases. For $PM_{2.5}$ the median correlation was *r* = 0.75 for all subjects, and r = 0.84 for all non-ETS exposed subjects. This indicates that, in these individual longitudinal time-series cases, the personal exposure to fine PM is highly correlated with the concentration of ambient fine PM. For comparison, Janssen (1998) obtained cross-sectional correlation coefficients by a Monte Carlo analysis. The values shown in the last column of Table 5-7 were obtained for each cohort by taking one random sample from each of the individual subject data sets (with replacement), and repeating the procedure a total of 1000 times.

Janssen et al. (1999b) report on a personal monitoring study of 13 non-randomly chosen school children, ages 10 to 12 years, in the rural town of Wageningen, the Netherlands. These children were sampled on one school day per week for a total of eight weeks. Nine of these children lived with parents and relatives who did not smoke tobacco in any form, and their data were chosen for analysis. Each of the nine children had five, six or seven 24-hour observations of personal exposure to $PM_{2.5}$ within the eight days monitored. The ambient $PM_{2.5}$ was collected at a central monitoring site on these same days for comparison using an identical monitor. Because there were widely different numbers of children with data on any given day in this time series (1 to 9), the missing data for each child was estimated using the E-M algorithm, and the results are shown in Table 5-8 along with their mean exposure and corresponding ambient concentration.

Figure 5-10 shows the relation of the estimated mean total PM of the children as a function of the simultaneous ambient $PM_{2.5}$ measured at the central station. The regression R^2 of the $PM_{2.5}$ daily mean exposures with the daily ambient PM is 97.8%, and the intercept is $12\mu g/m^3$. This analysis of children who were constrained by design to have the same time-activities at school and at home, where there were no major indoor sources of $PM_{2.5}$ that could vary from day to day, shows that in the absence of large variability of non-ambient sources of $PM_{2.5}$, variations in total personal exposure to $PM_{2.5}$ is virtually controlled by the variations of ambient $PM_{2.5}$.

Janssen et al. (1998a) report on a study of non-randomly chosen adult's exposure to PM_{10} in the Netherlands during the two winter periods of 1994. A total of 37 nonsmoking adults (18♂, 19♀), living with nonsmokers, average age 64-y, were monitored with personal PM_{10} monitors with simultaneous monitoring of the local ambient PM_{10}. One subset of 13 adults was

TABLE 5-8. PERSONAL EXPOSURES TO PARTICULATE MATTER (PM $_{2.5}$) OF NON-SMOKE EXPOSED CHILDREN IN WAGENINGEN, NL, AND STATIONARY AMBIENT MONITORING DATA (SAM). MISSING VALUES ESTIMATED ( )

Day	Person ID									Mean Personal	SAM
	01	03	05	08	09	11	13	14	15		
1	19.8	(8.0)	12.5	13.5	14.6	17.2	19.9	18.3	13.1	15.21	6.24
2	29.5	15.9	17.1	15.0	20.7	17.0	13.7	17.1	(10.5)	17.39	6.61
3	15.3	11.2	28.3	22.9	(40.9)	(29.2)	11.9	(17.0)	11.2	20.88	12.15
4	(27.1)	(16.6)	(21.1)	20.5	(29.4)	(25.9)	(18.3)	(20.0)	(15.0)	21.54	12.51
5	(41.2)	20.2	15.8	19.6	19.5	19.7	15.0	15.7	13.4	20.01	15.70
6	29.3	26.0	30.8	21.0	24.4	28.7	22.2	26.7	(20.1)	25.47	20.56
7	34.1	29.3	35.9	26.7	30.7	42.1	29.4	29.0	26.7	31.54	31.67
8	(51.3)	53.7	(41.1)	(30.7)	(35.5)	(45.2)	(49.0)	34.8	40.7	42.44	45.24

Source of Data: Janssen et al. (1999b).

monitored in the period January through March 1994, and another subset of 24 adults was monitored in the period October - December, 1994. Because there was no overlap of these two monitoring periods we analyzed each cohort separately.

The data sets for the adults are shown in Tables 5-9 and 5-10, for the 13 and 24 adult cohorts, respectively. In both cases the E-M algorithm could not be used to estimate the missing values because of the sparse coverage of these data. The extensive missing data caused the estimation routines to converge for several values in the negative concentration domain, which has no physical meaning. The method chosen for analysis was to use a linear model that was fitted to these data which included terms for days and persons, but no interaction terms.

This model we chose is equivalent to running an unbalanced two-way analysis of variance (ANOVA) on these data to estimate the marginal distribution of the means of the daily personal exposure data. Because we are only obtaining estimates of the model parameters (not testing for significance), the correlations between the people can be ignored (Winer, 1962). The last columns in Tables 5-9 and 5-10 show the estimated means that were used in the regression analysis.

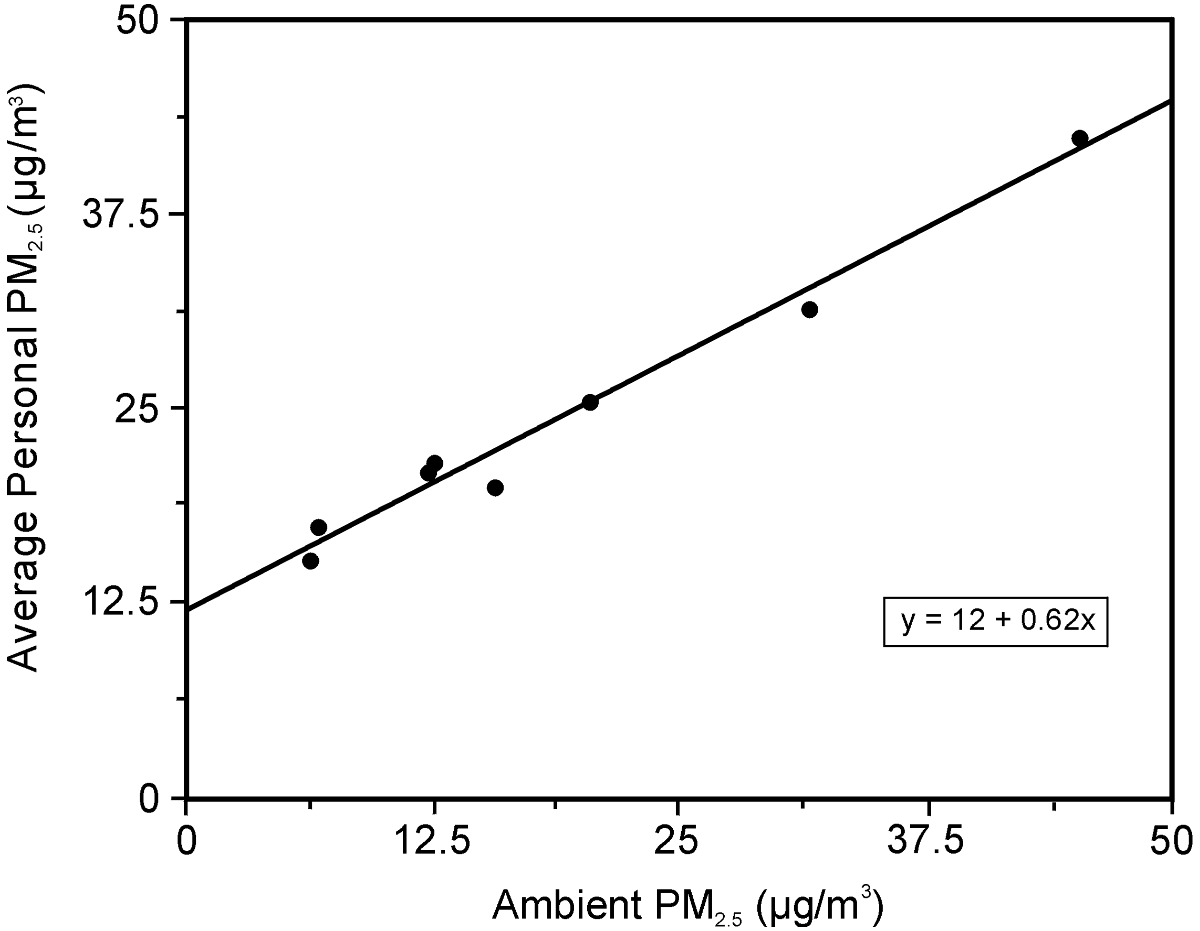

Figure 5-10. Completed mean personal $PM_{2.5}$ exposure of children not exposed to tobacco smoke at home in Wageningen, NL, versus the simultaneous ambient $PM_{2.5}$ measured in their community.

Source: Janssen et al. (1999b).

A linear regression was performed on these data with the ANOVA estimates of the daily PM exposure means and the ambient PM_{10} concentrations. The mean PM exposures (y) plotted against the ambient PM concentrations (x) are shown as Figures 5-11A,B. For the 13 adults the results provide a linear regression of y = 36.4 + 0.760 x, with R^2 = 0.424, r = 0.65; for the 24 adults, the regression is y = 34.3 + 0.543 x, with R^2 = 0.600, r = 0.74. The average Amsterdam slope of (0.76 + 0.54)/2 = 0.65 indicates that approximately 65% of an increase in

TABLE 5-9. PERSONAL PM_{10} EXPOSURE ($\mu g/m^3$) OF 13 ADULTS IN AMSTERDAM, NL SOURCE OF DATA: JANSSEN ET AL. (1998A)

		Person ID														
Day	Ambient	101	102	103	104	105	107	109	110	111	113	114	116	118	Mean of Personal Raw Data	Mean of Personal Estimated*
102	80.3						143.4					71.8			107.6	90.6
103	40.4						94.7								94.7	-
202	45.2				45.1								56.2		50.7	52.4
203	53.3				58.3	50.5		125.9					87.1	58.8	78.1	70.2
702	36.2	59.5	[68.4]	46.5	40.7		172.9	87.5				[93.0]			81.8	66.4
902	37.2					43.9		75.1		32.8			79.1	38.6	53.9	60.8
903	28.5	40.3			35.3	39.7			[45.2]		33.1			57.4	41.1	55.2
1402	75.0		[66.1]						[87.3]	47.0	65.2	88.7	72.9		68.5	81.5
1403	30.6		[95.6]	172.9						42.1	40.4	70.4			81.7	88.8
1503	29.7			65.3			[117]		[68.4]				75.2	38.7	44.8	58.1
1701	19.4		[70.9]			39.9									39.9	40.7
2001	61.9						89.5	139.1	104.3				95.5		107.1	77.8
2102	63.0	94.3	[95.2]			149.3		163.2		100.5				80.9	117.6	124.7
2103	33.6		[76.8]				82.6	84.8			28.3	[70.3]			65.2	48.1
2203	32.5			78.1	23.3	22.5			[58.6]					39.5	40.9	65.2
2401	25.8	29.9								58.2	26.4	[99.9]			38.2	41.1
2701	23.3			116.6	54.6	35.7	54.2						79.3	48.1	64.8	56.7
2802	48.0	75.0	[108]	112.1					[80.0]	62.7	49.0	84.8			86.3	87.6
2803	41.0			83.2	45.3			103.9		37.8	30.5	57.6	54.8		59	58.0
2903	47.9								[69.7]						[69.7]	-
3003	33.1	37.9												62.4	50.2	68.9
3101	35.0	27.5						123.3	[70.7]	34.7	50.7				59.1	69.4

The data marked [ ], representing smoke exposure at home, were not used in the ANOVA. No estimate of the mean could be made for day 103 because it had only one datum point; person 102 was smoke exposed at home for all sampled days and was excluded from all analyses; on day 2903 there were no non-smoke exposed data.

* - Estimated mean of all subjects' non-smoke PM exposure as computed by U.S. EPA via a 2-way ANOVA.

TABLE 5-10. PERSONAL PM_{10} EXPOSURE ($\mu g/m^3$) OF 24 ADULTS IN AMSTERDAM, NL
SOURCE OF DATA: JANSSEN ET AL. (1998A)

		Person ID																									
Day	Ambient	301	302	303	306	307	308*	310	312	313	315	316	317	318	321	322	325	327	331	333	334	336	337	338	339	Mean of Personal Raw Data	Mean of Personal Estimated*
112	42.5								29.7	73.7	78.3	42.1					71.7	57.4				61.7		86.0	109.8	67.8	63.7
311	46.7			37					38.9	36.1	83.7											73.9		56.8	86.2	58.9	58.2
512	29	31.8						58.2							50				31.3	40.3			45.0			42.8	47.1
612	24.8												29.2	60.7		55.6										48.5	54.7
711	84.5	67	99.6			66.2	50.2	51.7								77.7	114.4		55.8	75.6	59.6					71.8	70.1
812	22.9	31.3		17.6		61.6			38.3	31		33.9						44.0				26.5		59.8	68.1	41.2	42.7
1011	44.9			43.9	100.6				45.9		85.7		72	80.6				50.3						[112.4]		68.4	76.6
1212	40.1		31.5		43.9		[41.6]				50.4		51.1	42.4	34.6	45.7			44.2	75.4	50.7					47.0	46.8
1411	35.2	45.3	50.4				[23.3]	32.1								66.1	[86.6]		34.1	61.6	63.4					50.4	49.1
1512	63.9			70.5		75.6		36.7	45.8						52.2			69.9				75.7	65.7	85.8		64.2	69.0
1710	32.7		51.1		53.8		[92.2]	55.5			54.6															53.8	49.4
1711	31								27.7	30.8		52.8	36	28.9											69.4	40.9	44.4
1912	20.4	40.8					[90.9]	66.9			49.5	69.6	24	34		51.4	71.6						42.7		84.9	53.5	51.0
2010	77.5	129.2		58.6		101.4			82.1			73.1						80.1	81.8							86.6	95.4
2111	67.5		109.9		68.8						52.4						87.1	48.3	40.9	68.9	51.8				75.6	67.1	59.3
2212	25.8																71.5						50.6		92.7	71.6	54.6
2410	34									63.4					59.2		70.0			35.6	56.6	61.3		34.0		54.3	49.3
2411	29.8	45.5		34.2		49.4		33.3		49.7			22.7	21.6							104.3			52.2		45.9	50.9
2710	32.2			11.5	52.2		[35.8]		88.3				30.8	18.1				32.6					46.6			40.0	49.5
2811	27.6		30.2		81.3	60.2	[71]								34.4	57.7			51.5	51.1			57.1			52.9	51.1
3110	29.5	46.8	42.8			40.7									35.8	79.8			31.0	42.8						45.7	45.1

[ ] - smoker present at home
* - Estimated mean of all subjects' non-smoke PM exposure as computed by U.S. EPA via a 2-way ANOVA.

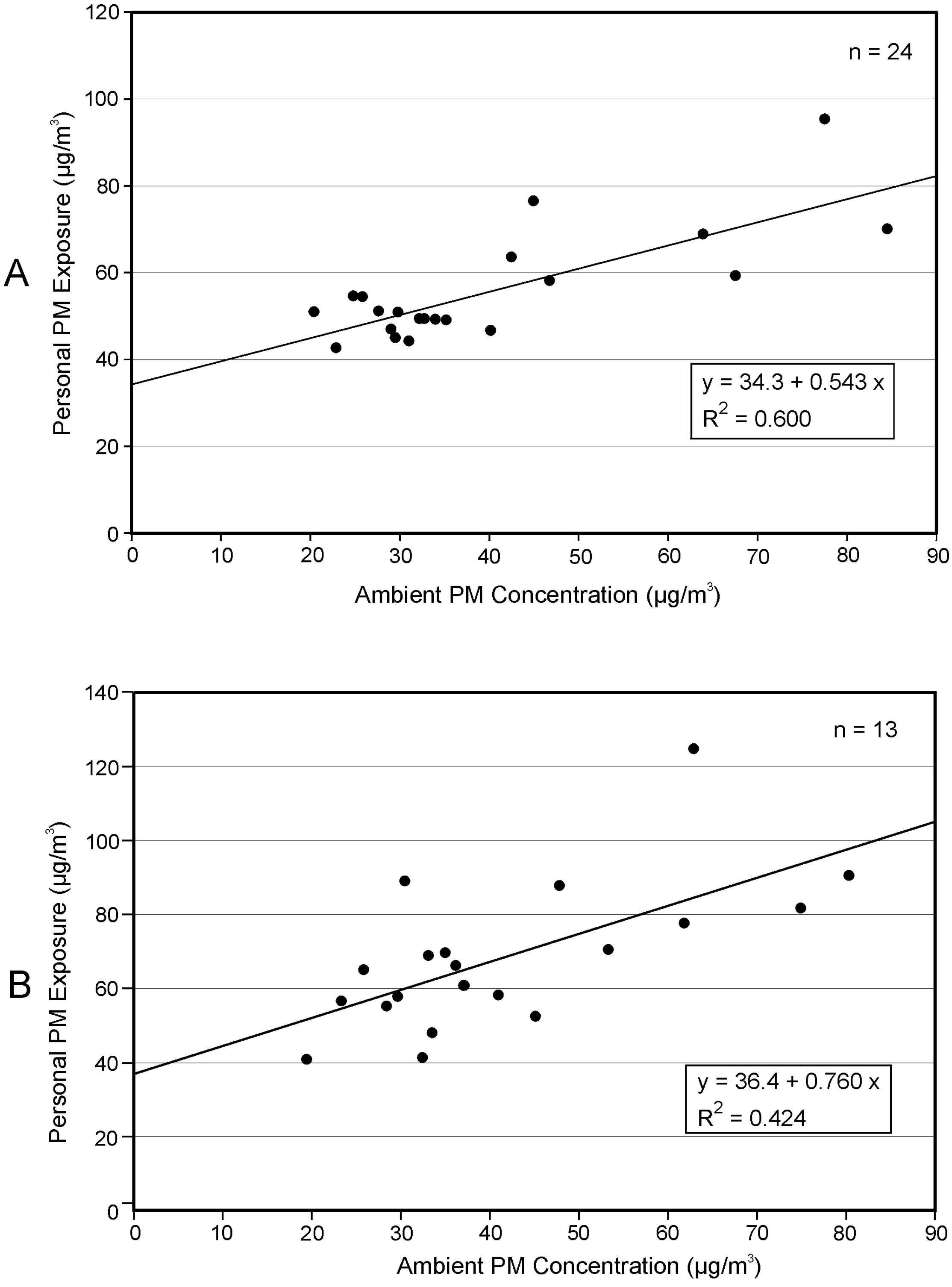

Figure 5-11A,B. Completed mean personal PM_{10} exposures of two groups of adults (n = 24 [A] and n = 13 [B]) not exposed to tobacco smoke at home in Amsterdam, NL, versus the simultaneous ambient PM_{10} measured in their community.

Source of data: Janssen et al. (1998a)

ambient PM_{10} is reflected as an increase in the exposure to PM_{10} of the subjects in this study. These correlation coefficients for adults who were not smoke-exposed at home, are both higher than the estimated mean cross-sectional correlation of r = 0.50, shown in Table 5-7.

The Janssen et al. (1999b) personal exposure intercept of 12 $\mu g/m^3$ for $PM_{2.5}$ corresponds to the average portion of the daily $PM_{2.5}$ exposure that is uncorrelated with the ambient $PM_{2.5}$ concentration, primarily while the subjects were indoors. This quantity represents the combination of indoor emissions of $PM_{2.5}$ and the children's 'personal cloud' of $PM_{2.5}$ stirred up by their activities, and the net effect of experimental errors in ambient PM measurement. If the children's personal clouds for coarse PM were much greater than their personal clouds for fine PM as in the PTEAM study (Özkaynak et al., 1996a), and there was much more coarse PM generated indoors than fine PM (there was no cigarette smoke exposure at home or in school), then their intercept for personal PM_{10} exposure could be much greater and of the order of the Lioy et al. (1990) intercept of 41 $\mu g/m^3$ or the Janssen et al. (1999b) intercepts of 34 and 36 $\mu g/m^3$ for PM_{10}. Values of this order are much larger than the Tamura et al. (1996a) intercept value of 11 $\mu g/m^3$ for PM_{10}. This difference may be due in part to the relative cleanliness of the Tokyo homes of the seven elderly Japanese subjects compared to the Phillipsburg, NJ and Wageningen, Netherlands homes, and the lower physical activity levels of these elderly people compared to the activities of the monitored children and working adults in the Netherlands.

The results of these three regressions show that the variations in personal exposure for these non-randomly chosen subjects who have similar life styles (habits and activities) from day to day, and who are not exposed to tobacco smoke on a routine basis, are driven by the variations in the ambient PM concentration. This finding, originally expounded by Janssen et al. (1995), supports the plausibility of the use of fluctuations of ambient PM concentration as a surrogate for fluctuations in human exposure to PM of ambient origin for subjects residing in the community surrounding an ambient monitoring station. However, this plausibility is weakened by the non-random choice of subjects and sampling periods which strictly limit the finding to the subjects sampled on the days sampled.

5.11 EXPOSURES TO AMBIENT $PM_{2.5}$ OF PEOPLE BELIEVED TO BE SUSCEPTIBLE TO THE EFFECTS OF AMBIENT $PM_{2.5}$

The study of the historic air pollution episodes reveals that those people most subject to the mortality effects of exposure to ambient $PM_{2.5}$ are the elderly with pre-existing cardio-pulmonary lesions (U.S. Environmental Protection Agency, 1996). Although it has been established in the previous section that, in general, peoples' exposures to PM of ambient origin are highly correlated with ambient PM in their community, prior to 1996, very few studies of the elderly and apparently susceptible people had been performed. For example, the Tamura et al. (1996a) study was of elderly people with no known cardio-pulmonary disease.

The question to be addressed here is 'Do elderly people with cardio-pulmonary disease have the same relationship of their exposure to PM of ambient origin as do the members of the general public who have been studied to date, as reported in the preceding section?' It may be possible that the elderly or infirm modify their physical activities and living conditions in such a manner as to influence the relationship of their exposures to ambient PM with the ambient PM concentrations of their community. If so, differences in exposure estimate errors between susceptible-diseased groups and non-susceptible-healthy groups may result in differential misclassification which has implications for the validity and interpretation of epidemiologic studies (Armstrong et al., 1992). The studies described in the following section address studies of this apparently susceptible cohort.

Williams et al. (1999a) measured the personal exposures to $PM_{1.5}$ of five elderly subjects living at a retirement center in Baltimore, MD in January-February, 1997 for ten consecutive days. Some of these subjects were under medical treatment for cardio-pulmonary conditions at the time of this study, and they represent a non-random sample of elderly subjects living in an environment of a retirement center. Each subject carried a personal $PM_{1.5}$ monitor described by Williams et al. (1999b), and the ambient $PM_{2.5}$ was monitored simultaneously outside the retirement center by a dichotomous sampler. Three subjects (1-3) lived apart in separate efficiency apartments in a new unit and the two other subjects (4, 5) lived apart in an older unit, in two separate smaller rooms, each with an attached bathroom. The three newer apartments had either a picture window or double windows and the two older single-rooms had only one window. Thus, even though none of the residents reported opening windows during the study, the newer units may have had a larger window-perimeter leakage area for air exchange directly with the outdoor air. The new and old units also had different air handling systems in their two general living areas which were connected by staircases and elevators. The authors reported that there were no special air cleaners installed in either of these two air handling systems.

The collected data are shown in Table 5-11 with the missing values estimated by the E-M algorithm (Mage et al., 1999) shown within parentheses ( ). Because of the different air handling systems for their living areas, the E-M algorithm was applied separately to these data for subjects 1 - 3, and then to these data for subjects 4 and 5. These different air handling systems, and the difference in window leakage areas, may be a partial explanation of why subjects 1 - 3 had positive correlations of their exposures with the ambient PM ($r = 0.91, 0.12, 0.70$ respectively), and subjects 4 and 5 had negative correlations of their exposures with the ambient PM ($r = -0.55, -0.05$ respectively). The mean $PM_{1.5}$ exposure vs ambient $PM_{2.5}$ for all five subjects is shown as Figure 5-12, with an R^2 of 27%. The range of nine observations of ambient $PM_{2.5}$ is fairly narrow (8 to 23 $\mu g/m^3$) and inclusion of the last day of data with an ambient $PM_{2.5}$ value of 32 $\mu g/m^3$ raises the correlation of their mean PM exposure with the ambient PM from $r = 0.269$ to $r = 0.522$. It is expected that all these correlations would have been higher than shown if both the ambient monitor and the personal monitor measured PM with the same nominal size cut.

Bahadori (1998) and Bahadori et al. (1999) report on a pilot study of the PM exposure of ten non-randomly 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. - 8 p.m.), for six consecutive days. These same pollutants were monitored simultaneously indoors and outside their homes. These homes were all air conditioned with lower air exchange rates (mean $a = 0.57$/h), 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 to the PTEAM study in Riverside, CA, where no air conditioners were in use and the air exchange rate was much higher (mean $a > 0.97$/h). In the PTEAM study the mean indoor $PM_{2.5}$ was 98% of the mean ambient $PM_{2.5}$ (Clayton et al., 1993).

Because each person carried a $PM_{2.5}$ or a PM_{10} personal monitor for only three 12-h periods, no Pearson correlations of personal PM vs ambient PM were reported for the individual subjects. However, these data were combined into two groups of 30 and Bahadori et al. (1999) report the correlations found between personal and outdoor concentrations when data were analyzed

TABLE 5-11. PERSONAL EXPOSURES TO $PM_{1.5}$ OF FIVE ELDERLY RESIDENTS OF A RETIREMENT CENTER IN BALTIMORE, MD, AS A FUNCTION OF AMBIENT $PM_{2.5}$ CONCENTRATION ($\mu g/m^3$)

Day	Ambient $PM_{2.5}$	Person 1 Exposure	Person 2 Exposure	Person 3 Exposure	Person 4 Exposure	Person 5 Exposure	Mean Exposure
1	14.8	21	31	(32.0)	(33.1)	31	29.6
2	9.2	22	16	(38.7)	39	27	28.5
3	14.2	17	35	18	40	43	30.6
4	14.0	25	20	(39.5)	18	30	26.5
5	22.6	33	38	(39.6)	32	30	34.5
6	21.2	32	29	44	26	35	33.2
7	11.6	27	33	37	51	19	33.4
8	8.0	12	35	30	39	45	32.2
9	14.5	29	45	(35.2)	38	58	41.0
10	32.0	50	(29.5)	57	(24.7)	(34.2)	39.1
Correlation		r = 0.907	r = 0.122	r = 0.702	r = -0.550	r = -0.050	r = 0.522

( ) Missing data estimated by U.S. EPA using E-M algorithm (U.S. Environmental Protection Agency, 1996; Mage et al., 1999).

Source of data: Williams et al. (1999a).

cross-sectionally were r = 0.09 for $PM_{2.5}$ and r = -0.08 for PM_{10}. The authors suggest that "personal-outdoor correlations would be stronger if data were to be analyzed longitudinally. However, this analysis could not be performed due to insufficient data." That relationship, if true, would be consistent with that in U.S. Environmental Protection Agency (1996) where it was shown how combining personal exposures for an individual with those for other individuals, leads to a degradation of the correlation coefficient.

Rojas-Bracho et al. (1999) report the results of a 1996/1997 study of the personal exposures to $PM_{2.5}$ and PM_{10} of 18 COPD patients in the Boston, MA metropolitan area. The study design was based on the pilot study by Bahadori et al. (1999) in Nashville, TN. The subjects were also not chosen as a random sample from the population of COPD patients in the Boston area, but were recruited via local physicians, from COPD exercise groups, as well as by newspaper advertisements. Therefore the results of the study strictly only apply to the 18 subjects on the days sampled, and cannot be inferred to relate to Boston area COPD patients in general.

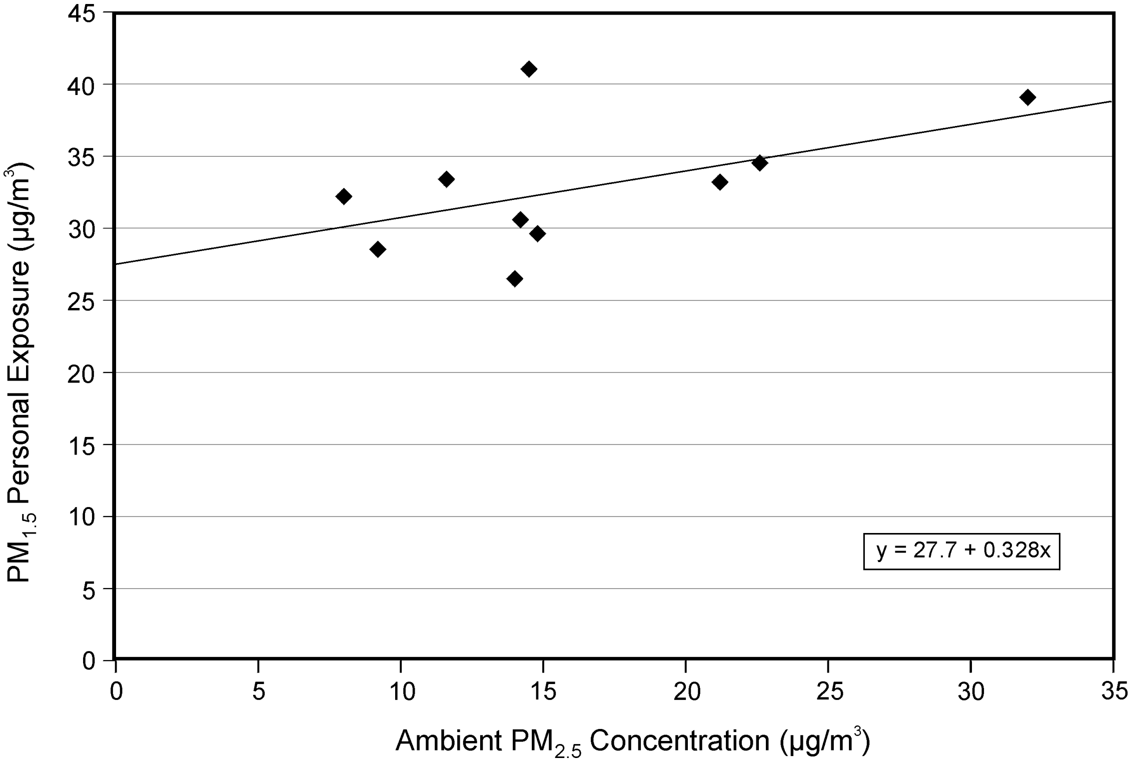

Figure 5-12. Mean personal exposures to $PM_{1.5}$ of five elderly residents of a retirement home in Baltimore, MD, as a function of ambient $PM_{2.5}$ concentration. Source of data: Williams et al. (1999a).

Each subject carried a personal monitor that sampled both $PM_{2.5}$ and PM_{10} for 12-hours per day for one, two or three consecutive 6-day periods between 8 a.m. and 8 p.m., while $PM_{2.5}$ and PM_{10} were also measured inside and outside their homes during the same time period. Subjects were monitored for either summer only (2), winter only (2) or in both summer and winter(14). The regression coefficients (R^2) between the daytime personal exposure and daytime outdoor PM measures for the 15 subjects with more than one week of sampling are shown in Table 5-12a. The 0.85 maximum value in the set is for the one subject who was only sampled in the summer period. As expected, the combining of summer and winter data reduced the correlation between personal and outdoor PM data because air exchange rates in Boston are decreased in the winter to save heat. The article does not report the difference between summer and winter correlations for the other 14 subjects.

TABLE 5-12A. SUMMARY OF CORRELATIONS BETWEEN DAYTIME PERSONAL PM EXPOSURES AND DAYTIME OUTDOOR PM CONCENTRATIONS FOR 15 COPD PATIENTS DURING COMBINED SUMMER AND WINTER PERIODS IN BOSTON, MA

Person ID	Weeks sampled in Summer (S) and Winter (W)	Number of valid paired observations	R^2 $PM_{2.5}$ Personal vs Outdoor	R^2 PM_{10} - $PM_{2.5}$ Personal vs Outdoor
1	S 1, W 1	10	0.58	0.11*
2	S 2, W 1	10	0.21	0.10
3	S 1, W 1	17	0.13	0.06*
4	S 1, W 1	9	0.44	0.26*
5	S 1, W 1	12	0.28	0.02*
6	S 1, W 1	11	0.01	0.31
9	S 2, W 1	12	0.65	0.00
10	S 2, W 1	17	0.49	0.00
11	S 2, W 1	17	0.32	0.00*
12	S 1, W 1	17	0.02	0.09
13	S 2	10	0.85 (maximum value)	0.00* (9 observations)
14	S 2, W 1	16	0.83	0.00
16	S 1, W 1	12	0.52	0.12
17	S 2, W 1	17	0.01*	0.05*
18	S 2, W 1	17	0.37	0.39

* Correlation coefficient (r) is negative.

Source: Rojas-Bracho et al. (1999).

Table 5-12a shows that the personal exposures to $PM_{2.5}$ were all positively correlated with the ambient PM, except for subject 17 (the slope of the regression line is negative). However, for the difference between PM_{10} and $PM_{2.5}$, representing the coarse mode fraction between 2.5 and 10 microns AD (neglecting cutpoint imprecision), there were 7 negative correlations, one zero correlation, and 7 positive correlations, which is an expected result if there is little or no correlation, on average, between ambient coarse PM and personal exposure to coarse PM for such people who spend the majority of their time indoors where coarse PM is generated by daily activities.

5.12 PERSONAL EXPOSURE TO CONSTITUENTS OF PM: SULFATES AND ACIDITY

PM sulfates are species that exist in the ambient atmosphere from primary emissions of combustion products of fossil fuels containing sulfur, from formation by photochemical oxidation of gaseous sulfur species, and from non-anthropogenic sources (e.g. volcanic activity and wind-blown soil). In the indoor environment, where ammonia is present, the only common major source of sulfate may be resuspension by human activity of PM containing ammonium sulfates and soil sulfates that were tracked into the home. In some homes an unvented kerosine heater using a high-sulfur fuel may be a major winter contributor (Leaderer et al., 1999a).

Trijonis et al. (1980) reported surface monitoring sulfate data from the U.S. EPA Regional Air Pollution Study (RAPS) of the greater St. Louis, MO metropolitan area including portions of Illinois. The authors reported that all site-to-site correlation coefficients of 24-h sulfate data were greater than 0.84. Suh et al. (1993) reported a study of personal exposure to PM sulfate of children living in State College, PA during a summer season. Figure 5-13 shows the excellent agreement between the personal exposure and ambient sulfate concentration. The regression slope of 0.87 falls below the 1:1 line because sulfates, although primarily of $< 1\ \mu$m AD, deposit on inner home surfaces with a value of k of order 0.16/hr (Özkaynak et al., 1996b). This leads to a value of $[Pa\ /\ (a + k)]$ of slightly less than 1 in the summer when homes are not air conditioned and sealed tightly ($a >> 0$ and $P \approx 1$).

If the home is sealed to conserve energy with air conditioning use, the air exchange parameter a is decreased. If the return-air to the air conditioner is filtered, or passes through an electrostatic precipitator, then the deposition parameter k is increased as some sulfates may be removed. This leads to a decrease in the parameter $[Pa/(a + k)]$, as shown by the data on Figure 5-13 where the open circles representing the air conditoned homes fall below the data for the non air conditioned homes. The overall regression coefficient for these data from non air conditioned homes is $R^2 = 0.92$, indicating how well personal exposure to this material of almost exclusively ambient origin correlates with ambient concentration.

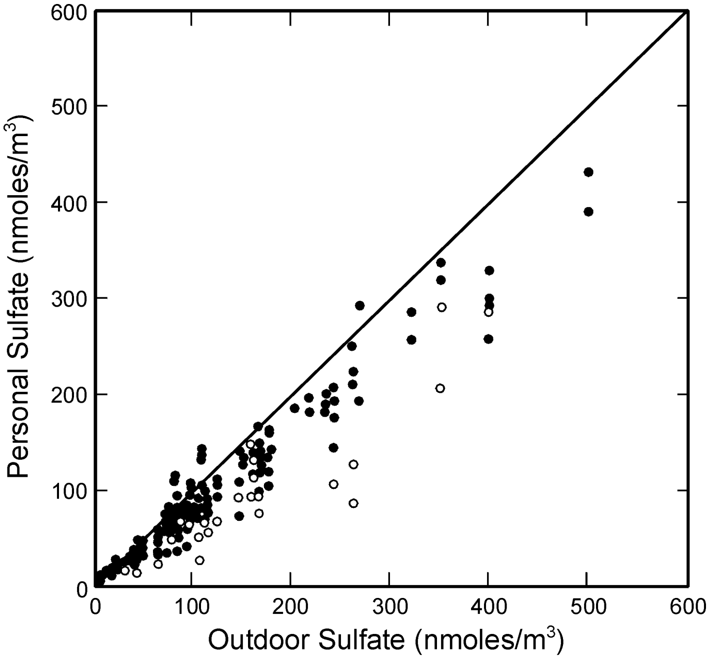

Figure 5-13. Personal versus outdoor $SO_4^=$ in State College, PA. Open circles represent children living in air conditioned homes; the solid line is the 1:1 line.

Source: Suh et al. (1993).

Leaderer et al. (1999a) compared sulfates in indoor and outdoor air for homes with air conditioning (A/C) and without A/C during summer periods in southwestern Virginia. The A/C homes had lower indoor/outdoor sulfate ratios, averaging 0.71, as compared to the ratio of 0.86 in the homes without A/C. Two possible reasons cited for the lower sulfate ratio in the A/C homes, were a lower home air exchange rate from sealing the A/C homes to conserve energy, and the presence of an in-line filter within the A/C system. These factors can contribute to the removal of sulfates by enhanced gravitational deposition and filtration, respectively. A third possible reason for lower PM concentrations in A/C homes was noted by Tung et al. (1999) who reported that enhanced thermal diffusion of particles to surfaces may become a major factor when there is a large temperature difference between the air and the contact surfaces, as in the case of a Virginia summer when the A/C indoor air is much colder than the walls and windows of a home.

The effect of air conditioning may be important to consider when comparing responses to air pollution in cities with different percentages of air conditioned homes. For example, if cities A and B have identical ambient air pollution concentrations and city A is completely air conditioned while city B has no need for air conditioning, the subjects in city A will be exposed to less ambient PM than the subjects in city B, and consequently, if the subjects in city A have less symptoms, the ambient PM in city A may appear to be less toxic. See the discussion of the effect of assumed protection by going indoors when smog warnings are issued, from the 1969 PM AQCD (National Air Pollution Control Association, 1969) mentioned in Section 5.1.1.

Özkaynak et al. (1996a,b) and Janssen et al. (1999c) report that in the U.S. 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 concentration in both the indoor and outdoor air. Therefore, where there are no indoor sources of fine mode sulfates, and no enhanced air cleaning systems operating, one may deduce the same relationship between personal exposure to PM of ambient origin (C) and ambient concentrations (Co) in an indoor microenvironment for other materials in the same aerodynamic size range as the fine mode sulfates found in the atmosphere.

Larssen et al. (1993) report such a study of traffic generated PM in Oslo, Norway. They made measurements of indoor and outdoor fine fraction $PM_{2.5}$ and coarse fraction (PM_{10} - $PM_{2.5}$) in a closed and uninhabited apartment facing on a busy street. Figure 5-14 presents three examples of their daily data. In the absence of indoor sources, these data show that with low air exchange rates (not monitored), the PM equilibrium parameter $[P\ a / (a + k)]$ is of order 5-10% for the coarse PM fraction and about 80% for the fine PM fraction.

Tung et al. (1999) developed a methodology to measure the particulate penetration coefficient (P) through a building shell by measuring simultaneously the air exchange rate (a), and the indoor and outdoor PM concentrations as the indoor PM equilibrates with the outdoor PM in the absence of any PM sources within the indoor microenvironment (microenvironment). The PM deposition parameter (k) is then estimated by the measured decay rate of the PM (e.g., $a + k$) minus the measured air exchange rate (a), and the penetration is computed as $P \approx C\ (a + k) / (Ca\ a)$. The authors demonstrated their technique using a large enclosed office as the simulated building microenvironment, while it was unoccupied at night with all mechanical ventilation shut off. The office had two closed doors leading to a corridor with closed louvers

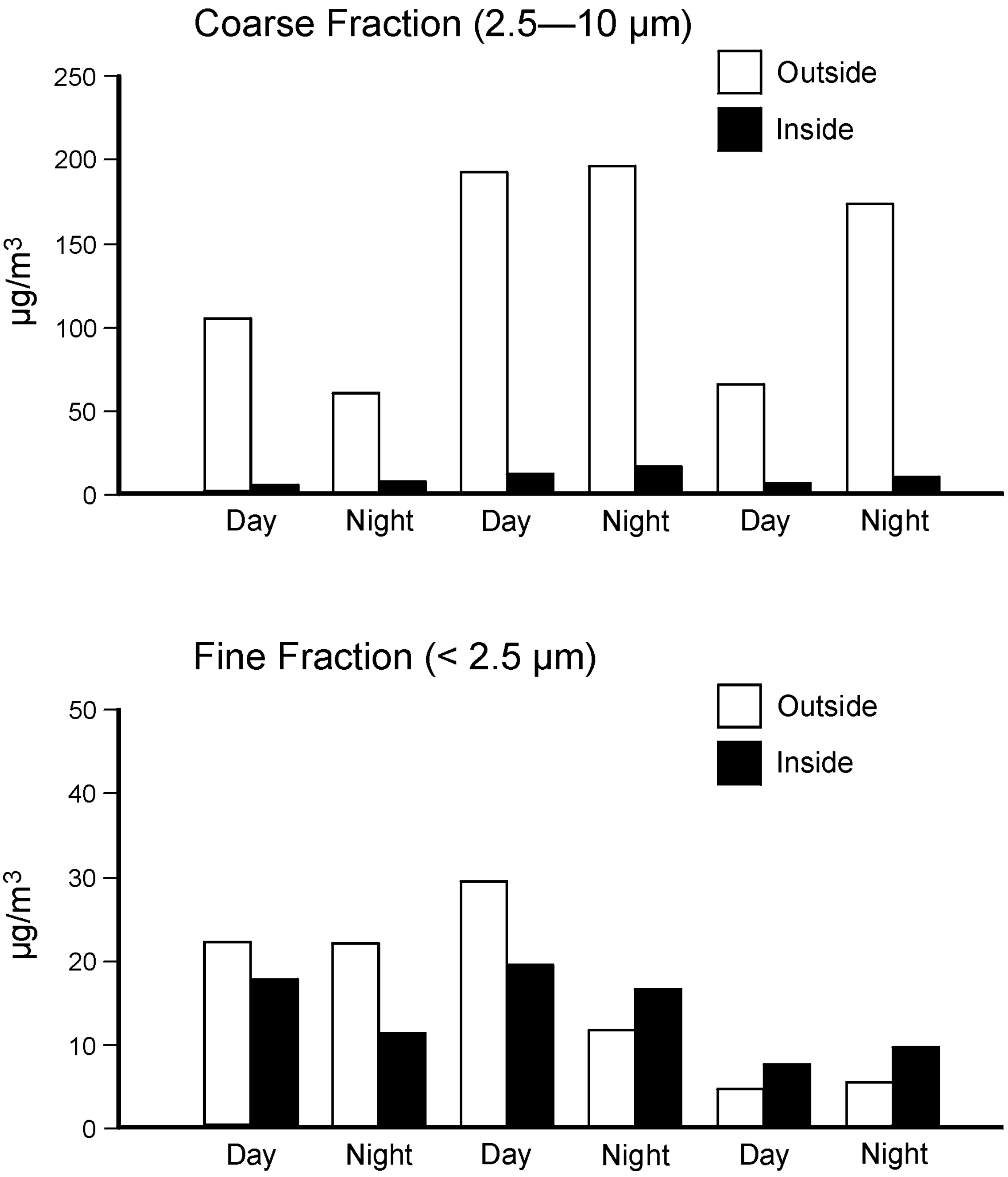

Figure 5-14. Results from simultaneous measurements of the indoor PM_{10} concentration and the immediate outdoor PM_{10} concentration of an uninhabited apartment in a building fronting to a busy street in Oslo, Norway.

Source: Larssen et al. (1993).

above them, and the corridor PM simulated the ambient PM. In three tests of the procedure the penetration of PM_{10} into the office had an average value of $P \approx 0.8$ corresponding to an average air exchange rate of $a \approx 0.4$/h.

Ormstad et al. (1997) measured PM_{10} indoors and outdoors for 29 occupied homes in Oslo, Norway. Using a 60 Lpm open face sampler, pointing 45° downward, they found that the median indoor/outdoor mass ratio was 1.43. $PM_{2.5}$ was not monitored, but the authors used transmission electron microscopy (TEM) to estimate that the vast majority of countable particles(> 90%) were under 2.5μm optical diameter. It is interesting to compare these data with the Larssen et al. (1993) data, cited just above. For a closed and unoccupied apartment in Oslo, the indoor/outdoor ratio was of order 0.2. The difference between these indoor/outdoor ratios (~1.4 vs ~0.2) may represent the effects of indoor PM generated and resuspended by occupants, and an increase in air exchange rate with door and window openings and closings by the occupants.

Brauer et al. (1989) measured personal exposures and ambient concentrations of acidic aerosols and gases using a personal annual denuder/filter pack sampling system. They found that personal exposures to aerosol strong acidity (H^+) were slightly lower than concentrations measured at a stationary site, and concentrations of sulfate and ammonium ions were similar to those measured at the stationary site.

In the absence of personal activity to resuspend or generate PM, and with a very low air exchange rate, the indoor PM fine fraction is virtually all of ambient origin and the PM coarse fraction is minimal due to its higher settling values (*k*) and lower penetration values (*P*). The caveat to this analogy is that while indoors, charged ambient particles and ultra-fine ambient PM (< 0.1 μm AD) may have greater electrostatic deposition and diffusion deposition than the larger sulfate particles (> 0.1 μm AD), which would inflate their deposition parameter *k*. Although the correlation between the ambient concentrations of such particles and the related exposure measurements may be much lower due to the fluctuations of the transient forces causing deposition, it remains that any exposure to these PM constituents which have no indoor sources, will be entirely caused by the PM of ambient origin.

5.13 CORRELATION OF AMBIENT PM AND PM EXPOSURE IN CROSS-SECTIONAL-TYPE STUDIES

The results for personal sulfate exposure and longitudinal (Type-1) personal PM exposure studies stand in contrast to the lack of correlation found in cross-sectional studies (Type-2) described in Chapter 7 of U.S. Environmental Protection Agency (1996). Typical of these studies is Spengler et al. (1985), which found virtually no cross-sectional correlation ($r \approx 0$) between personal exposure to $PM_{3.5}$ and ambient $PM_{3.5}$ concentration in the adjacent communities of Kingston and Harriman, in Eastern Tennessee. The reason for this difference can be visualized by comparison of the example data matrices for the Type-1 and Type-2 studies shown in Tables 5-12 and 5-13: The longitudinal Type-1 studies of Tamura et al. (1996a), Janssen et al. (1999b) and Lioy et al. (1990) correspond to Table 5-12. However, the Spengler et al. (1985) study and the PTEAM study (Clayton et al., 1993) were of Type-2, the class covered by Table 5-13.

TABLE 5-12. EXAMPLE OF A COMPLETED MATRIX FOR A TYPE-1 ANALYSIS OF PM EXPOSURE AND AMBIENT PM CONCENTRATION

	Person 1 PM Exposure	Person 2 PM Exposure	Person 3 PM Exposure	Person 4 PM Exposure	Ambient PM Concentration
Day 1	X	*(X)	X	X	X
Day 2	X	X	*(X)	X	X
Day 3	*(X)	X	X	X	X
Day 4	X	X	X	*(X)	X

*(X) missing data filled in by the E-M algorithm from assumption of bivariate normal distributions of daily personal exposures and each individual's exposure time series.

In the Spengler et al. (1985) study, subsets of people were sampled on subsets of days without any overlap. In the PTEAM study four different people were to be sampled on each consecutive day with no repeat sampling of any person, but some people's data were missed due to happenstance. Without any overlapping of sampling between all people one is unable to

TABLE 5-13. EXAMPLE OF AN INCOMPLETE MATRIX FOR TYPE-2 ANALYSIS OF PM EXPOSURE AND AMBIENT PM CONCENTRATION

	Person 1 PM Exposure	Person 2 PM Exposure	Person 3 PM Exposure	Person 4 PM Exposure	Ambient PM Concentration
Day 1	X	X	-*	-*	X
Day 2	X	X	-*	-*	X
Day 3	-*	-*	X	X	X
Day 4	-*	-*	X	X	X

*Missing data that cannot be estimated by E-M algorithm because there is no comparison data on how the personal PM exposures of Persons -3 and -4 relate to the simultaneous personal PM exposures of Persons - 1 and -2.

estimate the missing data by the E-M algorithm in these two studies. For example, if person-3 in an extensive data set always has the mean personal exposure of person-1 and person-2 we can estimate person-3's exposure as the mean of the person-1 and person-2 exposures on the day when person-3 was not sampled. However, if person-3 was never sampled simultaneously with persons -1 and -2 this relationship cannot be discovered. Consequently, the E-M algorithm cannot be applied to complete the Type-2 matrices of the form shown as Table 5-13.

In the PTEAM study all subjects were a set of randomly sampled residents of Riverside, CA aged 10 and above, who were self-declared nonsmokers. The daily PM exposure data from the subjects were averaged to create a time series of mean exposure values that were an estimate of the mean personal exposure of the Riverside cohort on those days. Most days had four observations but some days had only two or three observations, so the means of the four values are expected to have smaller confidence intervals than the means of the other values. Each missing personal PM exposure datum was estimated using the E-M algorithm. This amounts to finding a set of missing values that maintain an assumed bivariate normal correlation structure of the time series of completed (sets of 4) mean PM exposure data and ambient PM data.

The resulting table of average PM_{10} personal exposure and average ambient PM_{10} concentration of 43 days of data is as provided in Table 7-48 in U.S. Environmental Protection Agency (1996). Figure 5-15 shows these data, and the regression parameters are given in Table 5-14.

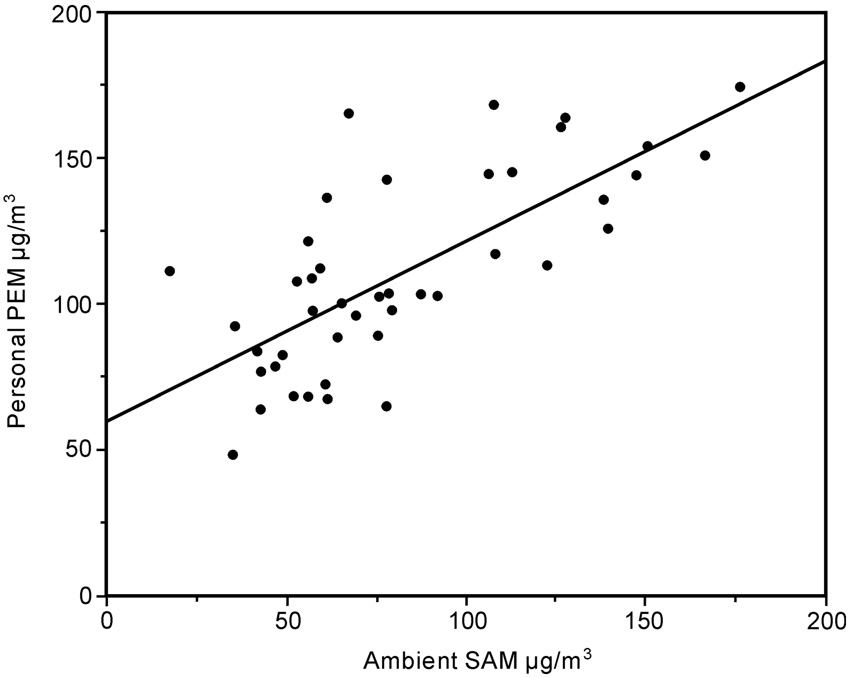

Figure 5-15. PTEAM mean 24-h PM_{10} data compared for personal PEM and SAM.

Source: U.S. EPA reanalyses of data reported on by Özkaynak et al. (1996a).

TABLE 5-14. RESULTS OF THE ANALYSIS OF THE PTEAM DAILY AVERAGE PERSONAL PM_{10} EXPOSURE DATA FROM RIVERSIDE, CALIFORNIA

Regression Model	Slope	Intercept
Linear, normal error	0.6174	59.7
Linear, lognormal error	0.6185	57.1
Orthogonal	0.8071	44.2
Linear adjusted for person error	0.9675	31.0
Measures of Association		**Value**
Correlation of averages		0.721
Fraction of variation explained by orthogonal regression		0.864

Source: U.S. Environmental Protection Agency (1996) reanalysis of PTEAM data (Özkaynak et al.,1996a,b).

The regression R^2 value for these averages is 0.52 which is much less than the regression R^2 values for the longitudinal time-series data averages of order 0.9 corresponding to a completed matrix (Table 5-12). This, in effect, is caused by the wider variance in the increment of non-ambient PM added to the PTEAM subjects' exposure to ambient PM, produced by the day-to-day variation of the indoor PM sources and personal activities of the different people who were sampled for only a single 24-hr period. For example, on day 1, the four people chosen may not live with smokers and have personal PM exposures at or moderately above the ambient PM value. On day 2, if some of the new subjects live with smokers, their personal exposures may be well above the ambient PM value.

The coherence of the time-series can be reduced by treating all such individuals together and the underlying high correlation of individuals with similar day-to-day exposure to PM of non-ambient origin is lost, as was shown by Figure 7-26 of the previous PM AQCD (U.S. Environmental Protection Agency, 1996). Janssen (1998) combined data from subjects with high longitudinal correlations, by randomly sampling from each individual's data set and combining them to create a cross-sectional data set. In each case, as shown in Table 5-7, the correlation coefficients were significantly reduced. It is this process of combining sets of people with assumed similar exposure to ambient PM but widely different exposures to non-ambient PM on different days that leads to the published studies that report little or no statistically significant correlation between personal exposure to the total PM and the corresponding ambient PM concentrations (e.g., Sexton et al., 1984; Spengler et al., 1985; Pellizzari et al., 1999).

5.14 EXPOSURE TO AMBIENT GASEOUS POLLUTANTS RELATED TO AMBIENT PM

Several gaseous pollutants, such as SO_2, NO (rapidly converted to NO_2) and CO, are often emitted at the same time as ambient PM is emitted from combustion sources. In addition, photochemical oxidants, such as ozone (O_3) are also formed in the atmosphere by the same processes that lead to formation of some of the photochemical aerosol species found in the fine-mode PM fraction (Seinfeld and Pandis, 1998). Weather also introduces a correlation effect as a stagnation inversion may cause all pollutant concentrations to rise, and a rain storm or frontal passage may cause all pollutant concentrations to fall. Consequently, these gaseous pollutants may have ambient concentrations that are correlated with the concentrations of various fractions of the ambient PM mixture [ultra-fine PM, fine-mode PM, or coarse-mode PM less than 10 μm AD].

If these gaseous species are capable of producing the same effect as an ambient PM fraction, and their ambient concentrations are correlated with ambient PM concentration, it becomes difficult to separate out which factor, if any, is causing the observed effect (Morris and Naumova, 1998; Chen et al., 1999). It is assumed that the generation of the primary pollutants CO, NO_2 and SO_2 in residential and occupational microenvironments is independent of ambient concentrations of those gases. However, there may be some locations where indoor emissions may be correlated with ambient concentrations as in the winter heating season. Assuming a linear system and no differential measurement errors, the health effects of indoor generated CO, NO_2 and SO_2 would also be independent of, and uncorrelated with, the health effects of the ambient PM. If these assumptions are valid, the presence of indoor sources of these gases should not confound the ambient PM mortality relationships reported in the literature.

An investigation (as yet unpublished) has been performed on the general correlation behavior of ambient PM and the ambient gaseous criteria pollutants in the U.S. (Shadwick et al., 1999). In order to examine the general geographic variability of the correlation coefficient, the U.S. EPA public Aerometric Information Retrieval System (AIRS) data base for the years 1992 - 1996 was reviewed (http://www.epa.gov/airs/airs2.html). Shadwick et al. (1999) chose the highest PM urban site and lowest rural PM site from each of the 50 states, Puerto Rico and Washington D.C. irrespective of the years of available data. The distributions of correlations between ambient PM_{10} and the 24-h concentrations of CO, NO_2, and SO_2, and ozone (8-h and 1-h), for urban and rural sites respectively, are shown in Figures 5-16a,b to 5-20a,b for the chosen urban and rural sites. For $PM_{2.5}$ only 38 sites were available for the entire U.S. so the urban and rural stations were combined for a joint analysis. The results for ambient $PM_{2.5}$ and the gaseous species CO, NO_2, SO_2 and ozone (8-h and 1-h), for combined urban and rural sites are shown in Figures 5-16c to 5-20c. These data are summarized in Table 5-15.

To estimate the relationship between exposure to ambient PM and exposures to the primary gases *of ambient origin*, their hourly averages along with an air exchange rate estimate would be required. For the highly reactive gases with strong sinks on indoor surfaces (such as ozone

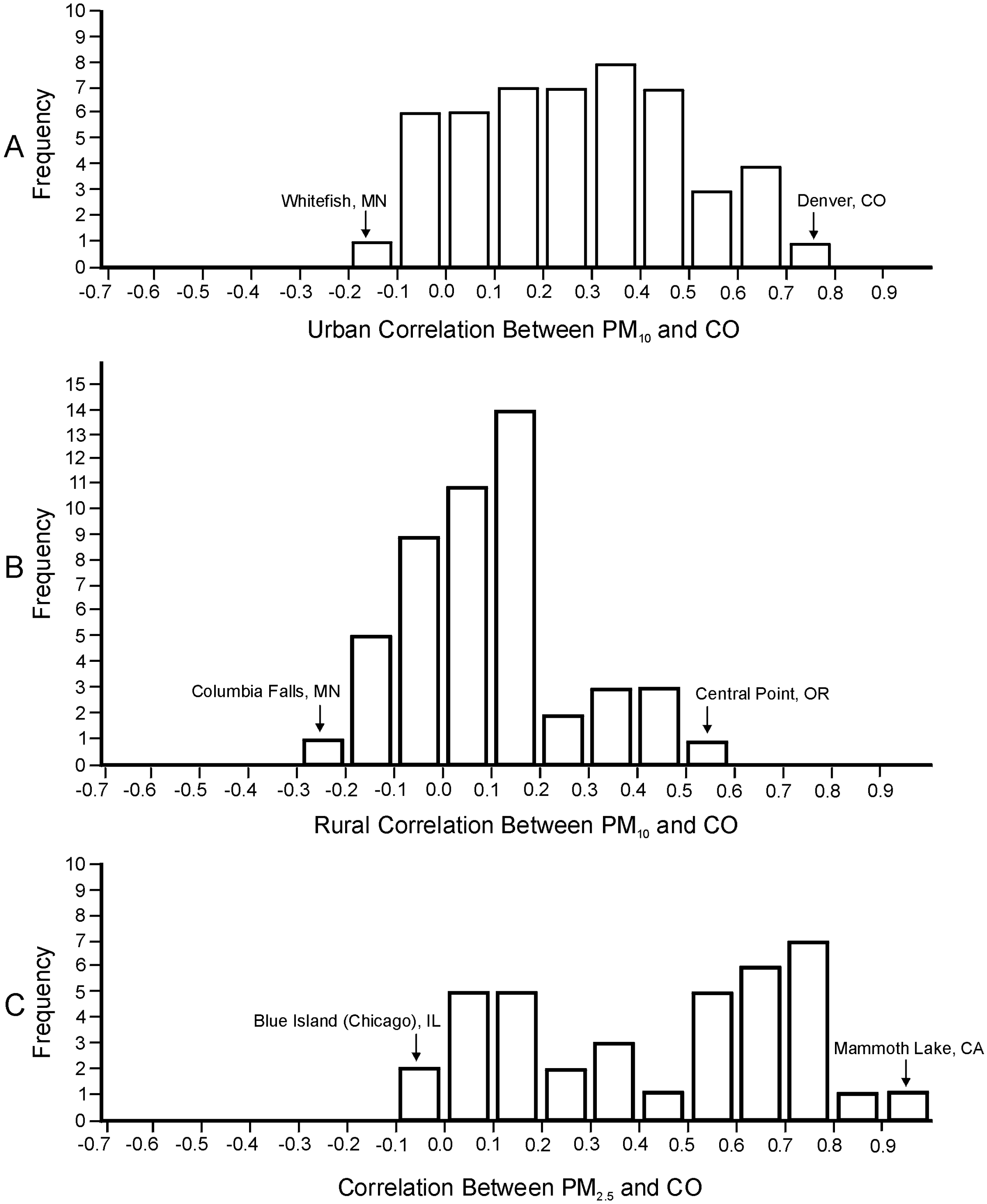

Figure 5-16. (a) Correlations of PM_{10}–CO for highest urban PM_{10} site per state; (b) correlations of PM_{10}–CO for lowest rural PM_{10} site per state; and (c) correlations of $PM_{2.5}$–CO.

Source: Shadwick et al. (1999).

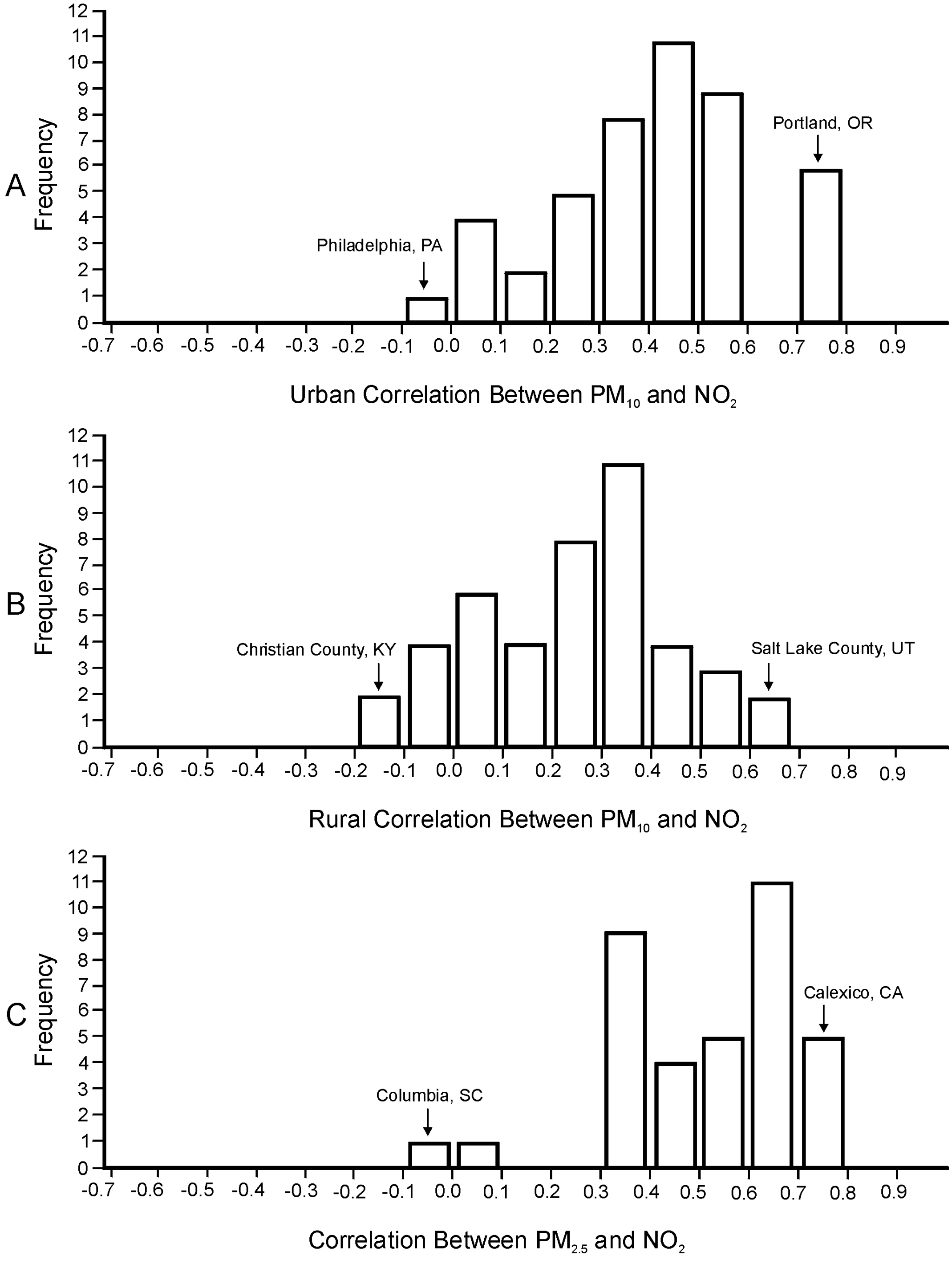

Figure 5-17. (a) Correlations of PM_{10}–NO_2 for highest urban PM_{10} site per state; (b) correlations of PM_{10}–NO_2 for lowest rural PM_{10} site per state; and (c) correlations of $PM_{2.5}$–NO_2.

Source: Shadwick et al. (1999).

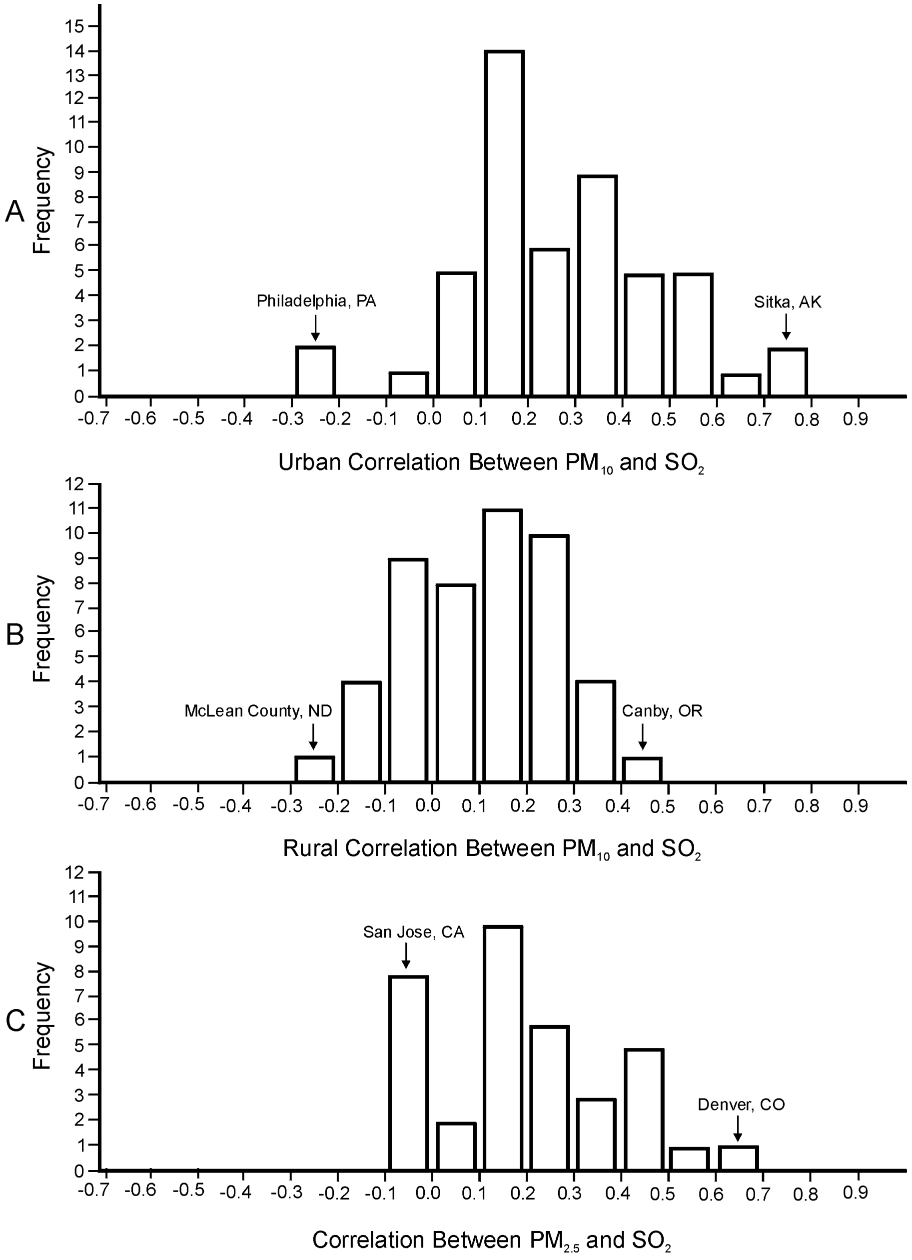

Figure 5-18. (a) Correlations of PM_{10}–SO_2 for highest urban PM_{10} site per state; (b) correlations of PM_{10}–SO_2 for lowest rural PM_{10} site per state; and (c) correlations of $PM_{2.5}$–SO_2.

Source: Shadwick et al. (1999).

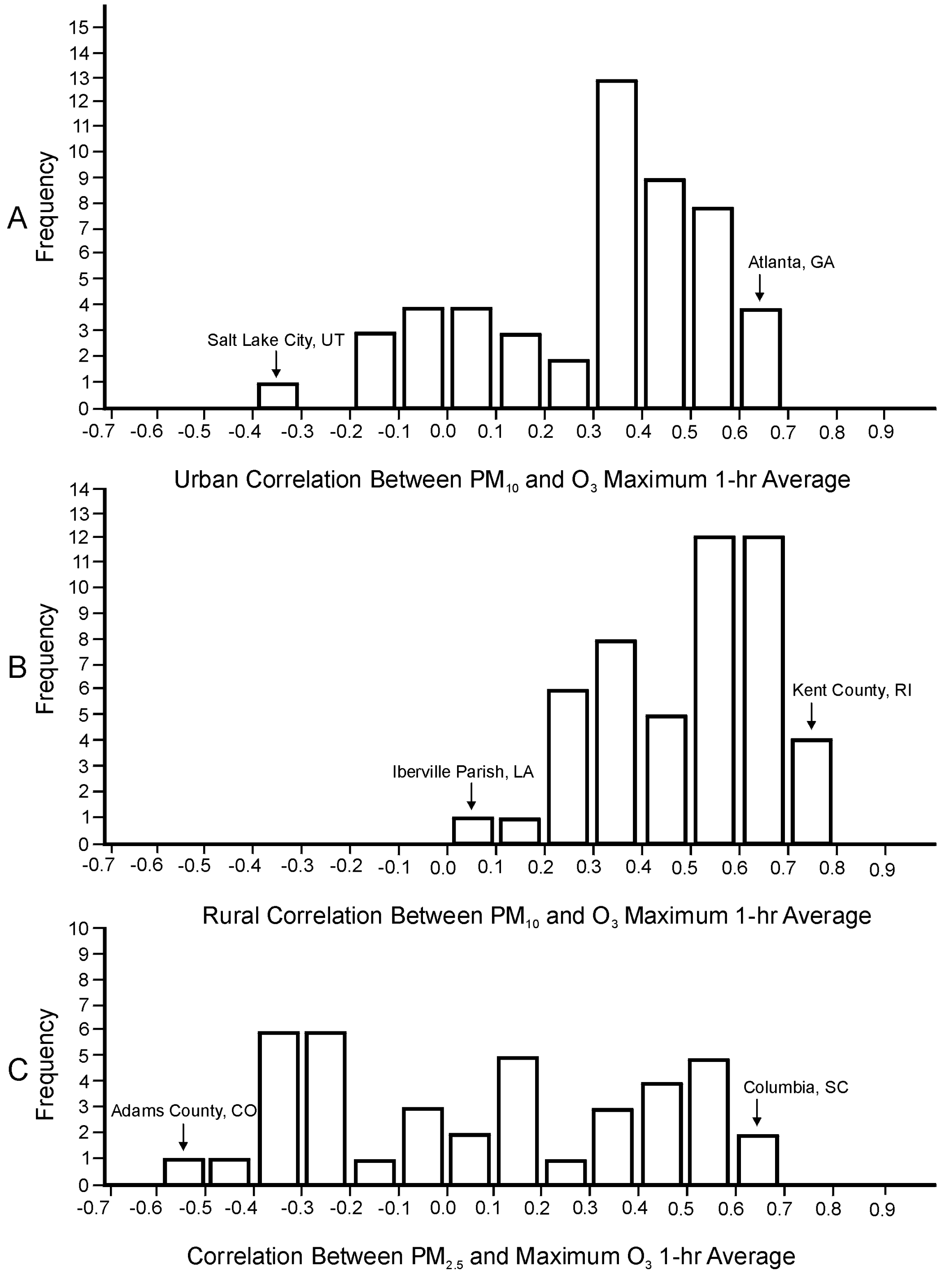

Figure 5-19. (a) Correlations of PM$_{10}$–O$_3$ 1-hr for highest urban PM$_{10}$ site per state; (b) correlations of PM$_{10}$–O$_3$ 1-hr for lowest rural PM$_{10}$ site per state and (c) correlations of PM$_{2.5}$–O$_3$ 1-hr.

Source: Shadwick et al. (1999).

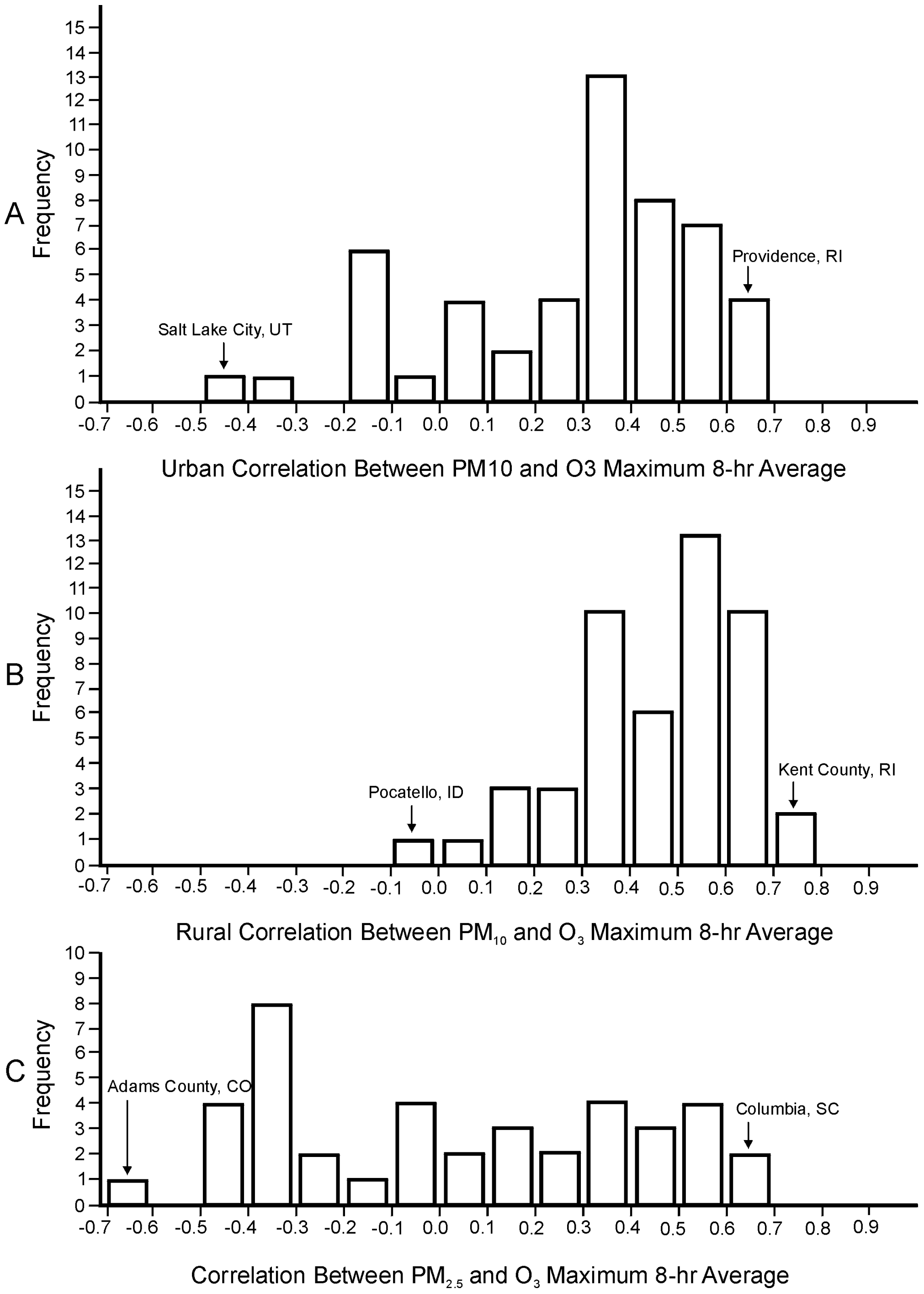

Figure 5-20. **(a) Correlations of PM_{10}–O_3 8-hr for highest urban PM_{10} site per state; (b) correlations of PM_{10}–O_3 8-hr for lowest rural PM_{10} site per state; and (c) correlations of $PM_{2.5}$–O_3 8-hr.**

Source: Shadwick et al. (1999).

TABLE 5-15. AVERAGE ANNUAL CORRELATIONS BETWEEN PM AND CRITERIA GASEOUS POLLUTANTS IN THE UNITED STATES (Std. Dev.)

Correlation PM vs Gas	vs CO	vs NO_2	vs SO_2	vs $O_{3\text{-}1h}$	vs $O_{3\text{-}8h}$
Urban PM_{10}	0.27 (0.22)	0.41 (0.21)	0.27 (0.21)	0.31 (0.25)	0.29 (0.26)
Rural PM_{10}	0.09 (0.18)	0.25 (0.21)	0.10 (0.13)	0.49 (0.17)	0.46 (0.18)
Combined $PM_{2.5}$	0.44 (0.29)	0.52 (0.18)	0.20 (0.20)	0.08 (0.36)	0.03 (0.38)

Source of Data: Shadwick et al. (1999).

which also oxidizes terpenes) their fractions of the ambient concentrations found indoors can be of order zero. In the absence of hourly PM data and air exchange rate data the estimation of a correlation between the ambient PM exposure and the exposure to the gases of ambient origin cannot be made without introducing assumptions about the hourly variability of ambient PM and air exchange rate. However, it is evident that the correlation between the personal exposures to ambient PM and personal exposures to ambient ozone, NO_2 and SO_2 must be closer to zero than the corresponding correlation of their respective atmospheric concentrations, because their different indoor deposition rates will create different and variable fractional exposures.

Carbon monoxide (CO), however, is virtually non-reactive in indoor micro-environments and it has no known surface sinks indoors. On average, a subject will be exposed to virtually 100% of the ambient CO concentration. Consequently the correlation between exposure to CO of ambient origin and exposure to PM of ambient origin will closely approach the correlation of the ambient PM concentration and the ambient CO concentration. However, the presence of indoor sources of CO, such as tobacco smoking, and outdoor in-vehicle exposures to traffic CO, will make the correlation between personal exposure to total CO and ambient PM much lower, in the same way that indoor sources of PM degrade the correlation of total PM exposure and ambient PM concentration.

Table 5-15 shows that on an annual basis PM_{10} is generally correlated positively with almost all gaseous criteria pollutants. The urban correlations are higher than the rural correlations for the daily averages of primary pollutants (CO, NO_2 and SO_2) and lower for the secondary pollutant ozone (1-h and 8-h). Examination of the corresponding histograms, with standard deviations of order 0.2, indicate that there is no general relationship; there are locations that can have no significant correlation (of order zero) and appreciable correlation (of order 0.5). Table 5-15 shows that $PM_{2.5}$ is, on the average, most strongly correlated with CO and NO_2, moderately correlated with SO_2, and not at all correlated with ozone in the combined urban and rural locations we have analyzed.

The correlations for $PM_{2.5}$ with ozone (maximum 1-h and maximum 8-h) for both urban and rural sites combined has the largest variance of all the data sets. The mean correlation is close to zero; however, the standard deviation of approximately 0.4 resulted from the fact that some locations were highly positively correlated, while others had low negative correlations. A possible explanation for a portion of this large variation in correlation between PM and ozone, may arise from the difference in number of years of data at each site, and the influence of motor vehicle traffic emissions of PM and NO. For example, Bernard et al. (1999) report that ozone and NO_2 in urban Montpellier, France had a highly negative correlation of $r = -0.96, p < 0.01$ in the short time period studied (November 13 − 20, 1995) as expected from the rapid gas phase reduction of ozone by NO. Consequently, if the U.S. monitoring stations for both PM and ozone are close to local traffic emissions that have the same diurnal pattern, then the PM may be a surrogate for accompanying NO emissions that would reduce the correlation of ozone with the measured PM.

These annual correlations between PM and criteria gaseous pollutants are relevant with respect to epidemiologic studies which analyze PM and health data over complete years of record. U.S. Environmental Protection Agency (1996) and Chen et al. (1999) discuss the variations in these gas-PM correlations between the summer and winter periods. Because of the different seasonal emissions and weather patterns, summer corresponds to a period of ozone maxima, and the primary combustion products (CO, SO_2) have their maxima during the winter, which often leads to seasonal variations of correlation. Therefore the results cited above may not be applicable to epidemiologic studies that analyze data by season, and a non-significant annual correlation of order zero may mask the presence of significant positive and negative correlations in the different seasons of the year.

In summary it appears that there is no general rule that applies to PM and the gaseous criteria pollutants. The possibility of confounding of a relation to ambient PM concentration by a gaseous ambient pollutant with a positive correlation in time to the ambient PM should be considered in epidemiologic studies.

5.15 CONFOUNDING BY INDOOR PM

It has been hypothesized that human exposure to indoor generated PM may be correlated with the ambient PM so that the health effects associated with the ambient PM concentration are in fact caused by the indoor generated PM and not the ambient PM (Crandall et al., 1996; Vedal, 1997). "For example, if study subjects closed their windows on days with higher levels of pollution, exposure to indoor pollutants might increase and actually be responsible for the increase in adverse health outcomes, and therefore confound the particle and health association" (Vedal, 1997). However this scenario may not apply to the situations in these studies because the ambient PM was virtually always below the PM NAAQS, and there were no episode warnings issued to the public to stay indoors to avoid high ambient PM pollution.

Hoek et al. (1989) reported respirable PM data (96% efficient collection of PM with a 4μm AD) indoors and outdoors before-during-after a moderate air pollution episode in the Netherlands in 1985, for which no smog warnings were issued. They found that indoor PM increased and then fell similarly in homes with 0, 1 and 2 smokers, in phase with the increase in ambient PM during the episode. Because Dutch homes with smokers have higher air exchange rates than homes without smokers (Lebret, 1985), Hoek et al. (1989) reasoned that "the increases in indoor concentrations observed during the episode were largely due to penetration of outdoor air, and not due to decreased ventilation, leading to increased concentrations of pollutants generated indoors, during the episode."

Mage et al. (1999) also tested this hypothesis of a decrease in air exchange rate leading to higher indoor PM from indoor sources by using the PTEAM data set from Riverside, CA (Clayton et al., 1993). When the PTEAM study was conducted in 1990, Riverside, CA was the region of the country with the highest annual average concentration of ambient PM_{10}. The PTEAM study utilized a constant emission source of perfluorocarbon tracer (PFT) and integrated charcoal PFT collectors for estimating air exchange rates. The measurements of the collected PFT were used to estimate the average number of air exchanges per hour (*a*) in each home during the resident's PM sampling period. Figure 5-21 shows that the measured air exchange rate had

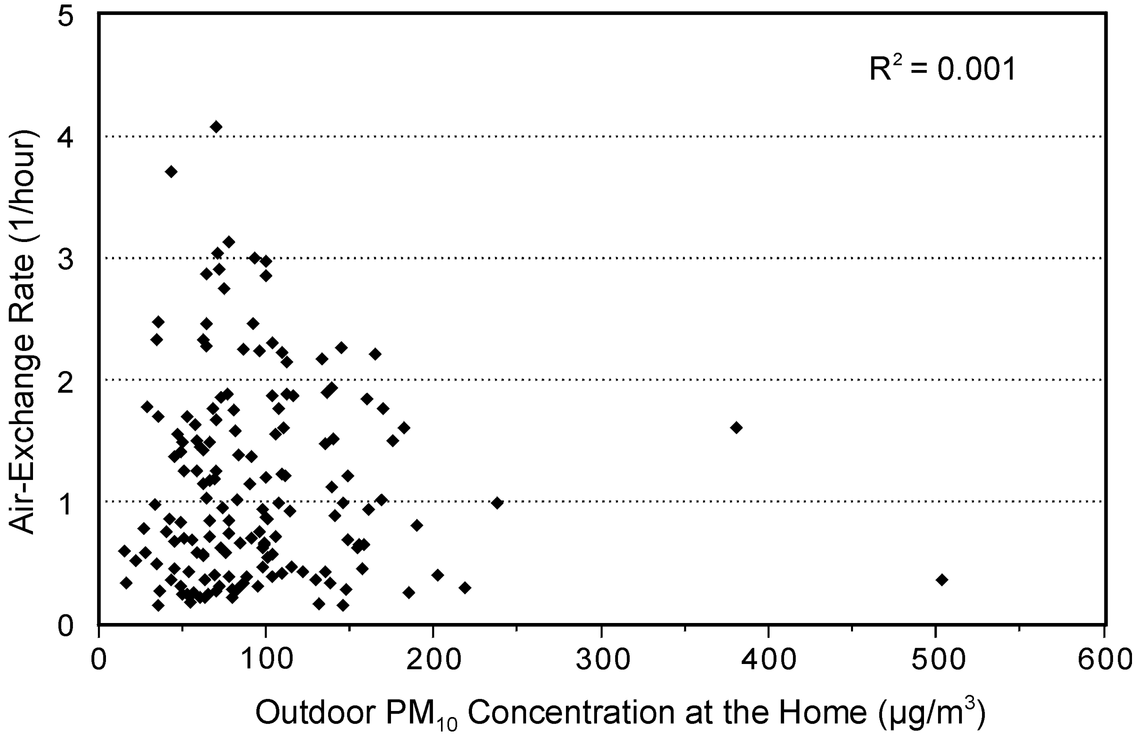

Figure 5-21. Air-exchange rate versus outdoor PM_{10} concentration at the home in the PTEAM study.

Source: Mage et al. (1999).

no statistically significant relation to the ambient PM_{10} during the daytime (r = - 0.04). Furthermore, each subject kept a time-activity diary so that the fraction of the time spent indoors and outdoors has been computed for each person. Özkaynak et al. (1996a) have determined the deposition parameter (k=0.65/h) and the penetration parameter ($P \approx 1$) for PM_{10} from these very same PTEAM data. Consequently we can estimate the exposure concentration of PM_{10} generated by indoor sources and personal activities (Ei) as,

$$\text{Ei} = \mathbf{E} - \text{Co}(a + k\,y)/(a + k) \tag{5-7}$$

Where **E** is the measured total personal exposure; Co ($a + k\,y$)/($a + k$) is the estimated personal exposure (Ea) to PM_{10} of ambient origin that also penetrates indoors ($P \approx 1$).

Figure 5-22 shows the quantity Ei for each subject vs the ambient concentration of PM_{10} (Co) that was measured outside their home at the same time. The regression has a slightly negative slope which is not significantly different from zero. Note the negative values for Ei in Figure 5-22 may be caused by the exposure and concentration measurement errors, and errors in the estimated parameters *P*, *a* and *k*. This suggests, at least for that Riverside cohort, that the personal exposure to a PM_{10} concentration of non-ambient origin does not appear to be positively correlated with the ambient PM_{10} concentration measured at that same time. We propose that this is the underlying general relationship between non-ambient generated PM and ambient PM concentration.

In order for there to be a positive correlation between exposure to indoor generated PM (Ei) and ambient PM (Co or Ca), people would have to smoke more cigarettes, dust and vacuum more, cook more, and perform more hobby-type activities indoors on days with higher ambient PM concentrations than on days with lower ambient PM concentrations. We expect that, where air quality standards are being met, people make their decisions to perform these personal activities without any conscious or unconscious consideration of the ambient PM concentration which is unknown to them (Hoek et al., 1989). Thus, the amount of non-ambient PM that people generate through their daily activities is expected to be independent of, and uncorrelated with, the ambient PM concentration in their community.

Because the concentrations of PM due to such indoor sources were not observed to be correlated with ambient PM concentration in either the Netherlands or Riverside, CA (the region of the U.S. with the highest ambient PM concentration at the time of the PTEAM study), it is reasoned that human exposure to non-ambient PM is likely to be independent of the concentration of PM of ambient origin. Therefore it would be independent of the human exposure to PM of ambient origin and not a confounder in the epidemiologic analysis. However, these indoor generated PM species can be effects modifiers as discussed in the following material.

Some PM species, and gaseous pollutants for which U.S. EPA has not established a short-term National Ambient Air Quality Standard (NAAQS), may also play a role as acute effect modifiers. Such a condition may occur with long-term exposure to a pollutant with a chronic effect without any apparent acute effects. That chronic exposure may make a subject more susceptible to the acute effect of a given exposure to PM of ambient origin. Chronic exposure to

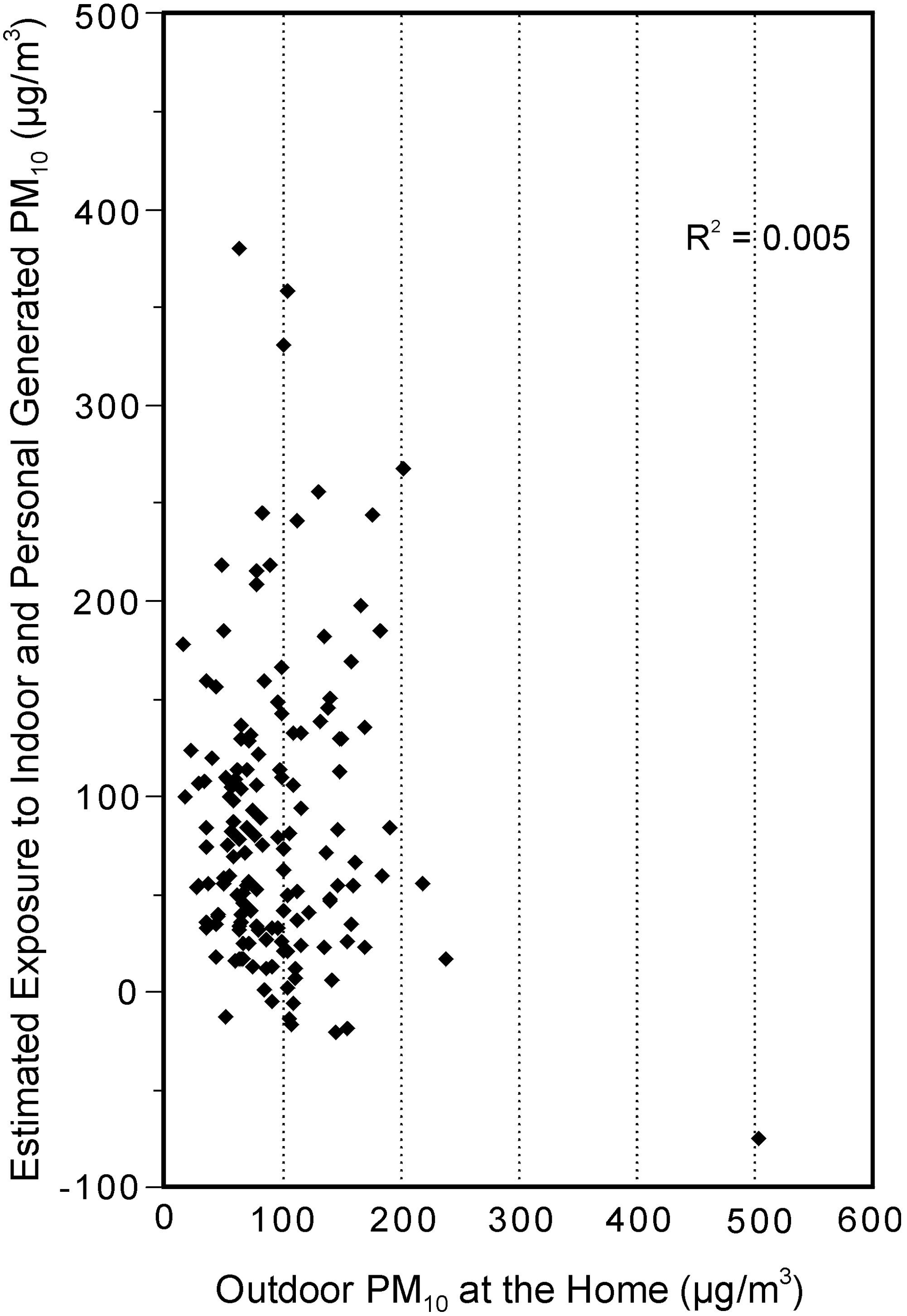

Figure 5-22. Estimated personal exposure to indoor and personally generated PM_{10} versus outdoor PM_{10} at the same home in the PTEAM study.

Source: Mage et al. (1999).

cigarette smoke, and chronic exposure to radon progeny and asbestos in PM of indoor origin, may cause malignant and non-malignant pulmonary disease which can make people more susceptible to the acute effects of ambient PM than otherwise healthy individuals (United Kingdom Ministry of Health, 1954). Therefore the daily concentration of such agents with chronic toxicity may be a surrogate for an underlying susceptibility to acute effects of ambient PM exposure in older subjects who lived in the monitored residence for a long period of time and who developed an underlying pulmonary insufficiency.

There are also possible short-term effects of exposure to "nuisance and inert" PM, occupationally generated PM, and unmonitored ambient PM in the upper portion of the coarse mode of PM with an AD > 10 μm (see Figure 5-1). PM species with biogenic or allergenic properties could irritate and sensitize the lung to the ambient PM_{10} (see Section 7.2 of U.S. Environmental Protection Agency, 1996) or increase the residence time of ambient PM_{10} in the lung. For example, if alveolar macrophages removed non-ambient particles and ambient particles of AD > 10 μm, instead of deposited ambient PM_{10} species, the rate of pulmonary clearance of the deposited ambient PM_{10} particles would be decreased.

The presence of effect-modification on mortality and morbidity is difficult to discern except perhaps in animal testing where controlled dose-response studies can be used to pick up modifications of responses to ambient PM exposures in the presence and absence of candidate agents. In epidemiologic studies, these effects would appear as statistically significant interaction terms, but at the present time such interaction effects have not been reported (see Chapter 12 of U.S. Environmental Protection Agency, 1996). The general-linearized-model (GLM) described by Liang and Zeger (1986) has been used for most all the epidemiologic studies discussed in Chapter 7 of this document. The GLM implies that the effect of exposure to 2 $\mu g/m^3$ of ambient PM is twice the effect of exposure to 1 $\mu g/m^3$ of the same mixture of ambient PM, and the effect of an exposure to a mixture of 1 $\mu g/m^3$ of ambient PM plus 1 $\mu g/m^3$ of non-ambient PM is equal to the effect of exposure to 1 $\mu g/m^3$ of the same ambient PM mixture, plus the effect of an exposure to 1 $\mu g/m^3$ of the same non-ambient PM mixture.

Semi-volatile constituents of PM exist in the atmosphere in a dynamic equilibrium between their vapor and condensed phases. For example, water vapor in an air mass at a given relative humidity (RH) is in dynamic equilibrium with the water content of the aerosol PM within that air mass. After a particle is collected, fluctuations in relative humidity cause fluctuations in the amount of the water adsorbed on the particle, so consequently, the Federal Reference Method for Particulate Matter (40CFR50 Appendices B, L, M, J) calls for filters to be weighed, following a 24-h dessication and equilibration period within a temperature and humidity controlled room, to reduce the water content of the collected particles.

Other species, such as some inorganic nitrates and organic compounds, have high enough vapor pressures, in the range of ambient temperatures, that they, like water, can coexist in both the vapor and aerosol phase. Consequently, a variable fraction of such species may be lost from the collected mass on filters during equilibration. Continuous monitors must also remove water associated with particles (particle-bound water). For example, the TEOM® monitor is operated with the filter at 50°C to remove particle-bound water. The TEOM® can record negative PM if mass volatilizes from the filter collecting the PM, faster than new PM adheres to it.

Because ambient concentrations of these semi-volatile species are not currently measured, and personal exposures to these constituents have not been reported in the literature, it is not known whether these effervescent PM species could contribute to the health effects associated with the non-volatile PM mass that is represented by the PM data in the epidemiology literature. Although one might not expect the health effects associated with the non-volatile PM mass to be caused by the unmeasured semi-volatile PM species, there may be a correlation between these two masses so the captured non-volatile PM mass may in some aspects be a surrogate for the mass of semi-volatile compounds that escaped from the collected PM.

In summary, this discussion supports the conclusion that the average concentrations of PM measured at a community ambient monitoring station are reasonably good surrogate-estimates of the average concentrations of PM of ambient origin to which people residing in that community are exposed, more so for fine mode PM than coarse mode PM. This agreement between exposure to ambient PM and ambient PM concentrations supports the plausibility of PM of ambient origin, or a constituent thereof, being responsible for the fluctuations of health effects that are correlated with fluctuations of ambient PM concentrations. The size distributions, the chemical compositions, and the related toxicities per unit mass of ambient PM may vary from city to city in a season, and from season to season in a city. In addition, different varieties of climates between cities may influence the amount of time people spend outdoors and the air exchange rates between their homes and the outdoor air, resulting in some cities having higher percentages of the ambient PM penetrating into the residences than the others (Gamble, 1998).

The resulting inter-urban differences of exposure to PM of ambient origin may explain a portion of the variance between the observed differences in mortality/morbidity per unit concentration of ambient PM that are reported in the literature and are discussed in Chapter 7 of this document.

5.16 IMPLICATIONS OF THE AMBIENT PM EXPOSURE RELATIONSHIPS FOR EPIDEMIOLOGIC ANALYSIS AND A SUMMARY OF THE CHAPTER CONCLUSIONS

The main conclusion of this chapter is that (a) exposures to PM of ambient origin are highly correlated with ambient PM concentrations; and; (b) exposures to emissions of PM of non-ambient origin (e.g., tobacco smoke, residential activity, occupational activity) have very low correlations with ambient PM concentrations. Therefore, it follows that the exposures to the concentrations of PM produced by non-ambient sources (e.g., indoor and/or occupational) are also uncorrelated with exposures to PM of ambient origin and the corresponding ambient PM concentrations. Consequently the finding that personal exposures to total PM (both ambient origin and non-ambient origin) are uncorrelated with ambient PM concentrations is not important. This is because the acute health effects, if any, caused by the exposure to non-ambient PM will have an equally low correlation with the acute health effects created by the personal exposure to PM of ambient origin.

As described in Section 5.14, ambient PM concentrations in the U.S. have a wide range of correlations in time with the ambient gaseous criteria pollutants that may produce or influence cardiac and pulmonary effects. It appears that there is no *a priori* reason to neglect their ability to confound the ambient PM vs health effect relationships. Therefore, these correlations need to be evaluated at each location where an epidemiologic study is conducted to determine whether they are significantly different from zero. The chapter conclusions are as follows:

1. Human exposure to PM of ambient origin for individuals in a community is often highly correlated ($R^2 > 0.5$) in time with concentrations of PM of ambient origin of the same size as measured in that community.
2. The longitudinal correlation coefficient for the ambient concentration of fine PM ($AD \leq 2.5\ \mu m$) with personal exposure to ambient fine PM is greater than the corresponding

correlation for the coarse fraction of ambient PM ($2.5\ \mu m < AD \leq 10\ \mu m$) as shown by studies of ambient sulfate concentrations and sulfate exposures.

3. People in a community surrounding an ambient monitoring station, over time, are exposed to relatively similar mixtures and concentrations of ambient $PM_{2.5}$.
4. People in a community are exposed to widely different mixtures and concentrations of non-ambient PM due to the diversity of smoking habits, personal activities such as hobbies, residential furnishings and appliances, and varying occupations.
5. Exposures to PM of indoor origin appear to be uncorrelated with exposures to PM of ambient origin.
6. The correlation of a single individual's sequence of daily personal exposures to total PM and ambient PM concentrations will be greater than the correlation that would occur had a different person been monitored on each of the same days [e.g., one person monitored consecutively for n days vs sequentially monitoring n different people, each for one day, over n days].
7. Ambient PM in the U.S. has average annual correlations with the ambient gaseous pollutants CO, ozone, NO_2, and SO_2 of order $r = 0.25$ with a standard deviation of order 0.25.
8. Although exposures to PM from indoor sources and occupational activities may not be correlated with ambient PM concentrations, these non-ambient PM species may possibly act as effect modifiers by making subjects more or less susceptible to exposure to PM of ambient origin.
9. There are only limited data available, from non-probability samples, to evaluate how well the exposures to PM of ambient origin for susceptible subgroups correlates with the ambient PM concentrations of similar AD size range as measured in their community.

In conclusion, day-to-day variation in the ambient concentration of fine particles is a good surrogate for the day-to-day variation in the community average personal exposure to fine particles of ambient origin. This relationship is not as clear for coarser particles (PM_{10} - $PM_{2.5}$) which do have more local sources. This supports the plausibility of ambient $PM_{2.5}$ concentration as a surrogate measure for personal exposure to $PM_{2.5}$ of ambient origin in time series studies, and provides the linkage necessary to more completely evaluate the impact of ambient PM regulation under Title I of the Clean Air Act Amendments.

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APPENDIX 5-A

Nomenclature

a	air exchange rate between indoors and outdoors
A	surface area for PM deposition in an indoor microenvironment
AD	aerodynamic diameter (not to be confused with actual dimensions or optical diameter)
C	indoor concentration of PM of ambient origin
Ca	ambient concentration of PM (virtually all PM of ambient origin) at a monitoring station
Co	outdoor concentration of PM at a residence, not necessarily equal to Ca
E	total exposure to PM of ambient origin and PM of non-ambient origin.
Ea	exposure to PM of ambient origin
Ei	exposure to PM of non-ambient origin (PM generated indoors)
ETS	environmental tobacco smoke (PM)
F(M)	a function of ambient PM mass deposited indoors (M)
HVAC	Heating-Ventiliation-Air Conditioning
k	deposition rate of PM onto indoor surfaces, 1/time
LOD	limit of detection
M	mass of PM of ambient origin deposited indoors
MDL	minimum detectable level
P	penetration factor for ambient PM from outdoors to an indoor microenvironment
PM_{AD}	particles collected by a monitor with a 50% collection efficiency at the given AD
Q_a	rate of resuspension of ambient PM in an indoor microenvironment
Q_{other}	PTEAM estimate of indoor PM emission rate from sources other than smoking and cooking
r	Pearson correlation coefficient
R^2	regression coefficient
SPSS	Scientific Probability Sampling Schema
T	time period of the study or the analysis
t	time, as a variable
v	alveolar ventilation rate

v	volumetric flow rate of air exchanged between indoors and outdoors
V	volume of well mixed indoor microenvironment
w	fraction of time spent outdoors at night in PTEAM (7pm - 7am)
x	fraction of time spent outdoors during the day in PTEAM (7am - 7pm)
y	fraction of time spent outdoors during a complete 24-h day
z	fraction of ambient concentration (Ca) to which a person is exposed during a 24-hour period
γ	resuspension rate of PM of ambient origin previously deposited in an indoor microenvironment
δio	delta function equal to 1 when subject is indoors and 0 when subject is outdoors, and δoi is vice versa
ϵ	spatial variation of ambient PM (Co - Ca)
σ	arithmetic standard deviation
μ	arithmetic mean