



# **Air Quality Criteria for Particulate Matter**

**Review  
Draft**  
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## **Volume I of III**

### **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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Environmental Criteria and Assessment Office  
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Office of Research and Development  
U.S. Environmental Protection Agency  
Research Triangle Park, NC 27711



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## FORWARD

As explained in Chapter 2 (Introduction), the present draft document, Air Quality Criteria for Particulate Matter, is being prepared to meet Clean Air Act provisions which require that the Administrator of the United States Environmental Protection Agency (U.S. EPA) periodically review and revise, as appropriate, the criteria and National Ambient Air Quality Standards (NAAQS) for particulate matter and other listed "criteria air pollutants". This criteria assessment, therefore, contains evaluations of new scientific information that has become available since the last prior criteria reviews for particulate matter were carried out by U.S. EPA in the 1980's, as also described in Chapter 2.

Responsibility for preparation of this External Review Draft of the subject Particulate Matter Air Quality Criteria Document (PM AQCD) falls within the mission of U.S. EPA's Environmental Criteria and Assessment Office in Research Triangle Park, NC. That office (ECAO/RTP) is a component of the Office of Health and Environmental Assessment (OHEA) within the Office of Research and Development (ORD), the scientific arm of U.S. EPA. Members of the U.S. EPA Project Development Team for Development of the present draft document are listed in ensuing pages of the front matter for this volume (I of III) of the document, and include both ECAO/RTP staff and a few other scientists on temporary assignment to ECAO/RTP.

The U.S. EPA Project Development team has carried out preparation of an overall Project Development Plan for preparation of the subject PM AQCD including identification of key issues to be addressed, planned content of the document, description of the process and schedule for preparation and review of draft materials, and identification of U.S. EPA staff scientists and non-EPA consultants expected to serve as authors of sections of the document. That Project Development Plan was reviewed by members and consultants of the Clean Air Act Scientific Advisory Committee (CASAC) listed on Pages xlv-xlvii, and it was appropriately modified in response to their comments and recommendations. The EPA Project Team has also coordinated and implemented the planning and execution of specific logistical arrangements, by which the writing, word processing, editing, and assembly of draft chapter materials and their preliminary peer review and subsequent revision to the present External Review Draft version have been accomplished.

## FORWARD (cont'd)

Initial drafts of various chapters (other than Chapters 1 and 13) were prepared mainly during summer/fall of 1994 and subsequently underwent preliminary peer review in early 1995, either (a) as part of public expert workshops held in January 1995 where most key chapters (4, 6, 7, 10, 11, 12) were discussed in open forum, or (b) via receipt of oral or written comments on the other chapters from internal EPA scientific staff and/or selected non-EPA experts. Revisions made in response to such preliminary reviews were then incorporated into revised chapters to produce this External Review Draft of the document.

The principal authors of materials contained in each chapter of the document are identified in the front matter for each of the three volumes of this External Review Draft, as shown on pages preceding this forward for Volume I chapters. Other contributors and reviewers, who provided comments on initial drafts of particular chapters or other information importantly considered as inputs to revisions incorporated into the chapters, are also identified under "Contributors and Reviewers" in the front matter materials for each volume. However, the evaluations and conclusions contained in this External Review Draft do not necessarily reflect the individual views of all identified authors, contributors, and reviewers.

The present External Review Draft of the subject PM AQCD has been prepared for release for public comment and review by CASAC, as mandated by the Clean Air Act. The public comment period, extending from May 1, 1995 to August 1, 1995, will be followed soon after by a public meeting of CASAC in early August, 1995 (specific site and dates to be announced in the Federal Register). Further revisions will then be incorporated into this draft document in response to public comments and CASAC peer review to produce a final version of this document by no later than January, 1996.

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# 1. EXECUTIVE SUMMARY

## 1.1 PURPOSE OF THE DOCUMENT

The purpose of this document is to present air quality criteria for particulate matter (PM) in accordance with the Clean Air Act (CAA). Two sections of the CAA (Sections 108 and 109) 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.

## 1.2 INTRODUCTION

Air Quality Criteria for Particulate Matter evaluates the latest scientific information useful in deriving criteria that form the scientific basis for U.S. Environmental Protection Agency (EPA) decisions regarding the National Ambient Air Quality Standards (NAAQS) for particulate matter (PM). This Executive Summary concisely summarizes key conclusions from the document which comprises thirteen chapters. The Executive Summary is followed by a general introduction in Chapter 2. Chapters 3 through 7 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. Chapter 8 describes effects on visibility, and Chapter 9 describes damage to materials attributable to PM. Chapters 10 through 13 evaluate information concerning the health effects of PM. More specifically, Chapter 10 discusses dosimetry of inhaled particles in the respiratory tract; Chapter 11 summarizes information on the toxicology of specific types of PM constituents, and includes experimental toxicological studies of animals and human clinical studies. Chapter 12 discusses epidemiological studies.

Chapter 13 integrates information on critical health issues derived from studies reviewed in the prior chapters. The following sections conform to the chapter organization of the criteria document.

### 1.3 PHYSICS AND CHEMISTRY OF PARTICULATE MATTER

Chapter three first describes the physical properties, chemistry, and chemical composition of PM. Next, the transport and transformation to secondary particulate matter are presented. Then, both dry and wet deposition are discussed. Finally, the physical and chemical considerations in particulate matter sampling and analysis are examined. The following brief comments present some basic characteristics of PM.

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 and elements, elemental carbon, organic compounds, and crustal compounds. Some atmospheric particles are hygroscopic and contain particle-bound water. The organic fraction is especially complex. Hundreds of organic compounds have been identified in atmospheric aerosols, including alkanes, alkanolic and carboxylic acids, polycyclic aromatic hydrocarbons, and nitrated organic compounds.

Particle diameters span more than four orders of magnitude, from a few nanometers to one hundred micrometers. Combustion-generated particles, such as those from power generation, from automobiles, and in tobacco smoke, can be as small as 0.01  $\mu\text{m}$  and as large as 1  $\mu\text{m}$ . Particles produced in the atmosphere by photochemical processes range in diameter from 0.05 to 2  $\mu\text{m}$ . Fly ash produced by coal combustion ranges from 0.1 to 50  $\mu\text{m}$  or more. Wind-blown dust, pollens, plant fragments, and cement dusts are generally above 2  $\mu\text{m}$  in diameter. Particles as small as a few nanometers and as large as 100  $\mu\text{m}$  have been measured in the atmosphere.

1       The composition and behavior of airborne particles are fundamentally linked with those  
2 of the surrounding gas. Although the term aerosol is often used to refer to suspended  
3 particles, aerosol is defined as a dilute suspension of solid or liquid particles in gas.  
4 Particulate material can be primary or secondary.

5       Primary particles are those emitted in particulate form and include wind-blown dust, sea  
6 salt, road dust, mechanically generated particles and combustion-generated particles such as  
7 fly ash and soot. The concentration of primary particles depends on their emission rate,  
8 transport and dispersion, and removal rate from the atmosphere.

9       Secondary particulate material may form from condensation of high temperature vapor  
10 or from vapors generated as a result of chemical reactions involving gas-phase precursors.  
11 Secondary formation processes can result in either the formation of new particles or the  
12 addition of particulate material to preexisting particles. Most atmospheric sulfate is formed  
13 from atmospheric oxidation of sulfur dioxide. Atmospheric nitrate is also essentially  
14 secondary, formed from reactions involving oxides of nitrogen to form nitric acid. A portion  
15 of the organic aerosol is also attributed to secondary processes. Secondary aerosol formation  
16 can depend on concentrations of other gaseous reactive species such as ozone or hydrogen  
17 peroxide, atmospheric conditions including solar radiation and relative humidity, and the  
18 interactions of precursors and preexisting particles with cloud or fog droplets. As a result, it  
19 is considerably more difficult to relate ambient concentrations of secondary species to sources  
20 of precursor emissions than it is to identify the sources of primary particles.

21       Airborne particulate matter can be anthropogenic or biogenic in origin. Both  
22 anthropogenic and biogenic particulate material can occur from either primary or secondary  
23 processes. Anthropogenic refers to particulate matter which is directly emitted or formed  
24 from precursors which are emitted as a result of human activity. Primary anthropogenic  
25 sources include fossil fuel combustion, fireplace emissions, and road dust. Secondary  
26 anthropogenic particulate material can be generated photochemically from anthropogenic  
27 SO<sub>2</sub>, NO<sub>x</sub>, or organic gases. Primary biogenic sources include leaf waxes and other plant  
28 fragments from plants. In addition, plants emit gaseous species such as terpenes. Terpenes  
29 are photochemically reactive, and in the presence of nitrogen oxides can form secondary  
30 organic particles. Other types of primary particulate material such as sea salt and wind-  
31 generated dust from soil undisturbed by man also are of non-anthropogenic origin.

## 1.4 SAMPLING AND ANALYSIS OF PARTICULATE MATTER AND ACID DEPOSITION

This chapter is intended to provide supplemental information to Chapter 3 and other discussions of aerosol measurement methodologies used in support of the existing PM<sub>10</sub> standards and/or potentially useful in considerations related to the possible need for development of a “fine particle” standard with an upper cut-point in the 1 to 3 μm range. The discussion of ambient PM monitoring methods is also included to enhance understanding of exposure data (and their interpretation) used in epidemiology analyses assessed in Chapter 12 of this document. An important contribution of the sampling and analytical sections is the extensive compilation of salient peer-reviewed technical references that can be consulted by the reader for more detailed information.

Chapter four briefly describes the technical capabilities and limitations of aerosol sampling and analytical procedures focusing on those that were used: (1) to collect data supporting other sections in this document; (2) to support the existing PM<sub>10</sub>, TSP, and Pb regulations; (3) to support health and welfare effects studies; and/or (4) have application to development of a possible fine particle standard; or (5) illustrate the attributes of several new technologies. The discussion of aerosol separation technologies is divided between (1) devices used to mimic the larger particle (> 10 μm) penetration rationales for the upper respiratory tract airways, and (2) those devices generally used to mimic smaller particle penetration (< 10 μm) to the thoracic regions. These device descriptions are followed by sampling considerations for their applications.

The applications of performance specifications to define these measurement systems for regulatory purposes are discussed, along with a number of critical observations suggesting that the current specification process does not always ensure the accuracy or representativeness necessary in the field.

The EPA program designating PM<sub>10</sub> reference and equivalent sampling systems is briefly described, along with a current list of designated devices. Selected measurement systems used to provide more detailed characterization of aerosol properties for research studies are discussed, with a focus on the determination of particle size distributions. Aerosol sampling systems for specialty applications, including automated samplers, personal

exposure samplers, and the sampling systems used in aerosol apportionment studies are briefly described.

## 1.5 SOURCES AND EMISSIONS OF SUSPENDED PARTICLES

Chapter five is organized to present first a concise summary of key information on PM emissions derived from the previous criteria review in the 1980's and then to provide a more extensive discussion of newer information appearing in recent years.

The main objectives of Chapter 5 discussions are:

- To identify the sources that are major contributors to suspended particle concentrations in the United States.
- To describe the particle sizes and chemical properties of source emissions.
- To evaluate the limitations and uncertainties of emissions rate estimates and source contributions for suspended particles and their gaseous precursors.

The ambient atmosphere contains both primary and secondary particles; the former are emitted directly by sources, and the latter are formed from gases (SO<sub>2</sub>, NO<sub>x</sub>, NH<sub>3</sub>, VOCs). Fugitive dust is a primary pollutant. Major sources of particle emissions are classified as major point sources, mobile sources, and area sources; these are anthropogenic. Natural sources also contribute to ambient concentrations.

The 1982 Criteria Document emphasized emissions from industrial sources, especially primary particles. SO<sub>2</sub> was the only precursor of secondary particles considered. Since 1982, many of these sources have been controlled, yet particle standards are exceeded in many areas.

Source and receptor models are used to quantify major contributions to excess PM<sub>10</sub> concentrations. Source models use emissions inventories and meteorological data to predict particle formation dispersion and particle concentrations measured at receptors. Receptor models use the chemical composition of emissions (finger points) and concentrations at receptor sites to estimate the contribution of sources. The latter are used to identify sources in non-attainment areas.

1 Fugitive dust is a major contribution to PM<sub>10</sub> at nearly all sampling sites, although the  
2 average fugitive dust source contribution is highly variable among sampling sites within the  
3 same areas, and is highly variable between seasons.

4 Primary motor vehicle exhaust makes up as much as 40% of average PM<sub>10</sub> at many  
5 sampling sites. Vegetative burning outdoor and residential wood burning are significant  
6 sources in residential areas. Fugitive dust from paved and unpaved roads, agricultural  
7 operations, construction, and soil erosion constitute ~90% of nationwide primary emissions.  
8 Fugitive dust consists of geological material that is suspended into the atmosphere by natural  
9 wind and by anthropogenic activities from sources such as paved and unpaved roads,  
10 construction and demolition of buildings and roads, storage piles, wind erosion, and  
11 agricultural tilling. There are obvious discrepancies between the proportion of fugitive dust  
12 in primary emissions and geological contributions to PM<sub>10</sub> calculated by receptor models,  
13 due to contributions from secondary aerosols, which are not included in the primary PM<sub>10</sub>  
14 emission estimates. Even when secondary aerosol is subtracted, however, other sources such  
15 as vegetative burning and wood combustion make larger relative contributions to ambient  
16 concentrations than is indicated by the emissions inventories. Fugitive dust estimates are  
17 especially affected by the general limitations of emissions inventories. All of the emissions  
18 have remained relatively constant over the 8-year period except for those from soil erosion.

19 The major non-fugitive dust emitters are other industrial processes and exhaust from  
20 highway vehicles. Fuel combustion from utilities, industrial, and other sources together  
21 contribute between 1 to 2% to total primary particle emissions. Industrial fuel combustion  
22 emissions were reduced by one-third and other fuel combustion emissions were reduced by  
23 one half between 1983 and 1992. On-highway vehicle emissions increased by 50%,  
24 primarily due to large increases in the number of vehicle miles traveled. Electric utilities  
25 account for the largest fraction of sulfur dioxide, nearly 70% of total emissions. These  
26 emissions have not changed substantially over the 10 years reported. Annual averages do not  
27 reflect the seasonality of certain emissions, residential wood burning in fireplaces and stoves,  
28 for example. Cold weather also affects motor vehicle exhaust emissions, both in terms of  
29 chemical composition and emission rates. Planting, fertilizing, and harvesting are also  
30 seasonal.



1 Mobile sources are major emitters of primary particles, oxides of nitrogen, and volatile  
2 organic compounds. They are also minor emitters of sulfur dioxide and ammonia. On-road  
3 motor vehicles using gasoline-and diesel-fueled engines are by far the largest component of  
4 mobile source emissions, and the emissions estimation methods are most highly developed  
5 for these vehicles. Studies show that while vehicle emissions models may function well  
6 under idealized conditions, they underestimate the effects of high emitting vehicles that may  
7 be major sources of VOCs. Motor vehicle exhaust contains high concentrations of organic  
8 and elemental carbon, but their ratios are much different from those found in wood  
9 combustion with the abundance of elemental carbon being nearly equal to the organic carbon  
10 abundance.

11 There are major discrepancies between the relative amounts of emissions and  
12 contributions to suspended particles found in many areas. Some major re-design is needed to  
13 create more accurate emissions models that can improve the quantification of source-receptor  
14 relationships. Emissions models are intended to estimate the emissions rates as a function of  
15 space and time of selected pollutants from point, area, and mobile sources. In contrast to an  
16 emissions inventory, which is a static catalogue of emissions estimates for a given  
17 geographical area and averaging time, an emissions model is capable of accessing activity  
18 data bases from a multitude of information-gathering agencies and determining actual  
19 emissions for relatively small regions and averaging times.

## 22 **1.6 ENVIRONMENTAL CONCENTRATIONS**

23 Chapter six summarizes PM concentrations over the United States, including the  
24 spatial, temporal, size, and chemical aspects. This chapter mainly aims to provide  
25 background information on U.S. PM concentrations to help set a context for discussions in  
26 later chapters on the characterization and quantification of PM health effects. The general  
27 approach in the chapter is to organize, evaluate, and summarize the existing large scale  
28 aerosol data sets over the United States. Emphasis is placed on complete national coverage  
29 as well as the fusion and reconciliation of multiple data sets.

30 The main organizing dimension used to structure Chapter 6 is space. Accordingly, PM  
31 concentrations are presented on global, continental, national, regional, and sub-regional or

1 urban scales. Within each spatial domain, the spatial-temporal structure, aerosol size and  
2 chemical composition are also presented. The presentation of aerosol pattern begins with a  
3 global and continental perspective. Next, national U.S. aerosol patterns are examined, as  
4 derived from non-urban and urban  $PM_{10}$  and  $PM_{2.5}$  monitoring networks, and the aerosol  
5 characteristics over seven subregions of the contiguous United States are examined in more  
6 detail. Ten year trends, seasonal patterns, as well as the  $PM_{2.5}/PM_{10}$  relationship and fine  
7 particle chemical composition are examined for each region. An ensuing section then  
8 focuses further on the sub-regional and urban-scale aerosol patterns over representative areas  
9 of the United States.

10 The aerosol concentration pattern over the United States has been reported by many  
11 aerosol researchers over the past decade. In particular the research groups associated with  
12 the IMPROVE aerosol monitoring networks have been prolific producers of high quality  
13 data, reports, and analysis of non-urban data. This section draws heavily on their  
14 contribution but the maps, charts, and computations have been re-done for sake of  
15 consistency with other (urban) data from the AIRS network. Each of the sections are  
16 augmented by suitable but not exhaustive references to the pertinent literature.

17 Table 1-1 summarizes, for illustrative purposes, annual average urban  $PM_{10}$  data from  
18 the AIRS Network by U.S. region. The annual means for all regions show declines from  
19 1985 to 1993. Tables 1-2 and 1-3 provide more specific illustrative information on 24-h  
20 mean, second highest maximum, and annual average values for  $PM_{10}$  concentrations in 1993  
21 for selected U.S. cities from various U.S. regions.

22 Next, a section on chemical composition of PM aerosols at urban and non-urban sites  
23 summarizes available data on the composition of atmospheric particles. Emphasis has been  
24 placed on the Harvard six-city study and the inhalable particulate network (1980-1981).  
25 However, data for fine particle mass and elemental composition only were available from  
26 these studies. Data for sulfate, nitrate, and elemental and organic carbon content are  
27 included from other studies to provide an overview of the chemical composition of the  
28 atmospheric aerosol in the United States. Extensive tables in this section provide detailed  
29 representation of atmospheric properties of aerosols to which U.S. populations are exposed.  
30 Unfortunately, data this complete are generally collected over limited time periods and are  
31 not of sufficient duration to be useful for most epidemiological

**TABLE 1-1. CHARACTERIZATION OF URBAN PM<sub>10</sub> DATA FROM AIRS NETWORK BY REGION FOR THE UNITED STATES**

Region	PM <sub>10</sub> (μg/m <sup>3</sup> )		SD <sup>a</sup>	Seasonality	Seasonal Variation %	PM <sub>2.5</sub> /PM <sub>10</sub>	Influences
	1993	1985					
Northeast	22	36	30%	Summer Peak July	20% <sup>b</sup>	62%	Canadian and Gulf airmasses, local sources, long range transport
Southeast	24	32	17%	Summer High July, August	37%	58%	Flat, poor regional ventilation
Industrial Midwest	25	38	28%	High June, August Low November, February	37%	59%	Winter cold Canadian airmasses. Summer moist Gulf Coast masses
Upper Midwest	25	31	19%	Slightly Lower Levels December/January	19%	38%	Agricultural Heartland windblown dust influence
Southwest	26	52	45%	April-June Peak October-November Peak August-September Dip		37%	low precipitation, coarse particle dominant, dust contribution to PM <sub>10</sub>
Northwest	25	50	45%	Peak December Low March-May	36%	59%	Meteorology highly variable
Southern California	32	45	40%	Peak November Low March	27%	50%	Air flow from Pacific, dry summer, low in remote Basin wide elevation

<sup>a</sup>Standard deviation among monitoring stations within regions.

<sup>b</sup>Seasonal range expressed as percent.

**TABLE 1-2. PM<sub>10</sub> LEVELS BY ANNUAL AVERAGE FOR SELECTED U.S. SMSAs FOR 1993**

Metropolitan Statistical Area	1990 Population	PM <sub>10</sub> WTD AM <sup>1</sup> (μg/m <sup>3</sup> )	PM <sub>10</sub> 2nd Max <sup>2</sup> (μg/m <sup>3</sup> )	O <sub>3</sub> (ppm) <sup>3</sup>
Santa Fe, NM	117,043	15	35	---
Amarillo, TX	187,547	16	29	-
Santa Rosa, CA	388,222	18	52	---
Springfield, MD	239,971	18	39	---
Casper, WY	61,226	18	41	---
Danbury, CT	187,867	19	46	0.14
Glens Falls, NY	118,539	19	44	---
Titusville Area, FL	398,978	19	57	---
New London Area, CT/RI	266,819	19	41	0.13
Bridgeport, CT	443,722	21	50	0.17
Fort Lauderdale, FL	1,255,480	21	71	---
Asheville, NC	174,821	22	58	---
Montgomery, AL	292,517	23	48	---
Honolulu, HI	836,231	24	58	---
Oakland, CA	2,082,914	26	71	0.13
Charleston, SC	506,875	26	58	---
San Francisco, CA	1,603,678	29	72	---
Dallas, TX	2,553,362	30	74	0.14
Louisville, KY	952,662	33	73	0.14
Baltimore, MD	2,382,172	35	70	0.15
Birmingham, AL	907,810	36	85	0.13
Mobile, AL	476,923	38	71	---
Orange County, CA	2,410,556	38	80	0.17
Phoenix, AZ	2,122,101	44	92	0.13
New York, NY	8,546,846	47	86	---

<sup>1</sup>Weighted Annual Mean

<sup>2</sup>Highest Second Maximum 24-hour Concentration

<sup>3</sup>Highest O<sub>3</sub> Second Daily Maximum 1-hour Concentration

**TABLE 1-3. SELECTED U.S. PM<sub>10</sub> LEVELS BY 2ND MAX PM<sub>10</sub> FOR 1993**

Metropolitan Statistical Area	1990 Population	PM <sub>10</sub> 2nd Max <sup>2</sup> (µg/m <sup>3</sup> )	PM <sub>10</sub> WTD AM <sup>1</sup> (µg/m <sup>3</sup> )	Note
St. Louis, MO	2,444,099	101	44	O <sub>3</sub> <sup>3</sup> 0.13
Los Angeles, CA	8,863,164	102	47	O <sub>3</sub> - 0.25, CO <sup>4</sup> - 14
San Diego, CA	2,498,016	105	34	O <sub>3</sub> 0.16
El Paso, TX	591,610	106	37	O <sub>3</sub> 0.14, CO-11
Medford, OR	146,389	106	41	---
Seattle, WA	1,972,961	119	35	---
Gary, IN	604,526	122	34	---
Flint, MI	430,459	127	24	---
Bakerville, CA	543,477	128	54	O <sub>3</sub> 0.16
Fresno, CA	667,490	131	53	O <sub>3</sub> 0.14
Denver, CO	1,622,980	142	41	---
Chicago, IL	6,069,974	147	47	---
Eugene, OR	282,912	151	28	---
Salt Lake City, UT	1,072,227	156	42	---
Spokane, WA	361,364	166	46	CO 12
Pittsburgh, PA	2,056,705	167	38	SO <sub>2</sub> <sup>5</sup> 0.155
Riverside, CA	2,588,793	172	73	O <sub>3</sub> 0.23
Steubenville, OH	142,523	177	40	SO <sub>2</sub> 0.244
New Haven, CT	638,220	178	52	O <sub>3</sub> 0.15
Provo, UT	263,590	209	40	CO 10
Philadelphia, PA	4,856,881	531	34	O <sub>3</sub> 0.14

<sup>1</sup>Weighted Annual Mean

<sup>2</sup>Highest Second Maximum 24-hour Concentration

<sup>3</sup>Highest O<sub>3</sub> Second Daily Maximum 1-hour Concentration

<sup>4</sup>Highest CO Second Maximum Non-overlapping 8-hour Concentration

<sup>5</sup>Highest SO<sub>2</sub> Second Maximum 24-hour Concentration

- 1 investigations. The tables do, however, provide insights as to the types of information that
- 2 could be collected as part of future monitoring efforts in support of human exposure
- 3 investigations. Table 1-4 provides illustrative data from an earlier 1987 study with regard to

**TABLE 1-4. CONCENTRATION RANGES OF VARIOUS ELEMENTS  
ASSOCIATED WITH PARTICULATE MATTER IN THE  
UNITED STATES ATMOSPHERE (ng/m<sup>3</sup>)**

Elements	Remote	Rural	Urban (USA)
As	0.007 to 1.9	1.0 to 28	2 to 2320
Cd	0.003 to 1.1	0.4 to 1000	0.2 to 7000
Ni	0.01 to 60	0.6 to 78	1 to 328
Pb	0.007 to 64	2 to 1700	30 to 96270
V	0.001 to 14	2.7 to 97	0.4 to 1460
Zn	0.03 to 460	11 to 403	15 to 8328
Co	0.001 to 0.9	0.08 to 10.1	0.2 to 83
Cr	0.005 to 11.2	1.1 to 44	2.2 to 124
Cu	0.029 to 12	3 to 280	3 to 5140
Fe	0.62 to 4160	55 to 14530	130 to 13800
Hg	0.005 to 1.3	0.05 to 160	0.58 to 458
Mn	0.01 to 16.7	3.7 to 99	4 to 488
Se	0.0056 to 0.19	0.01 to 3.0	0.2 to 30
Sb	0.0008 to 1.19	0.6 to 7	0.5 to 171

Source: Schroeder et al., 1987.

concentration ranges of various metals found in remote, rural, and U.S. urban areas as common specific airborne PM constituents.

Chapter 6 also includes a section on acid aerosols. Acid aerosols are secondary pollutants formed primarily through oxidation of sulfur dioxide (SO<sub>2</sub>), a gas emitted by the combustion of fossil fuels. Oxidation of SO<sub>2</sub> forms sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), the major component of acid aerosols. Sulfuric acid is formed to a lesser extent through the oxidation of sulfur species (H<sub>2</sub>S and CH<sub>3</sub>SCH<sub>3</sub>) from natural sources. H<sup>+</sup> is found in the fine particle size fraction i.e., particles with aerodynamic diameter (D<sub>p</sub>) < 1.0 μm. Although recent research has shown a typically high correlation between SO<sub>4</sub><sup>=</sup> and acidity, data from summertime sampling have shown that SO<sub>4</sub><sup>=</sup> is not always a reliable predictor of H<sup>+</sup> for individual events at a given site.

A major determinant of the lifetime of H<sup>+</sup> in the atmosphere is the rate of neutralization by ammonia (NH<sub>3</sub>). Ammonia reacts with H<sub>2</sub>SO<sub>4</sub> to form ammonium sulfate [(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>] and ammonium bisulfate (NH<sub>4</sub>HSO<sub>4</sub>). The major sources of ammonia in the

environment are animals and humans. In North America, ambient concentrations of  $H^+$  tend to be regional in nature with the highest concentrations found in the northeastern United States and southwestern Canada. Recent research has shown that regional transport is important to acid sulfate concentrations, as elevated levels of ambient  $H^+$  were measured simultaneously during a regional episode at multiple sites located from Tennessee to Connecticut.

Recent work has suggested that ultrafine particles may be responsible for some of the health effects associated with exposure to particulate matter, leading to an interest in the number concentration of ambient particles. A Chapter 6 section examines data on particle number concentration and the relationship between particle number and particle mass or volume. In some situations the ultrafine mode can be the dominant size range for selected components of atmospheric aerosol particles. One example is the case of metallic aerosols for which fine particles ( $D_p < 2.5\mu m$ ) concentrations can be dominated by the ultrafine mode despite the strength of the processes that tend to remove particles from this mode. While there is consensus that ultrafine metals are abundantly produced and emitted into the atmosphere, there are not much data on ambient concentrations of ultrafine metals. The few direct measurements available can be extended with some confidence using indirect methods; i.e., from particle counting techniques that have size information but no chemical information, or from filter collection methods that have limited size information but detailed compositional information.

## **1.7 EXPOSURE: AMBIENT AND INDOOR**

Chapter seven focuses on studies which include information on measurement of simultaneous personal PM exposures, indoor-residential PM concentrations, and ambient PM concentrations. The literature on concentrations of PM in indoor settings are also presented.

For any air pollutant, the total exposure of an individual consists of a variety of sequential exposures to a variety of microenvironments. They are typically, outdoor, indoors at-home, at-work, in-traffic, and many other indoor microenvironments. The principle of superposition is a useful mechanism to visualize the summation process. For any identified air pollutant, the ambient environment is one source of indoor pollution due to air exchange

1 and infiltration. Whether the ambient is a significant or dominant source of indoor pollution  
2 depends on the relative strength of indoor sources and sinks.

3 Particulate matter studies have detected a "personal cloud" related to the activities of an  
4 individual which may generate significant levels of airborne PM in his/her vicinity which  
5 may not be picked up by an indoor PM monitor at a distance. Other studies have identified  
6 significant sources in the home, e.g. cooking and smoking.

7 In PM of size fractions that include coarse particles, some studies have identified  
8 statistically significant relationships between personal exposures and particle concentrations  
9 from fixed-site ambient or indoor monitors, and other studies have not, probably due to  
10 overwhelming effects of indoor sources, "personal clouds" and other individual activities.  
11 For PM of a fine size fraction - such as sulfates, there seems to be more of a relationship  
12 between ambient concentration and personal exposure, than for coarser PM, perhaps because  
13 of the ability of fine PM to penetrate into indoor settings.

14 For a study population in which there is a detectable correlation between personal  
15 exposures and ambient concentrations, the ambient concentration can predict the mean  
16 personal exposure with much less uncertainty than it can predict the personal exposure of any  
17 given individual in the population.

18 The three largest studies of indoor air particles in the U.S. have all found that the  
19 single largest indoor source of fine ( $PM_{3.5}$  or  $PM_{2.5}$ ) particles is cigarette smoke. The  
20 estimate of the impact of smoking on a home PM levels ranges from about 30 to 45  $\mu g/m^3$ ,  
21 and of a single cigarette from 1 to 2  $\mu g/m^3$  for a 24-h period. Homes without smoking have  
22 indoor particle concentrations (both  $PM_{10}$  and  $PM_{2.5}$ ) that are sometimes below and  
23 sometimes above the outdoor levels. At low outdoor levels (as in most of the cities in the 6-  
24 City and New York State studies) indoor concentrations are generally higher—at high  
25 outdoor levels, they are slightly lower. Indoor concentrations are considerably higher during  
26 the day, when people are active, than at night.

27 The second largest source of indoor particles, as determined by the PTEAM Study, is  
28 cooking. Estimates of the effect of cooking ranged from about 10 to 20  $\mu g/m^3$ . A few small  
29 studies confirm the effect of cooking on indoor particle levels, both  $PM_{10}$  and  $PM_{2.5}$ . The  
30 two other large-scale studies did not directly test for the effect of cooking, although the



1 residual indoor concentrations in multivariate calculations led the authors to suggest that  
2 cooking could have contributed to the residual.

3 Kerosene heater use was determined to contribute about  $15 \mu\text{g}/\text{m}^3$  to indoor  
4 concentrations in one county but not the other in the New York State study. Also, a later  
5 effort using mass-balance calculations was unsuccessful in determining a contribution to  
6 particle mass from kerosene heater use in either county, although a somewhat smaller set of  
7 homes may have been responsible for this result. Gas stoves, wood stoves, and fireplaces  
8 were found to have no noticeable impact on total concentrations of particles, although many  
9 studies show an increase in PAH concentrations and some show an increase in mutagenicity  
10 of indoor air due to these combustion sources.

11 Vacuuming, dusting, and sweeping were found to contribute slightly but with doubtful  
12 significance to indoor levels in the PTEAM Study. House volume had a significant but small  
13 effect on particle concentrations, with values of  $-1$  to  $-2 \mu\text{g}/\text{m}^3$  per 1,000 cubic feet. Air  
14 exchange rates were also significant at times, but with different impacts depending on the  
15 relative indoor and outdoor concentrations—at high outdoor concentrations, increased air  
16 exchange resulted in increases in the indoor air particle levels.

17 Unknown indoor sources were found to account for a substantial fraction (25%) of  
18 indoor concentrations (both  $\text{PM}_{2.5}$  and  $\text{PM}_{10}$ ) in the PTEAM study. This suggests a need for  
19 further research to determine the source or sources of these particles.

20 Decay rates for fine ( $\text{PM}_{2.5}$ ) particles were determined to be about  $0.4 \text{ h}^{-1}$  compared to  
21  $1 \text{ h}^{-1}$  for coarse particles, with an intermediate estimate of  $0.65 \text{ h}^{-1}$  for  $\text{PM}_{10}$ . For a home  
22 with no indoor sources and a typical air exchange rate of about 0.75, this would imply that  
23 fine particles indoors would be about  $0.75/(0.4+0.75) = 65\%$  of the outdoor value at  
24 equilibrium, indoor  $\text{PM}_{10}$  would be about 54% of outdoor levels, and indoor coarse particles  
25 would be about 43% of outdoor levels. Since few homes were observed to have  
26 concentrations this low, it can be inferred that few homes are free of important indoor  
27 sources of particles.

28 Studies in buildings also indicated that smoking was the major indoor source of  
29 particles, with a geometric mean of 44 versus  $15 \mu\text{g}/\text{m}^3$  (arithmetic mean of 70 versus  
30  $18 \mu\text{g}/\text{m}^3$ ) observed for smoking versus nonsmoking areas in 38 Pacific Northwest buildings.

1 This difference of 29 to 52  $\mu\text{g}/\text{m}^3$  is similar to the difference of 30 to 45  $\mu\text{g}/\text{m}^3$  estimated  
2 from the three major studies of U.S. homes.

3 Indoor air quality models have been employed with increasing success to estimate  
4 source emission rates and particle decay rates. Cigarettes smoked in homes with normal  
5 activities emit about 14 mg/cigarette, a result that agrees well with various chamber studies  
6 with smokers or smoking machines. Cooking was estimated to emit 4 mg/min, a result that  
7 needs confirmation. Elemental emission profiles have been determined for both smoking and  
8 cooking, with potassium and chloride being major markers for smoking, and iron and  
9 calcium for cooking. Particle decay rates have been estimated for homes to range between  
10 0.4 and 1.0  $\text{h}^{-1}$ . Studies in telephone equipment buildings and museums have established  
11 particle deposition velocities for sulfates and other ions, although differences in the estimates  
12 suggest that further research is needed.

## 15 1.8 EFFECTS ON VISIBILITY AND CLIMATE

16 Chapter eight discusses factors affecting visibility, ways to measure it, historical trends,  
17 and methods to determine its value. Particulate matter effects on climate are also discussed.  
18 Much of the information contained in the section on visibility is a summary of information  
19 from the previous 1982 Criteria Document for Particulate Matter and Sulfur Oxides.

20 Traditionally, visibility has been defined in terms of the distance from an object that is  
21 necessary to produce a minimum detectable contrast between that object and its background.  
22 Although visibility is often defined by this "visual range," it includes not only being able to  
23 see or not see a target, but also seeing targets at shorter distances and appreciating the details  
24 of the target, including its colors. Visibility impairment can manifest itself in two ways: (1)  
25 as a layer of haze (or a plume), which is visible because it has a visual discontinuity between  
26 itself and its background, or (2) as a uniform haze which reduces atmospheric clarity. The  
27 type and degree of impairment are determined by the distribution, concentrations, and  
28 characteristics of atmospheric particles and gases, which scatter and absorb light traveling  
29 through the atmosphere. Scattering and absorption determine light extinction.

30 On a regional scale, the extinction of light is generally dominated by particle scattering.  
31 In urban areas, absorption by particles becomes important and occasionally dominant.

1 Extinction by particles is usually dominated by particles of diameter 0.1 to 2  $\mu\text{m}$  (fine par-  
2 ticles). In general, scattering by particles accounts for 50 to 95% of extinction, depending  
3 on location, with urban sites in the 50 to 80% range and nonurban sites in the 80 to 95%  
4 range.

5 Available visibility monitoring methods measure different aspects of visibility  
6 impairment. Generally, contrast-type measurements (such as photography, telephotometry,  
7 and human eye observations) relate well to the perception of visual air quality, while  
8 extinction or scattering measurements (such as transmissometry and nephelometry) relate to  
9 the cause of visibility degradation. The above measurement methods can be used to approx-  
10 imate visual range.

11 Current knowledge indicates that fine particulate matter is composed of varying  
12 amounts of sulfate, ammonium, and nitrate ions, elemental carbon, organic carbon  
13 compounds, water, and smaller amounts of soil dust, lead compounds, and trace species.  
14 Sulfate often dominates the fine mass and light scattering, while elemental carbon is the  
15 primary light-absorbing species. Ammonium ion typically accounts for 5 to 15% of the fine  
16 mass and often correlates well with sulfate levels. Mean nitrate concentrations can represent  
17 up to 37% of the total fine particle mass in urban cities.

18 Visibility has value to individual economic agents primarily through its impact upon  
19 activities of consumers and producers. Most economic studies of the effects of air pollution  
20 on visibility have focused on the aesthetic effects which are believed to be the most  
21 significant economic impacts of visibility degradation caused by air pollution in the U.S. It  
22 is well established that people notice changes in visibility and that visibility conditions affect  
23 the well-being of individuals.

24 Particulate matter of submicron size in the earth's atmosphere perturbs the radiation  
25 field. There is no doubt that anthropogenic aerosols have the potential to affect climate; the  
26 question is by how much. There are two chief avenues through which aerosols impact the  
27 radiation budget of the earth. The direct effect is that of enhanced reflection of solar  
28 radiation by particles in a cloud-free atmosphere. Since aerosols, even those containing some  
29 absorptive component, are primarily reflective, their impact is felt as a negative radiative  
30 forcing (i.e., a cooling) on the climate system. Although there is some uncertainty in the  
31 global distribution of such aerosols and in the chemical and radiative properties of the

aerosols, the radiative effects can still be modeled within certain bounds. Estimates of this forcing range from  $-0.3 \text{ W m}^{-2}$  to about twice that value for current conditions over pre-industrial times.

The indirect forcing results from the way in which aerosols, in their role as cloud condensation nuclei (CCN), affect cloud microphysical properties. The most important is the effective radius of cloud droplets, which decrease as CCN concentrations increase. This effect is most pronounced when the concentration,  $N$ , is very low, and clouds are moderately reflective. Other effects are the enhancement of cloud lifetimes and also changes in the nucleating ability of CCN through chemical changes. Although estimates of the indirect effect are uncertain by at least a factor of 2, it appears to be potentially as important as the direct effect. On a global mean basis, anthropogenic emissions of anthropogenic aerosols could have offset substantially the positive radiative forcing due to greenhouse gas emissions.

The one crucial difference between aerosol forcing and greenhouse (gas) forcing is the atmospheric lifetime of aerosols and gases and hence, forcing. The aerosol forcing is fairly regional, whereas the greenhouse forcing is global. One should, therefore, expect inter-hemispheric differences in the forcing and perhaps climate response. However, climate models are not currently at the level of sophistication needed to determine climate response unambiguously. Global observations of surface temperature cannot separate natural and anthropogenic causal mechanisms, with few exceptions.

## 1.9 EFFECTS ON MATERIALS

Chapter nine briefly discusses the effects of particulate matter exposure on the aesthetic appeal and physical damage to different types of building materials and economic consequences, including background information on the physics and chemistry of atmospheric corrosion. Where possible, the chapter discusses only those effects associated with particle exposure; however, most of the data are on the effects of particles in combination with  $\text{SO}_2$ .

A significant detrimental effect of particulate matter pollution is the soiling of painted surfaces and other building materials. Soiling is defined as a degradation mechanism that can be remedied by cleaning or washing, and depending on the soiled surface, repainting. Available data on pollution exposure indicates that particulate matter can result in increased

1 cleaning frequency of the exposed surface, and may reduce the life usefulness of the material  
2 soiled. Data on the effects of particulate matter on other surfaces are even less well  
3 understood. Some evidence also shows damage to fabrics, electronics, and works of art  
4 composed of one or more materials, but this evidence is largely qualitative and sketchy.

5 The damaging and soiling of materials by airborne pollutants have an economic impact,  
6 but this impact is difficult to measure. The accuracy of economic damage functions is  
7 limited by several factors. One of the problems has been to separate costs related to  
8 particulate matter-related materials from other pollutants, as well as from those related to  
9 normal maintenance. Cost studies typically involve broad assumptions about the kinds of  
10 materials that are exposed in a given area and then require complex statistical analysis to  
11 account for a selected number of variables. Attitudes regarding maintenance may vary  
12 culturally, further confounding the problem of quantifying economic impact.

13 The nature and extent of damage to materials by particulate matter have been  
14 investigated by field and laboratory studies. Both physical and economic damage functions  
15 have been developed for specific damage/effect parameters associated with exposure to  
16 particulate matter. To date, only a few of these functions are relatively reliable in  
17 determining damage, while none has been generally accepted for estimating costs.

18 In recent years, fairly reliable damage functions for soiling of exterior wall paints have  
19 been developed. The available damage functions are few in number but represent a major  
20 fraction of the total surface that is exposed and sensitive to pollution damage.

21 Although there still remains a lack of sensitive materials distribution data, the  
22 geographic resolution of available data is about as good as that of environmental monitoring  
23 data. These limitations may hinder accurate estimates of total material damage and soiling,  
24 but they do not prevent estimates within ranges of error. Studies have used various  
25 approaches to determine pollutant-related costs for extra cleaning, early replacement, more  
26 frequent painting, and protective coating of susceptible materials, as well as other indicators  
27 of the adverse economic effects of pollutants. No study has produced completely satisfactory  
28 results, and estimates of cost vary widely.

## 1.10 DOSIMETRY MODELING OF INHALED PARTICLES IN THE RESPIRATORY TRACT

Particles are deposited in the respiratory tract by mechanisms of impaction, sedimentation, interception, diffusion, and electrostatic precipitation. Ventilation rates differ for various activity patterns in humans, for different ages, and among species. These ventilation differences coupled with differences in upper respiratory tract structure and in size, branching pattern, and structure of the lower respiratory tract among species and healthy versus diseased states result in significantly different patterns of airflow that in turn affect particle deposition in the respiratory tract regions. For a given aerosol, the two most important parameters determining deposition are the mean aerodynamic diameter and the distribution of particles about that mean. Subsequent clearance of a deposited dose is dependent on the initial site of deposition, physicochemical properties of the particles (e.g., dissolution half-time), and on time since deposition.

An accurate description of the exposure-dose-response relationship for the observed health effects of PM should account, to the extent possible, for these mechanistic determinants of particle disposition. Deposited dose may be an appropriate metric for "acute" effects (e.g., mortality), especially if the particles exert their primary action on the surface contacted. An alternative to consider is dose rate ( $\mu\text{g}/\text{min}$ ) per unit surface area because insoluble particles deposit and clear along the surface of the respiratory tract. "Chronic" effects (e.g., certain types of morbidity) may be better described by retained dose estimates because clearance is affected by the time since deposition and the aerosol solubility, characterized by dissolution-absorption half-times.

The human model chosen to make deposited and retained dose predictions is a semi-empirical compartmental model that is able to describe particle deposition and clearance by three routes (absorption into blood, transport to gastrointestinal tract, and transport to lymphatics). Two different models were used to model particle deposition and clearance in laboratory animals.

The predictions of deposited and retained doses show anticipated differences due to the influence of aerosol particle diameter and distribution, minute ventilation, and species-specific morphometry. For example, mouth breathing alters the deposition fraction of ambient aerosols in the tracheobronchial and alveolar regions when compared to nasal

breathing. The differences shown in these predictions for deposition point to the importance of characterizing the differences between genders and the impact of age on deposition. The chosen model has predicted differences between children of 1 year and adults across particle diameters ranging from the diffusion to aerodynamic range of approximately 2.5-fold in the tracheobronchial region and 2-fold in the alveolar region. The direction and magnitude are a function of aerosol particle diameter and distribution. Differences in ventilation and morphometry for diseased states can also be anticipated and recent studies and other model predictions show an increased deposition in subjects with chronic obstructive pulmonary disease.

The various species used in inhalation toxicology studies that serve as the basis for exposure-dose-response assessment do not receive identical doses in a comparable respiratory tract region when exposed to the same aerosol. Such interspecies differences are important because the toxic effect is likely more related to the quantitative pattern of deposition within the respiratory tract than to the exposure concentration; this pattern determines not only the initial respiratory tract tissue dose but also the specific pathways by which the inhaled material is cleared and redistributed. Thus, accounting for differences in dosimetry can change the apparent effect levels among species. To illustrate, for the same aerosol of 0.5  $\mu\text{m}$  MMAD and  $\sigma_g$  of 1.3, using deposition normalized to surface area for an effect in the tracheobronchial region, an exposure concentration of 100  $\mu\text{g}/\text{m}^3$  to rats and guinea pigs would predict a human equivalent exposure concentration of 939 and 79  $\mu\text{g}/\text{m}^3$ , respectively, assuming species sensitivity to the deposited tracheobronchial dose were equal. However, for chronic exposures to the same aerosol, retained alveolar dose ( $\mu\text{g}/\text{g}$  lung tissue) may be more appropriate as a dose metric. Assuming it is a relatively insoluble aerosol (i.e., assuming a dissolution-absorption half-time of 1,000 days), a human equivalent exposure concentration would be predicted to be 22 and 784  $\mu\text{g}/\text{m}^3$  based on the rat versus guinea pig, respectively.

These examples show that relevance of a particular animal model should be considered together with dosimetry and the appropriateness of the metric for a given health endpoint. In general, the objective should be to provide a metric that is mechanistically motivated by the observed health effect of interest for extrapolation.

Dosimetry modeling at the moment can address important mechanistic factors of particle deposition and clearance including the aerosol particle diameter and distribution, intra and interspecies differences in deposition as a function of ventilation and morphometry, and intra and interspecies differences in clearance rates. Use of dosimetry modeling and judicious choice of appropriate dose metrics should be used to interpret the observed health effects data related to PM<sub>10</sub> exposures.

Further, these predictions were based on the use of mass as the exposure metric. Recent data suggest that particle number, or possibly particle surface area, may be a more appropriate exposure metric because the fine mode aerosols are small in mass but have extremely high concentrations of particle numbers. Also, normalizing factors such as number of alveoli or number of macrophages may be more appropriate for certain pathogenesis mechanisms. Creating these dose metrics for various species will depend on the availability of morphometric information.

## **1.11 TOXICOLOGY OF PARTICULATE MATTER CONSTITUENTS**

Chapter eleven reviews results on exposure to specific PM constituents, based on controlled human clinical studies, selected occupational studies, and animal toxicology studies. It focuses on those studies published since the 1982 PM Criteria Document and includes coverage of specific PM species selected for discussion based on their being commonly present in ambient aerosols at concentrations  $\geq 1 \text{ ng/m}^3$ .

Particulate matter is a broad term that encompasses thousands of chemical species, many of which have not been investigated in controlled animal or human studies. However, even a full discussion of all the types of particles that have been studied is well beyond the scope of the chapter. Most of the animal toxicological and occupational epidemiological studies summarized used very high particulate concentrations, relative to ambient, even when animal-to-human dosimetric differences are considered. In spite of these difficulties, the array of animal studies does illustrate certain toxicological principles for particles. To identify but a few here, the data base clearly shows that the site of respiratory tract deposition (and hence particle size) clearly influences the health outcome and that toxicity is dependent on the chemical species.



## Effects of Controlled Exposure to Acid Aerosols

The effects of acid aerosols are primarily related to strong acidity (i.e.,  $H^+$  content). That is,  $H_2SO_4$  is more potent than  $NH_4HSO_4$  which is more potent than  $NH_4(H)_2SO_4$ . The size of acid aerosols also affects their potency, but the exact relationships are dependent upon the endpoint being examined.

Sulfuric acid affects pulmonary function. Healthy subjects are only affected by very high levels of acute exposure (around  $2,000 \mu g/m^3$ ), even if they exercise and gargle with acidic material to reduce neutralization by oral ammonia. Asthmatics, especially adolescent asthmatics, appear to be more sensitive. For example, a few, but not all studies, found that an acute exposure to around  $70 \mu g/m^3$  caused small decrements in the pulmonary function of adolescent asthmatics.

Sulfuric acid affects mucociliary clearance in humans and animals. The direction (i.e., increase or decrease) and the magnitude of the effect is dependent on the concentration and duration of exposure, as well as the specific region of the lung being measured. Humans exposed to levels of  $H_2SO_4$  as low as  $100 \mu g/m^3$  (1h) experienced a decrease in mucociliary clearance. Animal studies have shown that  $H_2SO_4$  can also affect alveolar clearance.

Chronic exposure to  $H_2SO_4$  causes a variety of structural changes in the lung. For example, mucus-secreting cells are affected and can be found in deeper regions of the lung than usual. Pulmonary function is also altered.

Several studies have sought to define interactions of acids with other pollutants, especially ozone. Work with animals has demonstrated additivity, synergism, and antagonism, depending upon the species, exposure, and endpoint. More recent human clinical studies found that acute exposure to  $100 \mu g/m^3$   $H_2SO_4$  may potentiate the response to ozone on pulmonary function.

## Complex Mixtures

The 1982 Air Quality Criteria Document for Particulate Matter and Sulfur Dioxide concluded from its review of studies on the genotoxicity and carcinogenicity of atmospheric particles that "all the major types of airborne particulate matter may contain adsorbed compounds that are mutagenic and/or carcinogenic to animals and may contribute in some degree to the human cancer associated with exposure to urban air pollution." Recent

1 research activity has added data that support this conclusion, but do not warrant that it be  
2 changed significantly.

3 The direct relevance of the evidence for the mutagenicity and tumorigenicity of extracts  
4 of particulate matter in experimental systems to exposure scenarios experienced by humans is  
5 uncertain at this time. Recent analytical epidemiological studies, that adjusted for tobacco  
6 smoking and other major potential risk factors, have found a weak to non-existent association  
7 between human lung cancer and indices of exposure to air pollution including particulate  
8 matter. Most investigators believe that the epidemiological evidence obtained thus far does  
9 not substantiate causality, although the hypothesis remains credible.

## 11 Diesel Emissions

12 Acute toxic effects caused by exposure to diesel exhaust are mainly attributable to the  
13 gaseous components (i.e., mortality from carbon monoxide intoxication and lung injury from  
14 respiratory irritants). When the exhaust is diluted to limit the concentrations of these gases,  
15 acute effects are not seen.

16 Ten different long-term (> 1 year) animal inhalation studies of diesel engine emissions  
17 have been conducted. The focus of these studies has been on respiratory tract effects in the  
18 alveolar region. Effects in the upper respiratory tract and in other organs were not found  
19 consistently in chronic animal exposures. The pathogenic sequence following the inhalation  
20 of diesel exhaust as determined histopathologically and biochemically begins with the  
21 phagocytosis of diesel particles by alveolar macrophages (AMs). These activated  
22 macrophages release chemotactic factors that attract neutrophils and additional AMs. As the  
23 lung burden of diesel particles increases, there is an aggregation of particle-laden AMs in  
24 alveoli adjacent to terminal bronchioles, increases in the number of Type 2 cells lining  
25 particle-laden alveoli, and the presence of particles within alveolar and peribronchial  
26 interstitial tissues and associated lymph nodes. The PMNs and macrophages release  
27 mediators of inflammation and oxygen radicals and particle-laden AMs are functionally  
28 altered resulting in decreased viability and impaired phagocytosis and clearance of particles.  
29 There is a substantial body of evidence for an impairment of particulate clearance from the  
30 bronchio-alveolar region of rats following exposure to diesel exhaust. The latter series of

1 events may result in the presence of pulmonary inflammatory, fibrotic, or emphysematous  
2 lesions.

3 The noncancer toxicity of diesel emissions is considered to be due to the particle rather  
4 than the gas phase, since the long-term effects seen with whole diesel are not found or are  
5 found to a much lesser extent in animals exposed to similar dilutions of diesel exhaust  
6 filtered to remove most of the particles. Chronic studies in rodents have demonstrated  
7 pulmonary effects at 200 to 700  $\mu\text{g}/\text{m}^3$ . No-effect levels have been reported ranging from 60  
8 to 260  $\mu\text{g}/\text{m}^3$ .

9 Several epidemiologic studies have evaluated the effects of chronic exposure to diesel  
10 exhaust on occupationally exposed workers. None of these studies are useful for a  
11 quantitative evaluation of noncancer toxicity because of inadequate exposure characterization,  
12 either because exposures were not well defined or because the possible confounding effects of  
13 concurrent exposures could not be evaluated.

14 The U.S. Environmental Protection Agency has developed a draft qualitative and  
15 quantitative cancer assessment for diesel emissions. The summary to follow was drawn from  
16 that document. This draft is currently undergoing external review by the public and the  
17 Clean Air Scientific Advisory Committee. As a result of limited evidence from  
18 epidemiological data, supported by adequate evidence for carcinogenicity of diesel engine  
19 emissions in animal studies, as well as positive evidence for mutagenicity, it was concluded  
20 that diesel engine emissions best fit into cancer weight-of-evidence Category B1. Diesel  
21 engine emissions are thus considered to be probable human carcinogens. This is in  
22 agreement with a 2A classification by the International Agency for Research on Cancer.

23 Using a dosimetry model that accounted for animal-to-human differences in lung  
24 deposition efficiency, lung particle clearance rates, lung surface area, ventilation, metabolic  
25 rate, as well as elution rates of organic chemicals from the particle surface, equivalent human  
26 doses were calculated on the basis of particle concentration per unit lung surface area.  
27 Following dosimetric adjustment, risk estimates were derived using a linearized multistage  
28 model. A unit risk estimate of  $3.4 \times 10^{-5}$  (the upper 95% bound of the cancer risk from  
29 lifetime exposure to 1  $\mu\text{g}/\text{m}^3$  diesel particulate matter) is recommended. This estimate is  
30 based on the geometric mean of estimates derived from three separate animal bioassays using  
31 Fischer 344 rats.

## Metals

A summary of the health effects of airborne metals follows. The descriptions are qualitative in nature. Most of the literature on these compounds deals with high concentration animal toxicological studies or occupational epidemiological studies.

The primary target for inhaled aluminum compounds is the respiratory tract. Commonly reported symptoms include asthma, cough, and decreased pulmonary function; fibrosis has also been reported. Laboratory animal studies support findings from human studies that aluminum acts via an irritant, rather than by an allergic, mechanism.

The respiratory tract is the primary target organ for antimony (trioxide) following inhalation exposure. Respiratory effects have been reported in workers chronically exposed to mg levels of antimony dust. Other reported effects include altered ECGs, gastrointestinal symptoms, ocular and dermal effects, and reproductive effects.

The toxicity data on inhalation exposures to arsenic are limited. Long-term occupational exposure leads to lung cancer and causes skin changes and peripheral nerve damage in workers. Respiratory tract tumors occurred in hamsters exposed to intratracheal doses of arsenic combined with a carrier dust.

Data on barium are extremely limited, with no epidemiological data available and no standard inhalation toxicity studies in animals. Occupational case studies, supported by histopathological studies in rats, indicate that the respiratory tract is a target for barium compounds.

The kidney and the respiratory tract are the primary target organs for cadmium by inhalation exposure in the human; toxicity is dependent on cumulative exposure, with renal tubular dysfunction and associated increased excretion in urine of proteins, amino acids, and essential metals being key outcomes of long-term exposures. Acute high-level exposure in humans causes intense respiratory tract irritation, and milder effects on pulmonary function follow chronic low-level exposure. Rat studies show that cadmium can cause lung cancer; there is evidence that lung cancer has been observed in humans following high occupational exposure.

The respiratory tract is the primary target for inhaled chromium compounds. Human and animal data agree on the nature of nasal effects. Laboratory animal studies have reported lung lesions and evidence of inflammation. Human and animal data agree that

1 Cr(VI) compounds cause lung cancer. Human studies have also reported early signs of renal  
2 damage with exposure to Cr(VI) compounds.

3 The respiratory tract is the major target for inhaled cobalt compounds. In humans, two  
4 major types of effects are observed, interstitial lung disease and asthma. Inflammation and  
5 decreased lung function have been observed in laboratory animals.

6 Limited data support the respiratory system as a major target for inhaled copper and  
7 copper compounds. In humans the data are limited to subjective reporting of respiratory  
8 symptoms and radiographic evidence of pulmonary effects after acute and chronic inhalation.

9 The respiratory tract is the primary target for iron oxides by inhalation exposure. In  
10 humans, respiratory effects have been reported in workers chronically exposed to iron dust.  
11 In laboratory animals, hyperplasia and alveolar fibrosis have been reported after inhalation or  
12 intratracheal administration of iron oxide.

13 The nervous system is the most sensitive target for elemental mercury following acute  
14 or chronic inhalation exposures. Effects range from reversible neurological symptoms to  
15 psychomotor and neurobehavioral changes and peripheral nerve dysfunction. Respiratory,  
16 gastrointestinal, and cardiovascular symptoms have also been reported in case reports and  
17 occupational studies with exposure to high concentrations of mercury. The kidney is a  
18 sensitive target toxicity following elemental mercury exposure in humans.

19 The nervous system and the respiratory tract are primary targets for inhaled manganese.  
20 Acute occupational exposures are associated with pneumonitis, while chronic exposures  
21 mainly impact the central nervous system. Limited information suggests that prenatal and/or  
22 postnatal exposure of laboratory rodents to inhaled manganese oxide may depress  
23 neurobehavioral activity.

24 Limited data on the inhalation of magnesium and its compounds support the respiratory  
25 tract as a target. Acute high-level exposure of humans or laboratory animals to magnesium  
26 oxide fume results in a reaction similar to zinc oxide metal fume fever. Suggestive evidence  
27 indicates chronic exposure to magnesium dusts may produce pneumoconiosis. In laboratory  
28 animals, fibrosis is observed with chronic exposure to high levels of magnesium dusts.

29 The respiratory tract appears to be the main target in humans and animals after  
30 inhalation exposure to molybdenum compounds; however, inhalation exposure to  
31 molybdenum has also been associated with nonspecific effects in humans including general

1 weakness and dizziness. Animal inhalation studies indicate that toxicity varies with the  
2 molybdenum compound.

3 The respiratory tract is the primary target for nickel compounds following inhalation  
4 exposure. In humans, respiratory effects include asthma and altered pulmonary function. In  
5 laboratory animals, inflammatory responses suggest an immunological response in the lungs.  
6 Immunological changes have been reported in refinery workers exposed to nickel. The  
7 potential for lung and nasal cancer was evident in occupational and laboratory animal studies.

8 When ingested in relatively low concentrations, potassium is an essential metal, but  
9 available data on inhaled potassium compounds are insufficient to assess toxicity. Similarly,  
10 with inhalation exposure, the respiratory tract is the target for selenium, another essential  
11 metal. In humans, respiratory effects have been reported in workers chronically exposed to  
12 selenium; and similar effects have been reported in laboratory animal studies.

13 Inorganic tin is relatively inert toxicologically, and effects are limited to mild  
14 respiratory effects, along with the formation of radio-opaque nodules in the lungs. No other  
15 target systems for inhalation exposure to inorganic tin have been reported. Limited data  
16 indicate the nervous, hepatic, renal, and respiratory systems are targets for inhalation  
17 exposure to organotin compounds. The respiratory tract is the primary target for titanium  
18 following inhalation exposure. No histopathology of other organs was found in rats  
19 chronically exposed to titanium tetrachloride at up to 6,000  $\mu\text{gTi}/\text{m}^3$ . Titanium is not  
20 translocated in the body, even with chronic exposure and high concentrations. Titanium  
21 dioxide inhalation results in pneumoconiosis in humans and signs of inflammation in  
22 laboratory animals.

23 The respiratory tract is the primary target for inhaled vanadium compounds. Vanadium  
24 damages alveolar macrophages, and toxicity is related to compound solubility and valence.  
25 Human occupational case studies and epidemiological studies indicate symptoms of  
26 respiratory distress. Symptoms of systemic effects have been observed following chronic  
27 occupational exposure and in laboratory animal studies.

28 Following inhalation exposure, the respiratory tract is the primary target for zinc,  
29 another essential metal. In humans, metal fume fever, characterized by respiratory  
30 symptoms and pulmonary dysfunction, was observed in workers and experimental subjects

during acute exposures to high levels of zinc oxide. Zinc can produce inflammatory responses in both human and animal species.

## **Silica**

Silica can occur in two chemical forms, amorphous and crystalline. Crystalline forms include quartz, which is the most prevalent; cristobalite; tridymite; and a few other rare forms. Freshly fractured crystalline silica is more toxicologically reactive than aged forms of crystalline silica or forms that may be coated with other chemical compounds. Amorphous silica is less well studied and may have similar toxic endpoints but is less potent than crystalline silica. With sufficient exposure, crystalline silica is toxic to the respiratory system. Acute high exposure in both humans and animals causes lung inflammation and, if the exposure is high enough, rapid onset of a fibrotic lung disease (acute silicosis) which can be fatal. Occupational studies show that chronic exposure to crystalline silica causes inflammation of the lung which is followed by fibrosis and a human fibrotic disease called silicosis which can lead to early mortality. Silicotic individuals are also at higher risk for other diseases, e.g., tuberculosis. Some occupational studies also show a concurrent incidence of lung cancer.

The role, if any, of silica-induced lung inflammation, fibrosis, and silicosis in the development of lung cancer is hypothesized but not adequately demonstrated. Crystalline silica interaction with DNA has been shown. Chronic exposure animal studies in rats also show a similar pattern of lung inflammation, fibrosis, and lung cancer. In 1987, the International Agency for Research on Cancer classified crystalline silica as a "possible" human carcinogen owing to a sufficient level of evidence in animal studies but inadequate evidence in human studies. The evidence for amorphous silica carcinogenicity was said to be inadequate for both humans and animals, placing it in Group 3 (agent not classifiable). While active surveillance of the U.S. population for fibrosis and silicosis is not standard practice, U.S. health statistics do not reveal a general population increase of crystalline silica diseases. However, there is an increase in these diseases among the occupational work force.

An assessment of the occupational risk of silicosis was made using recent studies from South Africa and Canada, both of which examined medical histories of over 2000 miners.

Both predicted zero risk for cumulative silica exposures of  $0.6 \text{ mg/m}^3 \bullet \text{ years}$  (equivalent to a 20-year workplace exposure to an average concentration of  $30 \text{ } \mu\text{g/m}^3$ ). At higher exposures, excess risk was observed in these workers (e.g., 2% risk at  $1.6 \text{ mg/m}^3 \bullet \text{ years}$ ). These effective occupational exposures are greater and the particle sizes smaller than those likely to be experienced by the public; however, the public would be expected to include susceptible subpopulations. Information gaps still exist for both the exposure-response relationship (especially in potentially susceptible subgroups) for levels of exposure within the general population.

## **Asbestos**

The mechanisms underlying the development of asbestos-induced pulmonary fibrosis in rats is complex. While the acute response to asbestos results in pulmonary inflammation and cell proliferation, the pattern of fibrosis following chronic exposures becomes more complex. It is likely that the retention of inhaled fibers and consequent accumulation of interstitial fibers concomitant with prolonged inflammation will contribute to the development of a diffuse and progressive pattern of pulmonary fibrosis. The pathogenesis of asbestos-related lung tumors clearly is a complex process and requires further investigation.

## **Ultrafine Particles**

Certain freshly-generated ultrafine particles when inhaled as singlets at very low mass concentrations ( $10 \text{ to } 50 \text{ } \mu\text{g/m}^3$ ) can be highly toxic to the lung. Mechanisms responsible for this high toxicity could include (1) high pulmonary deposition efficiencies of these particles (2) the large numbers per unit mass of these particles, (3) their increased surface area available for reaction, and (4) the presence of radicals on the particle surface, depending on the process of generation of the particles. Results of studies with ultrafine model particles indicate that particle number may be of more import as a dose parameter, than just particle mass.



## **1.12 EPIDEMIOLOGY STUDIES OF HEALTH EFFECTS ASSOCIATED WITH EXPOSURE TO AIRBORNE PARTICLES/ACID AEROSOLS**

Chapter twelve assesses epidemiological evidence relating human health effects to exposure to airborne particles, which constitutes some of the most crucial information assessed in this latest PM criteria review. Much new information has appeared since EPA's publication of the 1982 document on Air Quality Criteria for Particulate Matter, and sulfur oxides (PM/SO<sub>x</sub>), its second Addendum (1986), and a later Acid Aerosol Issue Paper (1989). A rapidly growing body of epidemiologic literature examines relationships between PM concentrations and human health effects, ranging from respiratory function changes and symptoms to exacerbation of respiratory disease and excess mortality associated with premature death.

The time-series mortality studies reviewed in this and past criteria documents provide evidence that PM-containing ambient air pollution can cause increases in daily human morbidity and mortality. The newly available epidemiology studies provide indications that very small increases in relative risk for such effects are associated with ambient air pollutant mixtures containing low or moderate concentrations of PM, as indexed by a variety of monitoring methods (e.g., black smoke, TSP, COH, PM<sub>10</sub>, PM<sub>2.5</sub>). This includes emerging new evidence indicating likely associations of health effects with PM across a wide range of routine ambient concentration levels seen in the United States and other countries, including levels that extend below present U.S. PM air quality standards.

The 1982 EPA criteria document earlier concluded that the most clearly defined effects on mortality arising from exposure to PM were sudden increases in the number of deaths occurring, on a day-to-day basis, during episodes of high pollution, as occurred in the Meuse Valley in 1930, in Donora in 1948, and in London in 1952. During the December, 1952 London episode 3,000 to 4,000 excess deaths were attributable to air pollution, with the greatest increase in the death rate most dramatic for those  $\geq 45$  years old and occurring most notably in those with chronic lung disease and heart disease due to pollution-induced cardio-respiratory problems. Other episodes with associated notable increases in mortality occurred in London during various winters from 1948 to 1962. Collectively, studies of these and other early episodes left little doubt that airborne particles contribute to mortality

1 associated with very high concentrations of urban aerosol mixes dominated by combustion  
2 products (e.g., from burning coal) and/or their transformation products (e.g.,  $\text{H}_2\text{SO}_4$ ).

3 Besides evaluating mortality associated with major episodes, the 1982 criteria  
4 document also focused on studies of more moderate day-to-day variations in mortality within  
5 large cities in relation to PM pollution. Various methodological problems were identified for  
6 most of the studies, precluding quantitative conclusions regarding exposure-response  
7 relationships of importance for deriving air quality standards. Among the main problems  
8 were inadequate measurement or control for potentially confounding variables and inadequate  
9 quantification of exposure to airborne particles and other associated pollutants (e.g., sulfates  
10 or acid aerosols). Despite such problems, the 1982 document concluded that the then  
11 available studies collectively indicated that mortality was clearly and substantially increased  
12 when airborne particle 24-h concentrations exceeded  $1,000 \mu\text{g}/\text{m}^3$  (as measured by the black  
13 smoke, or BS, method) in conjunction with sulfur dioxide ( $\text{SO}_2$ ) elevations in excess of  $1,000$   
14  $\mu\text{g}/\text{m}^3$  (with the elderly or others with severe preexisting cardiovascular or respiratory  
15 disease mainly being affected).

16 The 1986 addendum to the 1982 criteria document later considered several additional,  
17 then-new analyses of acute PM exposure mortality in London during the 1958-1959 through  
18 1971-1972 winter periods. After reviewing the new data analyses, and taking into account  
19 the previously reviewed London results and the above noted methodological considerations,  
20 the following conclusions were drawn:

- 21  
22 (1) Markedly increased mortality occurred, mainly among the elderly and chronically  
23 ill, in association with BS and  $\text{SO}_2$  concentrations above  $1,000 \mu\text{g}/\text{m}^3$ , especially  
24 during episodes when such pollutant elevations occurred for several consecutive  
25 days;
- 26  
27 (2) During such episodes, coincident high humidity or fog was also likely important,  
28 possibly by providing conditions leading to formation of sulfuric acid ( $\text{H}_2\text{SO}_4$ ) or  
29 other acidic aerosols;
- 30  
31 (3) Increased risk of mortality is associated with exposure to BS and  $\text{SO}_2$  levels in  
32 the range of 500 to  $1,000 \mu\text{g}/\text{m}^3$ , for  $\text{SO}_2$  most clearly at concentrations in  
33 excess of  $\approx 700 \mu\text{g}/\text{m}^3$ ; and
- 34  
35 (4) Convincing evidence indicates that relatively small, but statistically significant,  
36 increases in the risk of mortality exist at BS (but not  $\text{SO}_2$ ) levels below 500  
37  $\mu\text{g}/\text{m}^3$ , with no indications of any specific threshold level having been

demonstrated at lower concentrations of BS (e.g., at  $\leq 150 \mu\text{g}/\text{m}^3$ ). However, precise quantitative specification of the lower PM levels associated with mortality is not possible, nor can one rule out potential contributions of other possible confounding variables at these low PM levels.

In setting the current U.S. PM standards, the BS levels noted above were taken as indexing particles roughly in the same size range as inhalable particles reaching tracheobronchial or alveolar regions of the respiratory tract; and, taking into account other evidence of morbidity effects (e.g., worsening of chronic bronchitis symptoms), the U.S. 24 h primary NAAQS was set as  $150 \mu\text{g}/\text{m}^3 \text{PM}_{10}$ .

The decade or so since the 1986 EPA Addendum has seen the publication of numerous new time series analyses of associations between human mortality or morbidity and acute exposures to PM concentrations at or below the lower end of the range indexed by the above studies of London mortality or the level of the current U.S. 24-h standard. Some utilized TSP or other measures (e.g., COH, BS, etc.) as an indices of PM exposure, but during the last few years, the analyses have mainly focused on  $\text{PM}_{10}$  as a measure of PM.

### **Short-Term PM Exposure Mortality Studies**

Based on the new time-series analyses, numerous investigators have reported very small, but statistically significant associations between increased relative risk for mortality and various indices of PM (e.g., BS, COH, TSP,  $\text{PM}_{10}$ ,  $\text{PM}_{2.5}$ , etc.) for many different cities in the United States and in other countries, as well. The elderly ( $> 65$  yr old), particularly those with preexisting cardiopulmonary disease, are found to have distinctly higher risks than younger age groups. The small relative risk estimates for PM are generally reduced when other likely important (potentially confounding) factors are also controlled for in the models, but the PM association still usually remains statistically significant, although typically accounting for much less of the variance in mortality than temperature or combinations of variables used to index contributions of weather-related mortality. Thus, qualitatively, the newly emerging database appears to provide indications that polluted atmospheres containing relatively low concentrations of particles may contribute (along with other factors) to a very small increase in relative risk for human mortality, especially in the elderly with preexisting cardiopulmonary diseases.

1           It is important to note that differences in opinion exist within the scientific community  
2 with regard to: (a) how adequately other likely important confounding factors (including  
3 weather and copollutants) and/or other seasonal factors were controlled for across the various  
4 new analyses; and (b) interpretation of reported associations between increased relative risk  
5 estimates and indices of ambient PM concentrations. For example, introduction of one or  
6 more other commonly-present ambient air pollutants (e.g., SO<sub>2</sub>, O<sub>3</sub>, CO, NO<sub>x</sub>) into models  
7 of PM effects generally reduces the estimated PM effect, often by as much as 50% and, at  
8 times, to statistically non-significant levels. In a few studies, however, the size of the PM  
9 effect remained essentially the same or increased slightly with other copollutants in the  
10 model. Similarly, analyses of PM-mortality effects by season (winter, spring, summer, fall),  
11 as in a few studies, so far have yielded varying patterns of PM-mortality effects being  
12 significant in one or another season(s) but not all, with specific effective seasons differing  
13 from one locale to another. The copollutant and seasonality analyses results, in particular,  
14 have led to considerable debate in the scientific community, typified on the one hand by (a)  
15 skepticism about the size and the "realness" of reported low-level PM effects and, on the  
16 other hand, (b) countervailing views asserting that the effect of PM (or any other weakly  
17 contributing factor) on mortality can be made to "disappear" by overspecification of  
18 applicable models (i.e., by introduction of sufficient other, possibly extraneous, variables  
19 into the models or by more detailed breakdowns of data (e.g., by season) that may reduce  
20 the power to detect a PM effect).

21           No clear resolution of this debate or "consensus" opinion in the scientific community  
22 has yet crystallized, but some agreement appears to be emerging that the results for models  
23 containing only PM and no other copollutants may provide upper bound estimates for effects  
24 of ambient particle-containing mixes of pollutants, whereas results derived from analyses  
25 including other copollutants and extensive controls for weather, seasonality, and/or other  
26 likely important contributing factors should be viewed as lower-bound estimates of PM  
27 effects (which may be 50% or more lower than the upper bound or even include zero). Key  
28 points regarding derivation of quantitative estimates of PM-related mortality and morbidity  
29 effects, taking into account the types of uncertainties and scientific debate just noted are  
30 summarized below. Major emphasis is placed first on results derived from studies of PM<sub>10</sub>

as the PM indicator of most interest in relation to the current U.S. PM standards and, then, additional key quantitative points for PM<sub>2.5</sub> and acid aerosols are summarized.

#### **PM<sub>10</sub> Relative Risk Analyses**

This section discusses key findings from studies conducted since the 1986 PM criteria document addendum that have employed PM<sub>10</sub> in their analyses of the human mortality effects of acute exposures to PM, as discussed in more detail in Chapter 12. Some studies considered daily mortality in the entire population (i.e., all ages) and some by cause; some also considered subpopulations (e.g., the elderly).

Two earlier published summaries of the PM literature converted all results to a PM<sub>10</sub>-equivalence basis and provided quantitative intercomparisons and after such summaries used TSP as the reference PM metric. The results from such summaries suggest about a 1 percent change in acute total mortality for a 10 µg/m<sup>3</sup> change in PM<sub>10</sub>, but the estimates range from 0.3 to 1.6% (i.e., a factor of 5). While most of the 95% confidence intervals (CIs) of these estimates overlap, CIs of the highest and lowest estimates do not overlap, indicating significant differences between these estimates. Note that the effects indicated for a 10 µg/m<sup>3</sup> PM<sub>10</sub> change cannot be reliably converted to other PM increments (e.g., 50 or 100 µg/m<sup>3</sup> PM<sub>10</sub>), as differences in model specification (e.g., linear versus log models) will cause them to differ in their conversions to other particle concentration ranges. The reasons for the approximately five-fold effect estimate difference noted among studies are not obvious, but one factor appears to be the PM exposure averaging time, as estimates using multiple day PM<sub>10</sub> averages are all 1% or higher. This is not unexpected, given that any lagged effects from prior days of PM<sub>10</sub> exposure will be added to the effects estimate when a multi-day average is employed, increasing the estimated effect on a per µg/m<sup>3</sup> basis.

It is also important to note that other air pollutants were generally not addressed in deriving the coefficients reported by the above summaries. Differences among coefficients are to be expected, given that the composition (and, potentially toxicity) of the PM, as well as the demographic characteristics in each city, can be expected to differ. Moreover, the conversions from other PM metrics to PM<sub>10</sub> necessarily introduce much additional uncertainty. However, though not all of these results may therefore be the most appropriate available for quantifying a PM<sub>10</sub> effect, they do consistently indicate that there is an

1 association between acute exposure to ambient air mixes containing PM and increased daily  
2 mortality. Moreover, the by-cause results also reported in the summaries indicate that PM  
3 effect estimates are greater for respiratory causes, which lends support to the biological  
4 plausibility of the noted PM associations.

5 In an effort to more clearly quantify daily PM<sub>10</sub>-total acute mortality associations,  
6 Table 1-5 summarizes total mortality relative risk (RR) estimates reported for a 50 µg/m<sup>3</sup>  
7 increase in PM<sub>10</sub> estimated from nine studies reviewed in Chapter 12, which employed PM<sub>10</sub>  
8 data in their analysis of total mortality data (or which had on-site PM<sub>10</sub> reference data to  
9 convert other PM metrics with more certainty). The studies listed were selected for this  
10 analysis mainly because they can most readily be intercompared and provide direct data  
11 related to PM<sub>10</sub> levels. The RR's calculated were based upon a 50 µg/m<sup>3</sup> increase above the  
12 mean PM<sub>10</sub> 24-h concentration, which is approximately the order of magnitude of the typical  
13 difference between the mean and maximum in these cities evaluated and is fairly  
14 representative of the mean/max differences seen for most of the U.S. cities in Tables 1-2 and  
15 1-3. This is noted because in non-linear models as often employed in the studies discussed in  
16 Chapter 12, the RR estimate associated with a given µg/m<sup>3</sup> PM<sub>10</sub> increase will vary  
17 depending upon the baseline concentration to which it is added.

18 From results presented in Chapter 12, it is apparent that these studies generally have  
19 yielded at least marginally significant PM<sub>10</sub> coefficients, but the resultant excess risk  
20 estimates differ by a factor of five across these studies (from 1.5% to 8.5% per 50 µg/m<sup>3</sup>).  
21 The mean and maximum PM<sub>10</sub> concentration data are noted for each study. If the PM<sub>10</sub>  
22 coefficient decreased as the mean level of PM<sub>10</sub> decreased, then confounding as a function of  
23 varying PM level would be suggested. However, the data presented indicate that the  
24 variability in coefficients is not a function of PM<sub>10</sub> level, as sites with high or low PM<sub>10</sub>  
25 concentrations can report either high or low RR's. In Chapter 12, the statistical  
26 methodology characteristics of each study were concisely summarized, in order to determine  
27 if any factors are important to help explain the variability observed from study to study in the  
28 PM<sub>10</sub> RR estimate. As noted earlier, the RR estimate for acute mortality associated with  
29 short-term exposure to PM<sub>10</sub> is usually larger when other pollutants are not simultaneously  
30 considered in the model. Those studies which considered PM<sub>10</sub> both alone and with other  
31 pollutants in the model often yielded smaller, and usually more marginally significant, PM<sub>10</sub>

**TABLE 1-5. COMPARISON OF RELATIVE RISK (RR) ESTIMATES FOR TOTAL MORTALITY FROM 50  $\mu\text{g}/\text{m}^3$  CHANGE IN  $\text{PM}_{10}$ , USING STUDIES WHERE  $\text{PM}_{10}$  WAS MEASURED OR WAS CALIBRATED FOR THE SITE**

Study	Reference	$\text{PM}_{10}$ ( $\mu\text{g}/\text{m}^3$ )		Other Pollutants In Model	Lag Times, d	RR per 50 $\mu\text{g}/\text{m}^3$	95 Percent Confidence Interval
		Mean	Maximum				
Utah Valley, UT	Pope et al.(1992)	47	297	None	$\leq 4$ d	1.08	(1.05, 1.11)
				None, Winter	$\leq 4$ d	1.085	(1.03, 1.14)
				None, Summer	$\leq 4$ d	1.11	(0.92, 1.35)
				Max $\text{O}_3$ , Summer	$\leq 4$ d	1.19	(0.96, 1.47)
				Avg $\text{O}_3$ , Summer	$\leq 4$ d	1.14	(0.92, 1.41)
St. Louis, MO	Dockery et al. (1992)	28	97	None	$\leq 3$ d	1.08	(1.005, 1.15)
				$\text{O}_3$	$\leq 3$ d	1.06	(0.98, 1.15)
Kingston, TN	Dockery et al. (1992)	30	67	None	$\leq 3$ d	1.085	(0.94, 1.25)
				$\text{O}_3$	$\leq 3$ d	1.09	(0.94, 1.26)
Birmingham, AL	Schwartz (1993)	48	163	None	$\leq 3$ d	1.05	(1.01, 1.10)
Athens, Greece	Touloumi et al. (1994)	78	306	None	1 d	1.034	(1.025, 1.044)
				$\text{SO}_2$ , CO	1 d	1.015	(1.00, 1.03)
Toronto, ON Canada	Özkaynak et al. (1994)	40	96	None	0 d	1.025	(1.015, 1.034)
Los Angeles, CA	Kinney et al. (1995)	58	177	None	1 d	1.025	(1.00, 1.055)
				$\text{O}_3$ , CO	1 d	1.017	(0.99, 1.036)
Chicago, IL	Ito et al. (1995)	38	128	$\text{O}_3$ , CO	$\leq 3$ d	1.025	(1.005, 1.05)
Santiago, Chile	Ostro et al. (1995a)	115	367	None	1 d	1.04	(1.005, 1.06)
				None	$\leq 4$ d	1.07	(1.04, 1.10)
				None, Poisson	1 d	1.022 <sup>1</sup>	(1.003, 1.042)
				$\text{SO}_2$ , Poisson	1 d	1.026 <sup>1</sup>	(1.005, 1.047)
				$\text{NO}_2$ , Poisson	1 d	1.043 <sup>1</sup>	(1.020, 1.066)
				$\text{O}_3$ , Poisson	1 d	1.026 <sup>1</sup>	(1.005, 1.047)
Chicago, IL	Styer et al. (1995)	37	365	None	3 d	1.04	(1.00, 1.08)

<sup>1</sup>Calculated on a basis of 50  $\mu\text{g}/\text{m}^3$  increase from 50 to 100  $\mu\text{g}/\text{m}^3$ .

1 relative risks when other pollutants were also considered. This ranges from roughly a 20 to  
2 50 percent reduction in the estimate of excess risk associated with PM<sub>10</sub> (e.g., in Athens,  
3 Greece, the PM<sub>10</sub> RR declines from 1.07 to 1.03 per 100 µg/m<sup>3</sup> when other pollutants are  
4 considered). Such a reduction is to be expected when co-linear variables are added.

5 Older studies using BS or TSP often found high correlations between SO<sub>2</sub> and the PM  
6 indicator which reduced the apparent PM effect and attenuated its statistical significance.  
7 However, studies using a variety of PM indicators at cities where SO<sub>2</sub> levels were so low as  
8 to have little likelihood of SO<sub>2</sub> being a significant confounder of a PM effect found  
9 quantitatively similar significant PM effects. While there is some possibility that  
10 summertime PM effects may be partially confounded with those of other pollutants (e.g., O<sub>3</sub>)  
11 derived from motor vehicle fuel combustion or transformation products, winter effects of PM  
12 are clearly detectable when O<sub>3</sub> levels are much lower. If PM effects on mortality were so  
13 completely confounded with those co-pollutants so as to be undetectable, then one would  
14 need to invoke many different confounders in different studies of communities. While this  
15 explanation is not impossible, it appears highly unlikely, but cannot be precluded altogether  
16 since PM may derive from different sources in these studies, have varying size and chemical  
17 composition from one locale to another, and therefore may have different characteristics that  
18 affect health outcomes such as mortality.

19 Another factor clearly affecting the PM<sub>10</sub> RR estimates is the PM<sub>10</sub> averaging period.  
20 Most of the studies which utilized multi-day averages of PM<sub>10</sub> in their regressions (i.e., for  
21 Utah Valley; St. Louis; eastern TN; Santiago; Chicago; and Birmingham) yielded higher RR  
22 estimate studies. However, the increase indicated for these studies is not proportional to the  
23 averaging time. Indeed, in sub-analyses for Utah Valley data, the PM<sub>10</sub> mortality risk is  
24 indicated to be roughly doubled by using a five day average versus a single day  
25 concentration, and sub-analyses for Santiago also indicate approximately a doubling in the  
26 PM<sub>10</sub> RR when a 3 day average is considered (i.e., from RR = 1.04 for a single day PM<sub>10</sub>  
27 value to RR = 1.07 for a 3d average PM<sub>10</sub> value). This may be due to the fact that, since  
28 autocorrelation exists in the PM<sub>10</sub> concentrations from day to day, the single day  
29 concentration is "picking up" some of the effect of multi-day pollution episodes, even though  
30 they are not explicitly modeled. These results suggest that a multi-day rather than a



single-day average  $PM_{10}$  concentration may provide a more relevant index to gauge the effects of short-term PM exposures over several consecutive days.

Table 1-5 shows that total acute mortality relative risk estimate associated with a  $50 \mu g/m^3$  increase in the one-day 24-h average  $PM_{10}$  ranged from 1.015 to 1.085, depending upon the site (i.e., the  $PM_{10}$  composition and population demographics) and whether  $PM_{10}$  is modeled as the sole index of air pollution. Relative Risk estimates with  $PM_{10}$  as the only pollutant index in the model range from  $RR = 1.025$  to 1.085, while the  $PM_{10}$  RR with multiple pollutants in the model range from 1.015 to 1.025. As noted earlier, the former range might be viewed as approximating an upper bound of the best estimate, as any mortality effects of co-varying pollutants are likely to be "picked up" by the  $PM_{10}$  index. On the other hand, the latter multiple pollutant model range might be viewed as approximating a lower bound of the best estimate, as the inclusion of highly correlated covariates may weaken the  $PM_{10}$  estimate. Overall, consistently positive PM-mortality associations are seen throughout these analyses, even with the use of various modeling approaches and after controlling for major confounders such as season, weather, and co-pollutants. The 24-h  $50 \mu g/m^3$   $PM_{10}$  total mortality effect estimate most typically falls in approximately the  $RR = 1.025$  to 1.05 range (representing an expected 2.5 to 5.0% increase in risk of death over daily background mortality rates for which a  $50 \mu g/m^3$  increment in ambient  $PM_{10}$  concentration could be a contributing factor).

It is logical to assume that the bulk of the total mortality effects suggested by these studies are among the elderly. During the historic London, 1952 pollution episode the greatest increase in the mortality rate was among older citizens and those having respiratory diseases. An analysis of mortality in Philadelphia, PA during 1973 through 1980 comparing mortality during the 5% highest versus the 5% lowest TSP days also found the greatest increase in risk of death to be among those aged 65 to 74 and those >74 year of age (mortality risk ratios = 1.09 and 1.12, respectively, between high and low TSP days). Also, in a time series analyses of Philadelphia daily mortality during this period, the TSP-mortality coefficient was significantly higher ( $\beta = 0.000910 \pm 0.000161$ ) for persons > 65 yrs old than for the younger population ( $\beta = 0.000271 \pm 0.000206$ ). These coefficients indicate an effect size for the elderly roughly three times that for the younger population (10% versus 3%, respectively, for a  $100 \mu g/m^3$  increase in TSP). Also, two other recent  $PM_{10}$  analyses

(one for Sao Paulo, Brazil and the other for Santiago, Chile) directly considered the question of PM<sub>10</sub>-mortality associations among the elderly population ( $\geq 65$  years of age). The first of these two analyses evaluated PM<sub>10</sub>-mortality associations for the elderly in Sao Paulo during 1990 through 1991 in Sao Paulo. The reported PM<sub>10</sub> relative risk (RR = 1.13 for a 100  $\mu\text{g}/\text{m}^3$  increase) is higher than noted above for total mortality analyses addressing multiple pollutants (100  $\mu\text{g}/\text{m}^3$  RR  $\approx$  1.03 to 1.05), supporting past observations that the elderly represent a population especially sensitive to the health effects of air pollution. The second study in Santiago, Chile found a 24-h PM<sub>10</sub> 100  $\mu\text{g}/\text{m}^3$  RR estimate of 1.08, for the overall population but the RR estimates for a 100  $\mu\text{g}/\text{m}^3$  increase in PM<sub>10</sub> rose to an RR = 1.11 for the elderly (aged 65+) using the same model specification. Thus, these directly comparable estimates (i.e., using the same model specification and population) suggest that the elderly experience roughly a 40 percent higher excess risk from exposure to PM air pollution than the overall population.

Overall, considering the historical pollution episode evidence and the results of recent PM<sub>10</sub>-mortality analyses evaluating elderly populations, it seems evident that elderly adults represent a population especially at risk for mortality implications of acute exposure to air pollution, including PM.

Relatively few studies have directly examined the PM-mortality association in children. It is difficult, given the limited and somewhat conflicting results available at this time, to ascribe any such association to low-level PM pollution in particular. This is an area where further research is clearly needed to broaden the base upon which to assess the potential for PM to increase mortality among children.

In studies alluded to above and in others discussed in more detail in Chapter 12, a consistent trend was for acute PM exposure effect estimates to be higher for the respiratory mortality category than for total mortality from all (non-accident) causes. This lends support to the biological plausibility of a PM air pollution effect, as the breathing of toxic particles would be expected to most directly affect the respiratory tract. Of particular interest is comparison of relative risk values from those studies that made most direct and appropriate comparisons. In a Santa Clara study, the PM-respiratory mortality RR was 4.3 times as large as for deaths as a whole (i.e., 3.5/0.8); for Philadelphia, the PM (TSP)-respiratory mortality RR was 2.7 times as large as for total mortality (i.e., 3.3/1.2); for Utah Valley,

1 the PM<sub>10</sub>-respiratory mortality RR was 2.5 times as large as for deaths as a whole (i.e.,  
2 3.7/1.5); for Birmingham, AL, the respiratory mortality RR of PM<sub>10</sub> was 1.5 times as large  
3 as for deaths as a whole (i.e., 1.5/1.0); and for Santiago, Chile the reported excess  
4 respiratory mortality RR of PM<sub>10</sub> was 1.8 times as large as for deaths as a whole (comparing  
5 1.15/1.08 RR per 100  $\mu\text{g}/\text{m}^3$ ). Thus, in these studies, the PM RR for respiratory diseases is  
6 indicated to range from 50 to over 400% higher for respiratory disease categories than for all  
7 causes of death, indicating that increases in respiratory deaths are a major contributor to the  
8 overall PM-mortality associations noted previously. Moreover, since evidence suggests that  
9 an acute pollution episode is most likely be inducing its primary effects by stressing already  
10 compromised individuals (rather than, for example, inducing chronic respiratory disease from  
11 a single air pollution exposure episode), the above results indicate that persons with  
12 pre-existing respiratory disease represent a population especially at risk to the mortality  
13 implications of acute exposures to air pollution, including PM.

14 In overall summary, the time-series mortality studies reviewed in this and the previous  
15 1982 and 1986 PM criteria assessments provide reasonably strong evidence that increases in  
16 daily human mortality are associated with short-term exposures to air pollution mixes  
17 containing elevated PM levels. Recent studies provide indications that small increases in  
18 such risk occur in association with air pollution indexed by moderate increases of 24-h PM<sub>10</sub>  
19 ( $\sim 50 \mu\text{g}/\text{m}^3$ ) above routine ambient levels averaging around 50 to 100  $\mu\text{g}/\text{m}^3$ . Overall, the...  
20 PM<sub>10</sub> relative risk estimates derived from the most recent PM<sub>10</sub> total mortality studies  
21 suggest an acute exposure effect on the order of  $\text{RR} = 1.025$  to  $1.05$  in the general  
22 population for increases in ambient air pollution indexed by a 24-h average  $50 \mu\text{g}/\text{m}^3$  PM<sub>10</sub>  
23 increment, with higher (30-40%) relative risks indicated for the elderly sub-population and  
24 for those with pre-existing respiratory conditions.

## 25 26 **Fine Particles/Acid Aerosols Relative Risks**

27 As noted earlier and in both Chapters 11 and 12, some epidemiologic and experimental  
28 toxicology data point toward fine particles as a class or certain constituents (e.g., acidic  
29 aerosols) as possibly being key contributors to observed PM-mortality and/or PM-morbidity  
30 associations. Only a few epidemiologic studies provide direct comparisons between various  
31 PM indices, including fine particle and acidity measurements.

One such study investigated relationships between multiple air pollutants (including  $PM_{2.5}$ ) and total daily mortality during a one year period in St. Louis, MO and Kingston/Harriman, TN and surrounding counties. In Poisson regressions controlling for weather and season, previous day's  $PM_{10}$  was the only significant predictor of daily mortality ( $\beta = 0.00175 \pm 0.00067$ ), but the association dropped off at 3 days ( $\beta = 0.00042 \pm 0.00063$ ). Size-fractionated PM data were examined to determine whether this association could be attributed to either the fine ( $PM_{2.5}$ , aerodynamic diameter  $d_a < 2.5 \mu m$ ) or the coarse ( $2.5 \mu m < d_a < 10 \mu m$ ) component of the  $PM_{10}$  mass. The fine fraction ( $PM_{2.5}$ ) was positively associated with mortality ( $\beta = 0.00171 \pm 0.00096$ ,  $P = 0.075$ ). Coarse particles were also positively associated ( $\beta = 0.00247 \pm 0.00129$ ,  $P = 0.056$ ). Neither fine nor coarse particles showed a stronger association than the other when considered simultaneously.

Both daily  $SO_4$  and  $H^+$  concentrations were significantly correlated with  $PM_{10}$  (Pearson correlations 0.52 and 0.76, respectively). Sulfate ( $SO_4^{2-}$ ) as measured by the sulfur fraction of  $PM_{10}$  ( $\beta = 0.00608 \pm 0.00577$ ) and  $H^+$  ( $\beta = 0.00086 \pm 0.00118$ ) were positively, but not significantly, associated with daily mortality. Among other PM elements measured, those correlated with  $PM_{10}$  concentrations were also associated with mortality. In particular, aluminum, calcium, chromium, iron, and silica all had correlations with  $PM_{10}$  of 0.5 or higher and had positive associations with mortality. Neither  $SO_2$ ,  $NO_2$ , nor  $O_3$  was significantly associated ( $P > 0.30$ ) with total mortality.

## **Long-Term $PM_{10}/PM_{2.5}$ Exposure Mortality Studies**

### **Population-Based Cross Sectional Mortality Studies**

Ecological cross-sectional studies employing averages across various geopolitical units (cities, SMSAs, etc.) present data that examine relationships between community-wide PM levels and mortality. Such community-based studies seek to define (average) community characteristics associated with overall average health status—in this case, annual mortality rate.

One study analyzed 1980 total mortality in 98 SMSAs, using data on  $PM_{15}$  and  $PM_{2.5}$  from the EPA inhalable particle (IP) monitoring network for 38 of these locations, ranked the importance of the pollutants by relative statistical significance in separate regressions, and concluded that the results were "suggestive" of an effect of particles on mortality decreasing

1 with particle size; although in the basic model only  $\text{SO}_4^{2-}$  was statistically significant. In  
2 some other models tested,  $\text{PM}_{2.5}$  was also significant, and  $\text{PM}_{15}$  nearly so. However, if the  
3 effects are judged by elasticities rather than significance levels,  $\text{SO}_4^{2-}$ ,  $\text{PM}_{2.5}$ , and  $\text{PM}_{15}$   
4 would be judged as equivalent, with TSP ranking somewhat lower. Also, based on source  
5 apportionment techniques, particles from coal combustion and from the metals industry  
6 appeared to be the most important. The specific coefficients and significance levels obtained  
7 for TSP may be the result of the particular TSP data used, being based on a single  
8 monitoring station in each SMSA and thus not clearly fully representative of population  
9 exposures. Thus, alternative interpretations of these findings are certainly possible. In  
10 addition, because smoking, diet, and other socioeconomic or lifestyle variables were not  
11 considered in the regression model, the pollution coefficients may have been biased. Finally,  
12 the study did not specifically address the question of acute vs. chronic responses by exploring  
13 lagged pollution variables.

14 Data from up to 149 metropolitan areas (mostly SMSAs) were analyzed in another  
15 study of relationships between community air pollution and "excess" mortality due to various  
16 causes for the year 1980. Several socioeconomic models were used in cross- section multiple  
17 regression analyses to account for non- pollution effects. Two different sources of  
18 (measured) air quality data were used: data from the EPA AIRS database (TSP,  $\text{SO}_4^{2-}$ , Mn,  
19 and ozone) and data from the inhalable particulate (IP;  $\text{PM}_{15}$ ) network; the latter data  
20 ( $\text{PM}_{15}$ ,  $\text{PM}_{2.5}$  and  $\text{SO}_4^{2-}$  from the IP filters) were only available for 63 locations. All PM  
21 data were averaged across all monitoring stations available for each SMSA, with TSP data  
22 restricted to 1980 and based on an average of about 10 sites per SMSA. Using these models,  
23 statistically significant associations were found between TSP and mortality due to non-  
24 external causes with the log-linear models evaluated, but not with a linear model. Sulfates,  
25 manganese, inhalable particles ( $\text{PM}_{15}$ ), and fine particles ( $\text{PM}_{2.5}$ ) were not significantly ( $P <$   
26  $0.05$ ) associated with mortality with any of the parsimonious models, although  $\text{PM}_{2.5}$  and  
27 manganese were close with linear models ( $p=0.07$ ) and significance may have been affected  
28 by the use of smaller data sets. This study found  $\text{PM}_{2.5}$  to be the "strongest" PM index with  
29 linear models, but TSP with log-linear models. This study support previous findings of  
30 associations between TSP and premature mortality.

## Prospective Mortality Studies

Prospective studies consider data on the relative survival rates of individuals, as affected by age, sex, race, smoking habits, and certain other individual risk factors. This type of analysis has a substantial advantage over the above population-based studies, because identification of actual decedents allows stratification according to important risk factors such as smoking. However, since none of the prospective cohort studies had data on personal exposures to air pollution, these studies are also considered to be "ecological."

Several newer prospective studies are of most interest. One such study followed approximately 6,000 white, non-hispanic, nonsmoking, long-term California residents for 6 to 10 years, beginning in 1976. The study was designed to test the use of cumulative exposure data as an explanatory factor for disease incidence and chronic effects. Only TSP and ozone data were used to index pollution exposures; with reliance on oxidant concentrations in the early part of the monitoring record. In a follow-up analysis,  $\text{SO}_4^{2-}$ ,  $\text{PM}_{10}$  (estimated from site-specific regressions on TSP),  $\text{PM}_{2.5}$  (estimated from visibility), and visibility per se (extinction coefficient) were used to index PM exposure. No significant associations with nonexternal mortality were reported, and only high levels of TSP or  $\text{PM}_{10}$  were associated with symptoms of asthma, chronic bronchitis or emphysema. The finding of no association between long-term cumulative exposure to TSP or  $\text{O}_3$  and all natural-cause mortality may be interpreted as showing the absence of chronic responses after 10 years but not necessarily the absence of (integrated) acute responses, since coincident air pollution exposures were not considered.

Another prospective study analyzed survival probabilities among 8,111 adults first recruited in the mid-1970s in six cities in the eastern portion of the United States. The cities are: Portage, WI, Topeka, KS; St. Louis, MO; Steubenville, OH, Watertown, MA, and Kingston-Harriman, TN, two small towns southwest of Knoxville. These locations thus comprise a transect across Northeastern and Northcentral United States, from suburban Boston, through Appalachia, and into the upper Midwest. The adults were white, aged 25 to 74 at enrollment, and the final cohorts numbered 1,400 to 1,800 persons in each city. Follow-up periods ranged from 14 to 16 years, during which from 13 to 22% of the enrollees died. Of the 1,430 death certificates, 98% were located, including those for persons who had moved away and died elsewhere. The bulk of the analysis was based on

1 all-cause mortality and included individual characteristics of the members (and thus of the  
2 decedents), e.g. smoking habits, an index of occupational exposure, body mass index, and  
3 completion of a high school education. Air pollution effects were evaluated in two ways: by  
4 evaluating the relative risks of residence in each city relative to Portage (the city with the  
5 lowest pollution levels for most indices), and by including the community-average air quality  
6 levels directly in the models.

7 Based on statewide mortality data, substantial differences in survival rates would be  
8 expected across this transect of the Northeastern U.S. and were in fact observed. The long-  
9 term average mortality rate in Steubenville was 16.2 deaths per 1,000 person-years; in  
10 Topeka, it was 9.7, yielding a 67% variation in the range of annual average (crude) relative  
11 risk across the six cities. After individual adjustment for age, smoking status, education, and  
12 body-mass index, the range in average relative risk was reduced to 26%. The authors  
13 reported that "mortality was more strongly associated with the levels of fine, inhalable, and  
14 sulfate particles" than with the other pollutants (e.g., NO<sub>x</sub>, SO<sub>2</sub>, TSP), which they attributed  
15 primarily to factors of particle size. For those three PM indices, relative risk estimates and  
16 confidence limits based on the differences between air quality in Steubenville and in Portage  
17 were calculated. Only small differences were found between many pollutants, including SO<sub>2</sub>  
18 and NO<sub>2</sub>, owing in part to the strong collinearity present. Neither mortality associations with  
19 TSP nor with coarse particle fractions created by subtracting PM<sub>15</sub> from TSP or PM<sub>2.5</sub> from  
20 PM<sub>15</sub> were significant, suggesting that particles > 15 um may be less important. This  
21 outcome may reflect in part greater spatial variability within the communities for these  
22 measures. The non-sulfate portion of PM<sub>2.5</sub> had the tightest confidence limits (SO<sub>4</sub><sup>2-</sup> was  
23 multiplied by 1.2 before subtraction, assuming an average composition of NH<sub>4</sub>HSO<sub>4</sub>).  
24 However, all of the differences in relative risks and their confidence limits could have  
25 occurred due to chance, given the availability of only 6 observations. No relationship was  
26 found for aerosol acidity (H<sup>+</sup>), but only limited data were available.

27 The authors of this study appear to have made the most of the available individual data  
28 on some of the most important mortality risk factors. They were quite cautious in their  
29 conclusions, stating that the results only suggest that fine-particulate air pollution "contributes  
30 to excess mortality in certain U.S. cities." There are several other important outcomes:  
31

- None of the population subgroups examined appeared to be statically significantly more sensitive to air pollution than any other, although smokers had notably higher relative risk estimates (with wide confidence intervals) than non-smokers.
- The implied regression coefficients are much larger (about an order of magnitude) than those found in either type of population-based study noted earlier. This could be interpreted as evidence that the chronic effects of air pollution far exceed the acute effects, or that not all of the spatial confounding has been controlled. Use of linear models for non-linear effects (body-mass index) and failure to control for alcohol consumption, diet, exercise and migration may have contributed to the relatively large effects indicated for air pollution.
- If the measured responses to air pollution truly are due to chronic PM exposure it is logical to expect that cumulative exposure would be the preferred metric. However, pollution levels 10 years before this study began were much higher in Steubenville and St. Louis, as indexed by TSP from routine monitoring networks. For example, annual average TSP in 1965 in Steubenville was about three times the value used to index chronic exposure in the study. Estimates of previous levels of fine particles are more difficult, but atmospheric visibility data suggest that previous levels may have been higher in winter, but not necessarily in summer. These uncertainties make it difficult to accept quantitative regression results based solely on coincident monitoring data.

Because it seems unlikely that any of the above-noted shortcomings of this study could have resulted in bias sufficient to reduce the risk estimates to levels less than those found in acute mortality studies, the Six City study appears to provide support for the hypothesis that effects indexed by results of long-term air pollution studies must also reflect the presence of acute effects on mortality as integrated over the long term. Or, it may also be concluded that support has been shown for the existence of chronic effects; these two possibilities are not mutually exclusive. However, these conclusions must be qualified by the realization that not all of the relevant socioeconomic factors may have been properly controlled in this study.

In a very recently reported 1995 study, 7-year survival data (1982 to 1989) for about 550,000 adult volunteers obtained by the American Cancer Society (ACS) were analyzed. The Cox proportional hazards model was used to define individual risk factors for age, sex, race, smoking (including passive smoke exposure), occupational exposure, alcohol consumption, education, and body-mass index. The deaths, about 39,000 in all, were assigned to geographic locations using the 3-digit zip codes listed at enrollment into the ACS study in 1982. Relative risks were then computed for 151 metropolitan areas defined by these zip codes and were compared to the corresponding air quality data (ca. 1980) derived



1 from the EPA AIRS system for sulfates, as obtained from high-volume sampler filters for  
2 1980, and the Inhalable Particulate Network for fine particles (PM<sub>2.5</sub>), measured by  
3 dichotomous samplers during 1979-81. Causes of death considered included: all causes,  
4 cardiopulmonary causes, lung cancer, and all other causes.

5 The adjusted total mortality risk ratios for the ACS study (computed for the range of  
6 the pollution variables) were 1.15 (95% CL = 1.09 to 1.22) for sulfates and 1.17 (95% CL  
7 = 1.09 to 1.26) for PM<sub>2.5</sub>. When expressed as log-linear regression coefficients, these  
8 values were quite similar for both pollution measures: 0.0070 (0.0014) per  $\mu\text{g}/\text{m}^3$  for SO<sub>4</sub><sup>2-</sup>  
9 and 0.0064 (0.0015) for PM<sub>2.5</sub>, suggesting that particle chemistry may be relatively  
10 unimportant as an independent risk factor (it is possible that the SO<sub>4</sub><sup>2-</sup> results have been  
11 biased high by the presence of filter artifacts). However, the pollution coefficients were  
12 reduced by 10 to 15% when variables for climate extremes were added to the model.

13 This study took great care to control for those potential confounding factors for which  
14 data were available. Several different measures of active smoking were considered, as was  
15 the time exposed to passive smoke. The occupational exposure variable was specific to any  
16 of: asbestos, chemicals/solvents, coal or stone dusts, coal tar/pitch/asphalt, diesel exhaust,  
17 or formaldehyde. The education variable was an indicator for having less than a high-school  
18 education. However, the possible influences of other air pollutants were not discussed, and  
19 other risk factors not considered included income, employment status, dietary factors,  
20 drinking water hardness and physical activity levels, all of which have been shown to affect  
21 longevity. Another important caveat is that the ACS cohort is by no means a random sample  
22 of the U.S. population; it is 94% white and better educated than the general public, with a  
23 lower percentage of smokers than in the Six City Study. The (crude) death rate during the  
24 7.25 years of follow-up was just under 1% per year, which is about 20% lower than  
25 expected for the white population of the U.S. in 1985, at the average age reported for the  
26 study cohort. In contrast, the corresponding rates for the Six-City study discussed above  
27 tended to be higher than the U.S. average.

28 The results of the long-term prospective cohort studies are compared in Table 1-6. The  
29 results of the American Cancer Society (ACS) prospective study were qualitatively consistent  
30 with those of the Six City study with regard to their findings for sulfates and fine particles;  
31 but relative standard errors were smaller, as expected because of the substantially larger

TABLE 1-6. PROSPECTIVE COHORT MORTALITY STUDIES

Source	Health Outcome	Population	Time Period/ No. Units	PM Indicators	PM Mean ( $\mu\text{g}/\text{m}^3$ )	PM Range/ (Std. Dev.)	Sites Per City	Total Deaths	Model Type	PM Lag Structure	Other Pollutants	Other Factors	Relative Risk <sup>1</sup> at SO <sub>4</sub> = 15, PM <sub>15</sub> = 50, PM <sub>2.5</sub> = 25	RR. Confidence Interval	Elasticity
Abbey et al. (1991)	Total mortality from disease	Calif. 7th Day Adventist	1977-82 Defined by air monitoring sites	24 h TSP > 200	102	25-175 (annual avg)	NA	845	Cox proportional hazards	10 yrs	none	age, sex, race, smoking, education, airway disease	0.99 TSP <sup>1</sup>	(0.87-1.13) <sup>1</sup>	NS <sup>2</sup>
Dockery et al. (1993) p. 1758	Total mortality	White adult volunteers in 6 U.S. cities <sup>3</sup>	1974-91	PM <sub>15</sub> PM <sub>2.5</sub> SO <sub>4</sub>	29.9 18 7.6	18-47 11-30 5-13	1	1429	Cox proportional hazards	none	none	age, sex, smoking, education, body mass, occup. exposure hypertension <sup>4</sup> , diabetes <sup>4</sup>	1.42 PM <sub>15</sub> 1.31 PM <sub>2.5</sub> 1.46 SO <sub>4</sub>	(1.16-2.01) (1.11-1.68) (1.16-2.16)	0.25 0.22 0.23
Pope et al. (1995) Table 2	Total mortality	American Cancer Society, adult volunteers in U.S.	1982-89 PM <sub>2.5</sub> 50 cities SO <sub>4</sub> 151 cities	PM <sub>2.5</sub> SO <sub>4</sub>	18.2 11 <sup>5</sup>	9-34 4-24	1 1	20,765 38,963	Cox proportional hazard	none	none	age, sex, race, smoking, education, body mass, occup. exposure, alcohol consumption, passive smoking, climate <sup>5</sup>	1.17 PM <sub>2.5</sub> 1.10 SO <sub>4</sub>	(1.09-1.26) (1.06-1.16)	0.117 0.077

<sup>1</sup>For 1,000 h/yr > 200  $\mu\text{g}/\text{m}^3$ .<sup>2</sup>NS = non significant, confidence limits not shown.<sup>3</sup>Portage, WI; Topeka, KS; Watertown, MA; Harrisman-Kingston, TN; Steubenville, OH.<sup>4</sup>Used in other regression analyses not shown in this table.<sup>5</sup>Value may be affected by filter artifacts.

1 database. However, no other non-PM pollutant measures were investigated in the ACS  
2 analysis, so that no further progress was made in attempting to clarify relative contributions  
3 of PM or other possible "responsible" pollutants. Also of note were that the ACS regression  
4 coefficients were about 1/4 to 1/2 of the corresponding Six City values and were much closer  
5 to the corresponding values obtained in various acute mortality studies. Thus it is not clear  
6 to what extent chronic effects (as opposed to integrated acute effects) are indicated by these  
7 results and to what extent the limited air quality data base used was responsible for this  
8 outcome.

9 The California and Six-City studies both suffer from small sample sizes and inadequate  
10 degrees of freedom, which partially offset the specificity gained by considering individuals  
11 instead of population groups. All of them may have neglected some important risk factors.  
12 The studies of California nonsmokers by Abbey et al. (1991, 1994) that had the best  
13 cumulative exposure estimates found no significant mortality effects of previous air pollution  
14 exposure. The Six Cities and ACS studies agree in their findings of strong associations  
15 between fine particles and excess mortality. At this time, the long-term studies appear  
16 mainly to provide support for the existence of short-term PM-related mortality increases,  
17 which are not subsequently offset by decreases below normal rates. However, they do not  
18 exclude the possible existence of additional chronic exposure effects; nor do they provide  
19 convincing evidence as to the specific pollutant(s) involved; and they do not rule out the  
20 possible existence of pollutant thresholds.

## 21 22 **Morbidity Outcomes Associated With PM Exposure**

23 Dockery and Pope (1994) reviewed the effects of PM on respiratory mortality and  
24 morbidity. The authors considered five primary health endpoints: mortality, hospital usage,  
25 asthma attacks, respiratory symptoms and lung function. In order to include as many studies  
26 as possible, they converted both British smoke and TSP measurements to  $PM_{10}$ . Results  
27 from each study were converted to an estimated percent change in the health endpoint per  
28  $10 \mu g/m^3 PM_{10}$ . These converted results were then combined across studies of similar  
29 endpoints using the standard inverse variance weighted method (fixed effects model). The  
30 authors concluded that there was a coherence of effects across the endpoints, with most  
31 endpoints showing a one to three percent change per  $10 \mu g/m^3 PM_{10}$ . Pulmonary function

1 showed a smaller change of 0.15 percent for FEV and 0.08 percent for PEF. These  
2 smaller percent changes are to be expected because there is much less variation in pulmonary  
3 function measurements than in the other measures. The limitations of the methodological  
4 considerations as they pertain to quantitative assessment of the subject individual studies are  
5 discussed in Chapter 12. Dockery and Pope (1994) also noted such limitations in their  
6 review.

7 The primary difficulties in combining studies can be summarized as follows. Most  
8 studies used several endpoints and it is not clear that results for all of the different endpoints  
9 were reported. Most studies used different lag times or moving averages for the pollutants,  
10 and in some cases reported only those which gave positive results. For those studies which  
11 did report results for similar endpoints, many were analyzed with different statistical models.  
12 The short-term studies must take into account serial correlation, and this was done in a  
13 variety of ways in those studies which did adjust for it. For these reasons, key findings from  
14 most of the studies are only summarized here rather than combined formally.

#### 15 16 **Short-Term PM Exposure Hospital Admission Studies**

17 Hospitalization data can provide a measure of the morbidity status of a community  
18 during a specified time frame. Hospitalization data specific for respiratory illness diagnosis,  
19 or more specifically for COPD and pneumonia, index respiratory health status and provide  
20 outcome measures which relate to mortality studies for total and specified respiratory  
21 measures. Tables 1-7 through 1-10 summarize studies that associate hospitalization data with  
22 various measures of PM. Some of the same factors and concerns related to the mortality  
23 studies are at issue for these studies also.

24 Both COPD and pneumonia hospitalization studies show moderate, but statistically  
25 significant relative risks in the range of 1.06 to 1.25 in association with an increase of 50  
26  $\mu\text{g}/\text{m}^3$  in  $\text{PM}_{10}$  or its equivalent. There are also indications of a relationship with heart  
27 disease, admissions, but the evidence is less clear. Overall, these hospitalization studies are  
28 indicative of health outcomes related to PM. They are also supportive of the mortality  
29 studies, especially with the more specific diagnosis relationships.

TABLE 1-7. HOSPITAL ADMISSIONS STUDIES FOR RESPIRATORY DISEASE

Study	PM Type & No. Sites	PM Mean & Range	Ave. Count per Day	Model Type & Lag Structure	Other pollutants measured	Weather & Other Factors	Pollutants in model	Result* (Confidence Interval)
Burnett et al. (1994) All ages in Ontario, Canada, 1983-1988	9 monitoring stations measuring sulfate	sulfate means ranged from 3.1 to 8.2 $\mu\text{g}/\text{m}^3$	108	Lin. regress. on filtered data, 1-d lag best	Ozone	Temperature	none	1.03 (1.02, 1.04)
Thurston et al. (1994) All ages in Ontario, Canada, July and August, 1986-1988	3 monitoring stations measuring sulfate, TSP, and $\text{PM}_{10}$	mean sulfate ranged 38 to 124 (nmole/ $\text{m}^3$ ), $\text{PM}_{10}$ 30 to 39 $\mu\text{g}/\text{m}^3$ , TSP 62 to 87 $\mu\text{g}/\text{m}^3$	14.4	Linear regression on filtered data, 0-d lag best	Ozone, H+, $\text{SO}_2$ , $\text{NO}_2$	Temperature	none  ozone	$\text{PM}_{10}$ 1.09 (0.96, 1.22) $\text{PM}_{10}$ 1.01 (0.87, 1.15)
Thurston et al. (1992) All ages in Buffalo, Albany, New York City, July and August, 1988-1989	3 monitoring stations (one per city) measuring sulfate, H+	(values not given)	Buffalo, 24 Albany, 12, New York, 137	Linear regression on filtered data	Ozone, H+	Temperature	ozone	(not given for PM measures)
Schwartz (in press) Elderly in New Haven, 1988-1990	$\text{PM}_{10}$ monitoring stations averaged, no. of stations not given	mean = 41, 10% tile = 19, 90% tile = 67	8.1	Poisson log-linear regression, 19 day mov. ave. filter, 0-d lag best	Ozone (ppb): mean = 29; 10% tile = 16; 90% tile = 45; $\text{SO}_2$ (ppb): mean = 30; 10% tile = 9; 90% tile = 61	Temperature and dew point adjusted for in the moving average	none  $\text{SO}_2$ (2 day lag)	1.06 (1.00, 1.13) 1.07 (1.01, 1.14)
Schwartz (in press) Elderly in Tacoma, 1988-1990	$\text{PM}_{10}$ monitoring stations averaged, no. of stations not given	mean = 37, 10% tile = 14, 90% tile = 67	4.2	Poisson log-lin. regress. 19 day mov. ave. filter, 0-d lag best	Ozone (ppb): mean = 25; 10% tile = 13; 90% tile = 36; $\text{SO}_2$ (ppb): mean = 17; 10% tile = 6; 90% tile = 28	Temperature and dew point adjusted for in the moving average	none  $\text{SO}_2$ (2 day lag)	1.10 (1.03, 1.17) 1.11 (1.02, 1.20)

\* Relative risk calculated from parameters given by author assuming a 50  $\mu\text{g}/\text{m}^3$  increase in  $\text{PM}_{10}$  on 100  $\mu\text{g}/\text{m}^3$  increase in TSP.

**TABLE 1-8. HOSPITAL ADMISSIONS STUDIES FOR COPD**

Study	PM Type & No. Sites	PM Mean & Range	Ave. Count per Day	Model Type & Lag Structure	Other pollutants measured	Weather & Other Factors	Pollutants in model	Result* (Confidence Interval)
Sunyer et al. (1993) Adults in Barcelona, 1985-1989	15 monitoring stations measuring black smoke	winter 33% tile = 49, 67% tile = 77, summer 33% tile = 36, 67% tile = 55	12	Autoregressive linear regression analysis, 0-d lag best	Sulfur dioxide, winter 33%tile = $49\mu g/m^3$ , 67%tile = 77, summer 33%tile = 36, 67%tile = 55	min temp, dummies for day of week and year	none        SO <sub>2</sub>	winter: 1.15 (1.09,1.21) summer: 1.05 (0.98,1.12)  winter: 1.05 (1.01,1.09) summer: 1.01 (0.97,1.05)
Schwartz (1994f) Elderly in Minneapolis, 1986-1989	6 monitoring stations measuring PM <sub>10</sub>	mean = 36, 10% tile = 18, 90% tile = 58	2.2	Autoregressive Poisson model, 1-d lag best	Ozone, mean = 26 ppb, 10%tile = 11, 90%tile = 41	8 categories of temp. & dew pt., month, year, lin. & quad. time trend	none	1.25 (1.10,1.44)
Schwartz (1994e) Elderly in Birmingham, 1986-1989	1 to 3 monitoring stations measuring PM <sub>10</sub>	mean = 45, 10% tile = 19, 90% tile = 77	2.2	Autoregressive Poisson model, 0-d lag best	Ozone, mean = 25 ppb, 10%tile = 14, 90%tile = 37	7 categories of temp. & dew pt., month, year, lin. & quad. time trend	none	1.13 (1.04,1.22)
Schwartz (1994d) Elderly in Detroit 1986-1989	2 to 11 PM <sub>10</sub> monitoring stations, data available for 82% of possible days	mean = 48, 10% tile = 22, 90% tile = 82	5.8	Poisson autoregressive model using GEE, 0-d lag best	Ozone, mean = 21 ppb, 10%tile = 7, 90%tile = 36	Dummy vars. for temp, month, lin. & quad. time trend	ozone	1.11 (1.04, 1.17)

\* Relative risk calculated from parameters given by author assuming a 50  $\mu\text{g}/\text{m}^3$  increase in  $\text{PM}_{10}$  or 100  $\mu\text{g}/\text{m}^3$  increase in TSP.

TABLE 1-9. HOSPITAL ADMISSIONS STUDIES FOR PNEUMONIA

Study	PM Type & No. Sites	PM Mean & Range	Ave. Count per Day	Model Type & Lag Structure	Other pollutants measured	Weather & Other Factors	Pollutants in model	Result* (Confidence Interval)
Schwartz (1994f) Elderly in Minneapolis, 1986-1989	6 monitoring stations measuring PM <sub>10</sub>	mean = 36, 10%tile = 18, 90% tile = 58	6.0	Autoregressive Poisson mod., 1-d lag best	Ozone: mean 26 ppb; 10% tile 11; 90% tile 41	8 categories of temp. & dew pt., month, year, lin. & quad. time trend	none	1.08 (1.01, 1.15)
Schwartz (1994e) Elderly in Birmingham, 1986-1989	1 to 3 monitoring stations measuring PM <sub>10</sub>	mean = 45, 10% tile = 19, 90% tile = 77	5.9	Autoregressive Poisson mod., 0-d lag best	Ozone: mean 25 ppb; 10% tile 14; 90% tile 37	7 cat. of temp. & dew pt., month, year, lin. & quad. time trend	none	1.09 (1.03, 1.15)
Schwartz (1994d) Elderly in Detroit 1986-1989	2 to 11 PM <sub>10</sub> mon. stations, data for 82% of possible days	mean = 48, 10% tile = 22, 90% tile = 82	15.7	Poisson auto- regress. mod. using GEE, 0-d lag best	Ozone: mean 21 ppb; 10% tile 7; 90% tile 36	Dummy variables for temp, month, lin. & quad. time trend	ozone	1.06 (1.02, 1.10)

TABLE 1-10. HOSPITAL ADMISSIONS STUDIES FOR HEART DISEASE

Study	PM Type & No. Sites	PM Mean & Range	Ave. Count per Day	Model Type & Lag Structure	Other pollutants measured	Weather & Other Factors	Pollutants in model	Result* (Confidence Interval)
Schwartz and Morris (in press) Elderly in Detroit 1986-1989 Ischemic Heart Disease	2 to 11 PM <sub>10</sub> monitoring stations, data available for 82% of possible days	mean = 48, 10% tile = 22, 90% tile = 82	44.1	Poisson auto- regressive model using GEE, 0-d lag best	SO <sub>2</sub> , mean = 25 ppb, 10% tile = 11, 90% tile = 44 CO, mean 2.4 ppm, 10% tile 1.2, 90% tile = 3.8	Dummy vars. for temp, month, lin. & quad. time trend	none  ozone, CO, SO <sub>2</sub>	1.06 (1.02, 1.10)  1.06 (1.02, 1.10)
Burnett et al. (in press) All ages in Ontario, Canada, 1983-1988 Cardiac disease admission	22 sulfate monitoring stations	station means ranged from 3.0 to 7.7 in the summer and 2.0 and 4.7 in the winter	14.4	Linear regression on a 19 day linear filter, 1-d lag best	Ozone averaged 36 ppb	Temperature included in separate analyses by summer and winter	none  ozone	1.04 (1.03, 1.06)  1.04 (1.03, 1.05)

\* Relative risk calculated from parameters given by author assuming a 50  $\mu\text{g}/\text{m}^3$  increase in PM<sub>10</sub> on 100  $\mu\text{g}/\text{m}^3$  increase in TSP.

## Short and Long-Term Exposure Respiratory Disease Studies

Respiratory illness and the factors determining its occurrence and severity are important public health concerns. This effect is of public health importance because of the widespread potential for exposure to PM and because of the very common occurrence of respiratory illness. Of added importance is the fact that recurrent childhood respiratory illness may be a risk factor for later susceptibility to lung damage. The occurrence of lower respiratory morbidity in early childhood may be associated with impaired lung function and growth that appears to persist through adolescence, and certain physicians assert that infections, reactive airways, and inhaled pollutants (mostly cigarette smoke) are the most important risk factors in the development of chronic lung disease. Thus, factors such as the presence of PM (which increases the risk for respiratory symptoms and related respiratory morbidity) are important because of associated public health concern with regard to both the immediate symptoms produced and the longer term potential for increases in the development of chronic lung disease.

### *Acute Respiratory Disease Studies*

Acute respiratory disease studies include several different endpoints, but the majority of authors reported results on at least two of: (1) upper respiratory illness; (2) lower respiratory illness; or (3) cough (See Table 1-11). These relative risks are all estimated for an increase of  $50 \mu\text{g}/\text{m}^3$  in  $\text{PM}_{10}$  (24-h) or its equivalent. The results for upper respiratory illness are very inconsistent: two studies estimate a relative risk near 1.00 whereas four others obtain estimates between 1.14 and 1.55. The relative risks for lower respiratory illness are spread between 1.01 and 2.03, but all are positive. The relative risks for cough include two below 1.0 and go as high as 1.51. All of these are generally suggestive of a PM effect, but whereas the hospital admission studies were all done in a similar manner and resulted in very similar results, these studies used different designs and yield very inconsistent results.

### *Chronic Respiratory Disease Studies*

The three studies listed (Table 1-12) are based on a similar type of questionnaire but were done by two different groups of researchers. All three studies suggest a chronic effect



TABLE 1-11. ACUTE RESPIRATORY DISEASE STUDIES

Study	PM Type & No. Sites	PM Mean & Range	Ave. Rate per Day	Model Type & Lag Structure	Other pollutants measured	Weather & Other Factors	Other pollutants in model	Result* (Confidence Interval)
Schwartz et al. (1994) 300 elementary school children in Six-Cities in U.S., 1984-1988	PM <sub>10</sub> monitoring in each city	median 30 $\mu\text{g}/\text{m}^3$ 10th percentile = 13, 90th percentile = 53	3.1	Autoregressive logistic regression using GEE	Ozone, NO <sub>2</sub> , SO <sub>2</sub>	Temperature	none	1.51 (1.12, 2.05)
							SO <sub>2</sub>	1.39 (0.98, 1.96)
							ozone	1.49 (1.10, 2.01)
Pope et al. (1991), students in the Utah Valley, winter 1989-1990	PM <sub>10</sub> monitoring stations at 3 sites	mean = 46 $\mu\text{g}/\text{m}^3$ , range = 11 to 195	(not given)	Fixed effects logistic regression	Limited monitoring of NO <sub>2</sub> , SO <sub>2</sub> , and ozone. Values were well below the standard	Variables for temperature and time trend	none	Upper resp. 1.20 (1.03, 1.39)
								Lower resp. 1.28 (1.06, 1.56)
Pope et al. (1991), asthmatic children in the Utah Valley, winter 1989-1990	PM <sub>10</sub> monitoring stations at 3 sites	mean = 46 $\mu\text{g}/\text{m}^3$ , range = 11 to 195	(not given)	Fixed effects logistic regression	Limited monitoring of NO <sub>2</sub> , SO <sub>2</sub> , and ozone. Values were well below the standard	Variables for low temperature and time trend	none	Upper resp. 0.99 (0.81, 1.22)
								Lower resp. 1.01 (0.81, 1.27)
Pope and Dockery (1992), symptomatic children in the Utah Valley, winter 1990-1991	PM <sub>10</sub> monitoring stations at 2 sites	mean = 76 $\mu\text{g}/\text{m}^3$ , range = 7 to 251	(not given)	Autoregressive logistic regression using GEE	none	Variable for low temperature	none	Upper resp. 1.20 (1.03, 1.39)
								Lower resp. 1.27 (1.08, 1.49)
								Cough 1.29 (1.12, 1.48)

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TABLE 1-11 (cont'd). ACUTE RESPIRATORY DISEASE STUDIES

Study	PM Type & No. Sites	PM Mean & Range	Ave. Rate per Day	Model Type & Lag Structure	Other pollutants measured	Weather & Other Factors	Other pollutants in model	Result* (Confidence Interval)
Pope and Dockery (1992), asymptomatic children in the Utah Valley, winter 1990-1991	PM <sub>10</sub> monitoring stations at 2 sites	mean = 76 $\mu\text{g}/\text{m}^3$ , range = 7 to 251	(not given)	Autoregressive logistic regression using GEE	none	Variable for low temperature	none	Upper resp. 0.99 (0.78, 1.26) Lower resp. 1.13 (0.91, 1.39) Cough 1.18 (1.00, 1.40)
Hoek and Brunekreef (1993), respiratory disease in school children aged 7 to 12 in Wageningen, Netherlands, winter 1990-1991	Two to 4 monitoring stations measured PM <sub>10</sub>	max = 110 $\mu\text{g}/\text{m}^3$	(not given)	Autoregressive logistic regression using GEE	Max SO <sub>2</sub> = 105 $\mu\text{g}/\text{m}^3$ , max NO <sub>2</sub> = 127 $\mu\text{g}/\text{m}^3$	Variable for ambient temperature and day of study	none	Upper resp. 1.14 (1.00, 1.29) Lower resp. 1.06 (0.86, 1.32) Cough 0.98 (0.86, 1.11)
Schwartz et al. (1991) Study of acute respiratory illness in children in 5 German communities, 1983-1985	Two to 4 monitoring stations in each area measured TSP	medians ranged from 0.5 to 2.9 from 17 to 56 $\mu\text{g}/\text{m}^3$ , 10% tiles from 5 to 34, 90% tiles from 41 to 118		Autoregressive Poisson regression using GEE	median SO <sub>2</sub> levels ranged from 9 to 48 $\mu\text{g}/\text{m}^3$ , median NO <sub>2</sub> levels ranged from 14 to 5 $\mu\text{g}/\text{m}^3$	Most significant terms of day of week, time trend, and weather (terms not listed)	none (TSP was not significant when NO <sub>2</sub> added to model)	1.26 (1.12, 1.42)

TABLE 1-11 (cont'd). ACUTE RESPIRATORY DISEASE STUDIES

Study	PM Type & No. Sites	PM Mean & Range	Ave. Rate per Day	Model Type & Lag Structure	Other pollutants measured	Weather & Other Factors	Other pollutants in model	Result* (Confidence Interval)
Schwartz et al. (1994) Study of respiratory symptoms in 6 U.S. cities, 1984-1988	Daily monitoring of PM <sub>10</sub> , PM <sub>2.5</sub> at each city	median PM <sub>10</sub> = 30 µg/m <sup>3</sup> , 10% tile = 13, 90% tile = 53 median PM <sub>2.5</sub> = 18 µg/m <sup>3</sup> , 10% tile = 7, 90% tile = 37	(not given)	Autoregressive logistic regression using GEE	SO <sub>2</sub> , median = 4 ppb, 10% tile = 1, 90% tile = 18 NO <sub>2</sub> , median = 13 ppb, 10% tile 5, 90% tile = 24, ozone	temperature, day of week, city or residence	all two pollutant models were fitted with minimal effect on PM	Cough (PM <sub>10</sub> lag 1) 1.51 (1.12, 2.05) Upper resp. (PM <sub>10</sub> lag 2) 1.39 (0.97, 2.01) Lower resp. (PM <sub>10</sub> lag 1) 2.03 (1.36, 3.04)
Braun-Fahrlander et al. (1992) Study of preschool children in four areas of Switzerland	Daily monitoring of TSP	(not given)	4.4	Logistic regression	SO <sub>2</sub> , NO <sub>2</sub> , and ozone levels not given	city, risk strata, season, temperature	none	Upper resp. 1.55 (1.10, 2.24)
Roemer et al. (1993) Study of children with chronic respiratory symptoms in Wageningen, The Netherlands	Daily monitoring of PM <sub>10</sub>	6 days above 110 µg/m <sup>3</sup>	.094 incidence rate	Autoregressive logistic regression	SO <sub>2</sub> and NO <sub>2</sub> means not given	(not given)	none	Cough (not given, probably less than one)
Dusseldorf et al. (1994) Study of adults near a steel mill in The Netherlands	Daily monitoring of PM <sub>10</sub> , iron, sodium, silicon, and manganese	mean PM <sub>10</sub> = 54 µg/m <sup>3</sup> , range = 4 to 137)	(not given)	Logistic regression	Geometric mean iron = 501 ng/m <sup>3</sup> , manganese = 17 ng/m <sup>3</sup> , silicon = 208 ng/m <sup>3</sup>	(not given)	none	Cough 1.14 (0.98, 1.33)

TABLE 1-11 (cont'd). ACUTE RESPIRATORY DISEASE STUDIES

Study	PM Type & No. Sites	PM Mean & Range	Ave. Rate per Day	Model Type & Lag Structure	Other pollutants measured	Weather & Other Factors	Other pollutants in model	Result* (Confidence Interval)
Ostro et al. (1991) Study of adult asthmatics in Denver, Colorado November 1987 to February 1988	Two monitors provided daily measurements of PM <sub>2.5</sub>	22 $\mu\text{g}/\text{m}^3$ , range = 0.5 to 73	15 (out of 108)	Autoregressive logistic regression	nitric acid, sulfates, nitrates, SO <sub>2</sub> , and H <sup>+</sup>	day of survey, day of week, gas stove, minimum temperature	none	Cough 1.09 (0.57, 2.10)
Ostro et al. (1993) Study of non-smoking adults in Southern California	Apparently one site (Azusa). PM measurements included sulfate fraction and COHS	mean sulfate = 84.2/person for $\mu\text{g}/\text{m}^3$ , range = lower, 2 to 37 mean COHS = 12 per upper 100 ft, range = 4 to 26	10.2/person, upper	Logistic regression	ozone, mean = 7 pphm, range = 1 to 28	temperature, rain humidity	none	Sulfates: Upper resp. 0.91 (0.73, 1.15) Lower resp. 1.48 (1.14, 1.91)

\* Relative risk calculated from parameters given by author assuming a 50  $\mu\text{g}/\text{m}^3$  increase in PM<sub>10</sub> on 100  $\mu\text{g}/\text{m}^3$  increase in TSP.

TABLE 1-12. CHRONIC RESPIRATORY DISEASE STUDIES

Study	PM Type & No. Sites	PM Mean & Range	Overall Symptom Rate	Model Type & Lag Structure	Other pollutants measured	Other Covariates	Other pollutants in model	Result* (Confidence Interval)
Ware et al. (1984) Study of respiratory symptoms in children in 6 cities in the U.S. Survey done 1974-1977	Daily monitoring of TSP, SO <sub>2</sub> , NO <sub>2</sub> , and ozone at each city	City TSP means ranged from 39 to 114 µg/m <sup>3</sup>	Cough, .08, Bronchitis .08, Lower resp. .19	Logistic regression	SO <sub>2</sub> , NO <sub>2</sub> , and ozone	age, gender, parental education, maternal smoking	none	Cough 2.75 (1.92, 3.94) Bronchitis 2.80 (1.17, 7.03) Lower resp. 2.14 (1.06, 4.31)
Dockery et al. (1989) Study of respiratory symptoms in children in 6 cities in the U.S. Survey done 1980-1981	Daily monitoring of PM <sub>15</sub> , sulfate fraction at each city	City PM <sub>15</sub> means ranged from 20 to 59 µg/m <sup>3</sup>	Cough, .02 to .09, Bronchitis .04 to .10, Lower resp. .07 to .16	Logistic regression	SO <sub>2</sub> , NO <sub>2</sub> , and ozone	age, gender, maternal smoking	none	Cough 5.39 (1.00, 28.6) Bronchitis 3.26 (1.13, 10.28) Lower resp. 2.93 (0.75, 11.60)
Chapman et al. (1985) Study of persistent cough and phlegm (bronchitis) in adults in four communities in Utah. Survey done in 1976	Daily monitoring of TSP, and sulfate fraction at each city	Previous 5 year TSP ranged from 11 to 115 µg/m <sup>3</sup>	.02 to .05 by city	Logistic regression	SO <sub>2</sub> , NO <sub>2</sub>	smoking	none	Mothers 1.75 (1.21, 2.54) Fathers 1.94 (1.16, 3.25)
Neas et al. (1994) Study of children aged 7 to 11 from six cities in U.S. Survey done 1983-1986.	PM <sub>2.5</sub>	Not given	Not given	Logistic regression	NO <sub>2</sub>	household smoking, gas stove, age, gender	none  none	Cough 1.08 (0.76, 1.53) Bronchitis 1.32 (0.98, 1.79) Lower resp. 1.23 (0.98, 1.55)

\* Estimates calculated from data tables assuming a 50 µg/m<sup>3</sup> increase in PM<sub>10</sub> on 100 µg/m<sup>3</sup> increase in TSP.

of particulate matter on respiratory disease, but the studies suffer from the usual difficulty of cross sectional studies. The PM effect estimates are based on variations in exposure which are determined by different numbers of locations. In the first two studies there were six locations and, in the second, four. The results seen were consistent with a PM gradient, but it is impossible to separate out the effect of PM any other factors or pollutants which have the same gradient.

### **Short and Long-Term Exposure Pulmonary Function Studies**

Pulmonary function studies are part of a comprehensive investigation of the possible effects of any air pollutant. Measurements can be made in the field, they are noninvasive, and their reproducibility has been well documented; and guidelines for reference values and interpretative strategies of lung function tests have been prepared. Various factors are important determinants of lung functions. Lung function in children has been related to genetic factors that exert their greatest influence through general stature as measured by height and age. Growth patterns in children differ by gender and lung function declines with age among adults. Studies of the growth of pulmonary function and generalized growth models consider factors of how growth is statistically dependent on initial measures of function, and how it is related to respiratory illness in childhood. The effects of active smoking and passive smoking are also considered. Epidemiological studies relating ambient PM measures to decrements in pulmonary function represent a potentially important health effect.

The acute pulmonary function studies (Table 1-13) are suggestive of a short term effect resulting from particulate pollution. Peak flow rates show decreases in the range of 30 to 40 ml/sec to be associated with an increase of  $50 \mu\text{g}/\text{m}^3$  in  $\text{PM}_{10}$  (24-h) or its equivalent. The results appear to be larger in symptomatic groups such as asthmatics. The effects are seen across a variety of study designs, authors, and analysis methodologies. Effects using  $\text{FEV}_1$  or FVC as endpoints are less consistent.

The chronic pulmonary function studies are less numerous than the acute studies (Table 1-13). The one study with good monitoring showed no effect from particulate pollution. Cross sectional studies require very large sample sizes to detect differences because the studies cannot eliminate person to person variation which is much larger than the

TABLE 1-13. ACUTE AND CHRONIC PULMONARY FUNCTION CHANGES

Study Period, Population	PM Type & No. Sites	PM Mean & Range	Model Type & Lag Structure	Other pollutants measured	Weather & Other Factors	Pollutants in model	Decrease* (Confidence Interval)
Dockery et al. (1982)- School age children in Steubenville, OH, measured at three times between 1978 and 1980	Single station measuring TSP	up to 455 $\mu\text{g}/\text{m}^3$	individual regression analyses for each child, coefficients pooled across time	SO <sub>2</sub>	average temperature	TSP	FVC: 8.1 ml FEV <sub>0.75</sub> : 1.8 ml Note: decreases were statistically significant
Dassen et al. (1986) School age children in The Netherlands, measured in November, 1984 and January, 1985	Six station network measuring TSP, RSP (PM <sub>10</sub> )	TSP and RSP both exceeded 200 $\mu\text{g}/\text{m}^3$	multiple linear regression	SO <sub>2</sub>	technician, appliance, presence of colds	RSP	slopes not given but FVC, FEV <sub>1</sub> , and PEFR were significantly reduced during episodes
Quackenboss et al. (1991) - Asthmatic children aged 6 to 15 years in Tuscon, AZ, measured in May and November, 1988	Individual monitoring of homes of PM <sub>2.5</sub> , PM <sub>10</sub>		Random effects linear model	NO <sub>2</sub>	temperature, wind speed, dew point	PM <sub>2.5</sub>	PEFR: 375 ml/s Note: these are diurnal rather than daily changes
Pope et al. (1991) - Study of asthmatic children in the Utah Valley	PM <sub>10</sub> monitors in Orem and Lindon, Utah	PM <sub>10</sub> ranged from 11 to 195 $\mu\text{g}/\text{m}^3$	Weighted least squares regression	SO <sub>2</sub> , NO <sub>2</sub> , ozone	low temperature	PM <sub>10</sub>	PEFR: 55 ml/s (24, 86)
Pope and Dockery (1992) - Study of non- asthmatic symptomatic and asymptomatic children in the Utah Valley	PM <sub>10</sub> monitors in Orem and Lindon, Utah	PM <sub>10</sub> ranged from 11 to 195 $\mu\text{g}/\text{m}^3$	Weighted least squares regression	SO <sub>2</sub> , NO <sub>2</sub> , ozone	low temperature	PM <sub>10</sub>	Symptomatic PEFR 30 ml/s (10, 50) Asympto- matic PEFR 21 ml/s (4, 38)

TABLE 1-13 (cont'd). ACUTE AND CHRONIC PULMONARY FUNCTION CHANGES

Study Period, Population	PM Type & No. Sites	PM Mean & Range	Model Type & Lag Structure	Other pollutants measured	Weather & Other Factors	Pollutants in model	Decrease* (Confidence Interval)
Koenig et al. (1993) - Study of asthmatic and non-asthmatic elementary school children in Seattle, WA in 1989 and 1990	PM <sub>2.5</sub> calibrated from light scattering	PM <sub>2.5</sub> ranged from 5 to 45 $\mu\text{g}/\text{m}^3$	Random effects linear regression	none	height, temperature	PM <sub>2.5</sub>	Asthmatics FEV <sub>1</sub> 42 ml (12, 73) FVC 45 ml (20, 70) Non-asthmatics FEV <sub>1</sub> 4 ml (-7, 15) FVC -8 ml (-20, 3)
Hoek and Brunekreef (1993) - Study of children aged 7 to 12 in Wageningen, Netherlands	Single site measure black smoke. PM <sub>10</sub> was measured during episodes	range of PM <sub>10</sub> was 30 to 144 $\mu\text{g}/\text{m}^3$	SAS procedure AUTOREG	SO <sub>2</sub> , NO <sub>2</sub>	day of study	PM <sub>10</sub>	PEFR 41 ml/s (-8, 90)
Roemer et al. (1993) - Study of children with chronic respiratory symptoms in The Netherlands	Single site measure black smoke. PM <sub>10</sub> was measured using an Anderson dichot	range of PM <sub>10</sub> was 30 to 144 $\mu\text{g}/\text{m}^3$	multiple linear regression analysis	SO <sub>2</sub> , NO <sub>2</sub>	none	PM <sub>10</sub>	PEFR 34 ml/s (9, 59)
Pope and Kanner (1993) - Study of adults in the Utah Valley from 1987 to 1989	PM <sub>10</sub> was collected daily from the north Salt Lake site	PM <sub>10</sub> daily mean = 55 $\mu\text{g}/\text{m}^3$ , ranged from 1 to 181 $\mu\text{g}/\text{m}^3$	Linear regression on difference in PFT as a function of PM <sub>10</sub>	Limited monitoring of SO <sub>2</sub> , NO <sub>2</sub> , and ozone	low temperature	PM <sub>2.5</sub>	FEV <sub>1</sub> 29 ml (7, 51) FVC 15 ml (- 15, 45)
Neas et al. (1994) - Study of lung function in children in 6 cities in the U.S. Data collected from 1983-1988.	Daily monitoring of PM <sub>2.5</sub> , sulfate fraction at each city	not given	Linear regression using logarithm of PFT value	SO <sub>2</sub> , NO <sub>2</sub> , and ozone	city, gender parental education, history of asthma, age, height, weight	PM <sub>2.5</sub>	FVC and FEV <sub>1</sub> not changed. Values could not be converted to mls.

\* Decreases in lung function calculated from parameters given by author assuming a 50  $\mu\text{g}/\text{m}^3$  increase in PM<sub>10</sub> or 100  $\mu\text{g}/\text{m}^3$  increase in TSP.



1 within person variation. Thus the lack of statistical significance cannot be taken as proof of  
2 no effect.

### 3 4 **Comparison of Effects of PM<sub>10</sub> Versus PM<sub>2.5</sub> on Respiratory Disease and Pulmonary** 5 **Function**

6 The most direct comparison of effects of PM<sub>10</sub> versus PM<sub>2.5</sub> are possible when studies  
7 include both exposure measures in their analyses. This occurred in the Six City study for  
8 Steubenville children, the Tuscon study, and the Uniontown study for pulmonary function  
9 changes (Table 1-13). None of these studies directly showed that one of these PM measures  
10 was a significantly better predictor than the other for pulmonary function effects. The study  
11 did suggest that PM<sub>2.5</sub> may be better predictor of lung function change.

12 A few other studies used PM<sub>2.5</sub> as a measure of particulate exposure. One on lung  
13 function in asthmatic and non-asthmatic school children in Seattle (Table 1-13) found a  
14 slightly larger effect of PM<sub>2.5</sub> for asthmatics, but a slightly smaller effect for non-asthmatics  
15 when compared with the PM<sub>10</sub> studies. Also, the Ostro et al. (1991) study of respiratory  
16 disease in Denver found an effect that was in the middle of the range of effects found by the  
17 PM<sub>10</sub> studies.

18 Based on the above information, there is currently no obvious way by which to clearly  
19 distinguish morbidity effects of PM<sub>10</sub> versus PM<sub>2.5</sub>. Even the suggestive evidence leaves the  
20 scales in a balanced position.

### 21 22 **Mortality Effects of Acid Aerosols**

23 Few epidemiological studies have examined mortality data for an association with  
24 ambient particulate strong acid aerosol (H<sup>+</sup>) exposures. The scarcity of the analyses is due  
25 to the absence of adequate ambient acid measurement techniques in the past, and to the lack  
26 of routine acid aerosol monitoring in more recent years. Some studies now exist which  
27 suggest that human health effects may be associated with exposures to ambient acid aerosols,  
28 both: (1) as derived from reexamination of older, historically important data on air pollution  
29 episode events in North America and Europe and (2) as can be deduced from limited recent  
30 epidemiology studies carried out in the U.S., Canada, and Europe.

Historical and present-day evidence suggests that strongly acidic PM can be associated with both acute and chronic human health effects. Evidence from historical pollution for episodes, notably the London Fog episodes of the 1950's and early 1960's, indicates that extremely elevated daily acid aerosol concentrations (on the order of  $400 \mu\text{g}/\text{m}^3$  as  $\text{H}_2\text{SO}_4$ , or roughly  $8,000 \text{ nmoles}/\text{m}^3 \text{ H}^+$ ) may be associated with excess acute human mortality when present as a copollutant with elevated concentrations of PM and  $\text{SO}_2$ . In addition, Thurston et al. (1989) and Ito et al. (1993) both found significant associations between acid aerosols and mortality in London during non-episode pollution levels ( $\leq 30 \mu\text{g}/\text{m}^3$  as  $\text{H}_2\text{SO}_4$ , or  $\leq$  approximately  $600 \text{ nmoles}/\text{m}^3 \text{ H}^+$ ), although these associations could not be separated from those for BS or  $\text{SO}_2$ . The only attempts to date to associate present-day levels of acidic aerosols with acute and chronic mortality (Dockery et al., 1992; Dockery et al., 1993b, respectively) were unable to do so, but weaknesses in these analyses (in particular, too limited  $\text{H}^+$  data for the analysis) may have made associations undetectable. At very high concentrations that do not occur in the ambient air, mortality in laboratory animals can occur following acute exposure, due primarily to laryngeal or bronchoconstriction; larger particles are more effective in this regard than are smaller ones.

## **Respiratory Illness Effects of Acid Aerosols**

Historical and present-day evidence suggests that there can be both acute and chronic effects of strongly acidic PM on human health. Increased hospital admissions for respiratory causes were documented during the London Fog episode of 1952, and this association has now been observed under present-day conditions, as well. Thurston et al. (1992) and Thurston et al. (1994) have noted associations between ambient acidic aerosols and summertime respiratory hospital admissions in both New York State and Toronto, Canada, respectively, even after controlling for potentially confounding temperature effects. In the latter of these studies, significant independent  $\text{H}^+$  effects remained even after simultaneously considering the other major copollutant,  $\text{O}_3$ , in the regression model. In these studies,  $\text{H}^+$  effects were estimated to be the largest during acid aerosol episodes ( $\text{H}^+ \geq 10 \mu\text{g}/\text{m}^3$  as  $\text{H}_2\text{SO}_4$ , or  $\approx 200 \text{ nmoles}/\text{m}^3 \text{ H}^+$ ), which occur roughly 2 to 3 times per year in eastern North America. These studies provide evidence that present-day strongly acidic aerosols

1 may represent a portion of PM which is particularly associated with significant acute  
2 respiratory disease health effects in the general public.

3 Results from recent acute symptoms studies of healthy children indicate the potential for  
4 acute acidic PM effects in this population. While the 6-City study of diaries kept by parents  
5 of children's respiratory and other illness did not demonstrate  $H^+$  associations with lower  
6 respiratory symptoms except at  $H^+$  above 110 nmoles/ $m^3$  (Dockery et al., 1994), upper  
7 respiratory symptoms in two of the cities were found to be most strongly associated with  
8 daily measurements of  $H_2SO_4$  (Schwartz, et al. 1991).

9 Studies of the effects of chronic  $H^+$  exposures on children's respiratory health and lung  
10 function are generally consistent with effects as a result of chronic  $H^+$  exposure.  
11 Preliminary analyses of bronchitis prevalence rates as reported across the 6-City study locales  
12 were found to be more closely associated with average  $H^+$  concentrations than with PM in  
13 general (Speizer, 1989). A follow-up analysis of these cities and a seventh locality which  
14 controlled the analysis for maternal smoking and education and for race, suggested  
15 associations between summertime average  $H^+$  and chronic bronchitic and related symptoms  
16 (Damokosh et al., 1993). The relative odds of bronchitic symptoms with the highest acid  
17 concentration (58 nmoles/ $m^3$   $H^+$ ) versus the lowest concentration (16 nmoles/ $m^3$ ) was 2.4  
18 (95% CI: 1.9 to 3.2). Furthermore, in a follow-up study of children in 24 U.S. and  
19 Canadian communities (Dockery et al., 1993a) in which the analysis was adjusted for the  
20 effects of gender, age, parental asthma, parental education, and parental allergies, bronchitic  
21 symptoms were confirmed to be significantly associated with strongly acidic PM (relative  
22 odds = 1.7, 95% CI: 1.1 to 2.4). It was also found in the 24-Cities study that mean FVC  
23 and  $FEV_{1.0}$  were lower in locales having high particle strong acidity (Raizenne et al., 1993).  
24 Thus, chronic exposures to strongly acidic PM may have effects on measures of respiratory  
25 health in children.

26 The respiratory tract has an array of defense mechanisms to kill, detoxify, and  
27 physically remove inhaled material, and these defenses may be altered by exposure to  $H_2SO_4$   
28 at levels  $< 1,000 \mu g/m^3$ . Acid aerosols alter mucociliary clearance in human and laboratory  
29 animals, with effects dependent on exposure concentration and the region of the lung being  
30 studied. For example 1- to 2-h resting exposures of humans to  $100 \mu g/m^3$  accelerate  
31 clearance in large bronchi, but slows clearance in smaller more peripheral airways.

1 Clearance in asthmatics is also affected, but the results are not clearly interpretable. Long-  
2 term exposure also affects mucociliary clearance in animals. For example, in rabbits  
3 exposed intermittently for 125  $\mu\text{g}/\text{m}^3$   $\text{H}_2\text{SO}_4$  for 1 year, clearance was accelerated during  
4 exposure but was depressed 6 months after exposure ceased. These responses are complex  
5 and are accompanied by histological and chemical changes in mucus and epithelial secretory  
6 cells. Defenses, such as resistance to bacterial infection, may be altered by acute exposure  
7 to concentrations of  $\text{H}_2\text{SO}_4$  around 1,000  $\mu\text{g}/\text{m}^3$ .

8 Severe morphologic alterations in the respiratory tracts of animals occur at high acid  
9 levels. At low levels and with chronic exposure, the main response seems to be hypertrophy  
10 and/or hyperplasia of mucus secretory cells in the epithelium; these alterations may extend to  
11 the small bronchi and bronchioles, where secretory cells are normally rare or absent.

12 Limited data also suggest that exposure to acid aerosols may affect the phagocytic  
13 functioning of alveolar macrophages; the lowest level examined to date is 500  $\mu\text{g}/\text{m}^3$   $\text{H}_2\text{SO}_4$ .  
14 Alveolar region particle clearance is accelerated by repeated  $\text{H}_2\text{SO}_4$  exposures to as low as  
15 250  $\mu\text{g}/\text{m}^3$ ; higher levels retard clearance. Acute exposure of rabbits to lower concentrations  
16 (e.g., 75  $\mu\text{g}/\text{m}^3$   $\text{H}_2\text{SO}_4$ ) can affect other alveolar macrophage functions.

## 18 **Pulmonary Function Effects of Acid Aerosols**

19 Both acute and chronic exposure of laboratory animals to  $\text{H}_2\text{SO}_4$  at levels well below  
20 lethal ones will produce functional changes in the respiratory tract. The pathological  
21 significance of some of these are greater than for others. Acute exposure will alter  
22 pulmonary function, largely due to bronchoconstrictive action. However, attempts to  
23 produce changes in airway resistance in healthy animals at levels below 1  $\text{mg}/\text{m}^3$  have been  
24 largely unsuccessful, except when the guinea pig has been used. The lowest effective level  
25 of  $\text{H}_2\text{SO}_4$  producing bronchoconstriction to date in the guinea pig is 100  $\mu\text{g}/\text{m}^3$  (1-h  
26 exposure). In general, smaller size droplets are more effective in altering pulmonary  
27 function, especially at low concentrations. Yet even in the guinea pig, there are  
28 inconsistencies in the type of response exhibited towards acid aerosols. Chronic exposure to  
29  $\text{H}_2\text{SO}_4$  is also associated with alterations in pulmonary function (e.g., changes in the  
30 distribution of ventilation and in respiratory rate in monkeys). But, in these cases, effective  
31 concentrations are  $\geq 500$   $\mu\text{g}/\text{m}^3$ . Hyperresponsive airways have been induced with repeated

1 exposures to 250  $\mu\text{g}/\text{m}^3$   $\text{H}_2\text{SO}_4$  in rabbits, and have been suggested to occur following single  
2 exposures at 75  $\mu\text{g}/\text{m}^3$ .

3 Ten human clinical studies since 1988 have confirmed previous findings that healthy  
4 subjects do not experience decrements in lung function following single exposures to  $\text{H}_2\text{SO}_4$   
5 at levels up to 2,000  $\mu\text{g}/\text{m}^3$  for 1 h, even with exercise and use of acidic gargles to minimize  
6 neutralization by oral ammonia. Mild lower respiratory symptoms occur at exposure  
7 concentrations in the  $\text{mg}/\text{m}^3$  range, particularly with larger particle sizes.

8 There is no clearly established exposure-response relationship across studies. Asthmatic  
9 subjects appear to be more sensitive than healthy subjects to the effects of acid aerosols on  
10 lung function, but reported effective concentrations differ widely among studies. Adolescent  
11 asthmatics may be more sensitive than adult asthmatics, and may experience small  
12 decrements in lung function in response to  $\text{H}_2\text{SO}_4$  at exposure levels only slightly above peak  
13 ambient levels (e.g., less than 100  $\mu\text{g}/\text{m}^3$ ). Although the reasons for the inconsistency  
14 among studies remain largely unclear, individual variability in sensitivity and subject  
15 selection may be an important factors. Even in studies reporting an overall absence of  
16 effects on lung function, occasional asthmatic subjects appear to demonstrate clinically  
17 important effects. Two studies from different laboratories have suggested that responsiveness  
18 to acid aerosols may correlate with the degree of baseline airway hyperresponsiveness.  
19 However, based on very limited studies, the elderly and individuals with chronic obstructive  
20 pulmonary disease do not appear to be particularly more susceptible to the effects of acid  
21 aerosols on lung function than healthy adults.

22 Two recent studies have examined the effects of exposure to both  $\text{H}_2\text{SO}_4$  and ozone on  
23 lung function in healthy and asthmatic subjects. Both studies found evidence that 100  $\mu\text{g}/\text{m}^3$   
24  $\text{H}_2\text{SO}_4$  may potentiate the response to ozone, in contrast with previous studies. Recent  
25 summer camp (and schoolchildren) studies of lung function have also indicated a significant  
26 association between acute exposures to acidic PM and decreases in the lung function of  
27 children independent of those associated with  $\text{O}_3$  (Studnicka et al., 1995; Neas et al, 1995).

28 In view of uncertainties about differences between high acid concentrations needed to  
29 produce effects in animal studies and low concentrations found in the human environment,  
30 the epidemiologic evidence does not establish a clear role for acid aerosols as a primary  
31 agent contributing to ambient PM exposure effects on pulmonary function.

## Coherence of Epidemiologic Findings

Factors involved in evaluating both the data and the entire group of epidemiological studies, include the strength of association, the consistence of the association, as evidenced by its repeated observation by different persons, in different places, circumstances and time, and the consistency with other known facts (Bates, 1992). One can look for interrelationships between different health indices to provide a stronger and more consistent synthesis of available information. The various findings that support a picture of coherence would provide a stronger case with quantitative studies as opposed to qualitative studies. Other studies may be inappropriate to use in such a discussion, and the quality of the study should be considered. Bates (1992) states that the difficulty with discussing any index of internal coherence is that this requires a series of judgements on the reliability of the individual findings and observations. The outcome of a coherence discussion then is a qualitative presentation in the end, not quantitative. Thus, coherence cannot be formally measured.

Bates (1992) also noted that the strength of different health indexes are important as are difficulties in assessing exposure. Bates (1992) also suggests three areas to look for coherence: (1) within epidemiological data, (2) between epidemiological and animal toxicological data, and (3) between epidemiological, controlled human and animal data.

Coherence by its nature considers biological relationships of exposure to health outcome. The biologic mechanism underlying an acute pulmonary function test reduction in children is most likely not part of the acute basis for a change in the mortality rate of a population exposed in an older group of individuals. In looking for coherence one should compare outcomes that look at similar time frames—daily hospitalizations compared to daily mortality rather than monthly hospitalizations. Overall the data indicates that PM has a relationship with a continuum of health outcomes, but the studies may not establish a coherence between them. The underlying mechanisms may be different.

The principal health outcome for which coherence is desirable is mortality, the death rate in a population. This can be considered within the endpoint and/or in other endpoints. Of the various morbidity outcomes studied and discussed in the earlier part of the chapter, hospitalization studies reviewed in the chapter support this notion. The mortality studies suggest that these specific causes provide stronger relationships (i.e., larger RR estimates)

1 than total mortality. The outcome potentially most related is hospital admission for  
2 respiratory or cardiovascular causes in the older age group (i.e., > 65 years old). In a  
3 qualitative sense, the increased mortality found in that age group should also be paralleled by  
4 increased hospital admissions.

5 Partial coherence is established by those studies in which increased incidence of  
6 different health outcomes associated with PM are found in the same population, as is the case  
7 for the following examples, based on currently published studies:

- 8 ●Detroit: Mortality mainly in elderly populations, hospital admissions for respiratory  
9 causes and for cardiovascular causes in the elderly;
- 10 ●Birmingham: Mortality mainly in the elderly, hospital admissions for the elderly;
- 11 ●Philadelphia: Mortality and hospital admissions for pneumonia in the elderly;
- 12 ●Utah Valley: Mortality and hospital admissions for respiratory causes in adults.

13  
14 Also, pulmonary function, respiratory symptoms, and medication use in asthmatic subjects of  
15 all ages; hospital admissions for respiratory symptoms, pulmonary function, respiratory  
16 symptoms, and medication use in healthy school children, pulmonary function in  
17 symptomatic and asymptomatic children; and elementary school absences in children were  
18 found to be associated with PM exposures in Utah Valley. A similar study found a PM  
19 effect on pulmonary function in smokers with COPD in Salt Lake Valley. The Utah Valley  
20 population was largely non-smoking, so smoking was not likely to be a source of  
21 confounding.

22 While these multiple outcomes did not occur in strictly identical subgroups of each  
23 population, there was probably a sufficient degree of overlap to indicate that PM was a  
24 significant predictor of a wide range of health outcomes within a specific community. The  
25 symptoms serious enough to warrant hospitalization and the major part of the excess  
26 mortality occurred in the elderly sub-group of the population. However, a significant  
27 decrement in pulmonary function and increased incidence of symptoms associated with daily  
28 increases in PM occurred in children in Utah Valley, along with a "quality of life" effect  
29 measured by lost school days. Thus, there is evidence for increased risk of health effects  
30 related to PM exposure ranging in seriousness from asymptomatic pulmonary function  
31 decrements, to respiratory symptoms and cardiopulmonary symptoms sufficiently serious to

warrant hospitalization, and to excess mortality from respiratory and cardiovascular causes, especially in those older than 65 years of age.

Children may also be at increased risk of pulmonary function changes and increased incidence of symptoms associated with PM exposure. While we have arrayed these health outcomes in order of increasing severity, there is as yet little indication that there is a progression of effects in any single individual associated with increasing exposure to PM. The "exposure-response" relationship that is derived in most studies must be understood as characterizing population risk from population exposure. Additional studies are needed to define the relationship(s) among individual exposure to PM and other stress factors, individual risk, and individual progression among disease states. Differences in PM dosimetry in the developing, aged, or diseased respiratory tract may also contribute to increased susceptibility.

The coherence of the various health effects in humans could be established more conclusively from epidemiology studies if there were better evidence. We cannot prove that the people that suffered respiratory symptoms in response to PM exposure were among the same people who suffered pulmonary function decrements from PM exposure in the past, that those who were admitted to hospital for respiratory or cardiopulmonary causes in response to PM exposure were among those who had suffered respiratory symptoms or pulmonary function decrements from earlier PM exposures, nor that those who died from PM exposure were among those who had earlier shown other health endpoints associated with PM exposures. Such information could, in principle, be extracted from longitudinal data bases such as those collected by health care providers; however, although some such efforts are now being considered, the preferred design for such a study is a prospective design rather than a retrospective design. If and when these studies are completed, they could be useful in future PM health assessments.

### **1.13 BIOLOGICAL PLAUSIBILITY: POTENTIAL MECHANISMS OF ACTION**

Chapter 13, the Integrative Health Synthesis Chapter, incorporates key information of the types summarized in the several preceding sections of this chapter. It also importantly



1 discusses key points relating to evaluation of the biological plausibility of the new  
2 epidemiologic findings, the identification of special risk groups, and the interpretation of  
3 implications of reported relative risk estimates for associations between ambient PM exposure  
4 indices and mortality/morbidity effects. Each of these latter three topics are accorded  
5 separate sections in this Executive Summary, starting with this one on biological plausibility.

6 Epidemiologic studies have suggested that ambient particulate exposure may be  
7 associated with increased mortality and morbidity at PM concentrations below those  
8 previously thought to affect human health (Section 1.12 and Chapter 12). However, the  
9 biological plausibility of a causal relationship between low concentrations of PM and daily  
10 mortality and morbidity rates is neither intuitively obvious nor expected based on  
11 experimental studies of the toxicity of inhaled particles. As indicated in Chapter 11, chronic  
12 toxicity from poorly soluble particles has been observed based on the slow accumulation of  
13 large lung burdens of particles, not due to small daily fluctuations of one or another of the  
14 specific PM constituents discussed in that chapter. Two possible exceptions can be noted.  
15 Acute toxicity from inhaled particles has been demonstrated with acidic particles, but only at  
16 much higher particle concentrations than those observed in the recent epidemiology studies  
17 reporting an association between low-level PM concentrations and morbidity/mortality.  
18 Acute toxicity resulting in death has also been reported in rats inhaling singlet ultrafine  
19 particles ( $<0.05\ \mu\text{m}$ ) formed in the pyrolysis of perfluorinated compounds at concentrations  
20 of 60 to 200  $\mu\text{g}/\text{m}^3$  (Oberdörster et al., 1995; Warheit et al., 1990), but the significance of  
21 these findings for ambient human exposures is yet to be determined.

22 To approach the difficult problem of determining if reported associations between low-  
23 level PM concentrations and daily morbidity and mortality are biologically plausible, one  
24 must consider: the chemical and physical characteristics of the particles in the inhaled  
25 atmospheres; the characteristics of the morbidity/mortality observed and the affected  
26 population; as well as potential mechanisms that might link the two. Several salient  
27 considerations related to the evaluation of biological plausibility of the epidemiology findings  
28 are discussed below.

## Characteristics of Observed Morbidity and Mortality

If daily mortality rates are increased in association with elevated ambient particulate concentrations, what are the people dying of? Schwartz (1994) addressed this question by comparing causes of death in Philadelphia on high pollution days (average =  $141 \mu\text{g}/\text{m}^3$ ) with causes of deaths on lower pollution days (average =  $47 \mu\text{g}/\text{m}^3$ ). On the high pollution days there was a higher relative increase in deaths due to chronic obstructive pulmonary disease (COPD) (RR = 1.25), pneumonia (RR = 1.13), cardiovascular disease (RR = 1.09) and stroke (RR = 1.15). There was also an increase in reports of respiratory factors being contributing causes in the deaths and a higher relative age of those dying. The patterns of causes of death and age of those dying were found to be similar to the patterns observed in the London smog deaths of 1952.

Other studies on associations of morbidity with particulate pollution noted small decreases (2 to 2.5%) in pulmonary function (FVC or  $\text{FEV}_1$ ) in smokers on high pollution days ( $100 \mu\text{g}/\text{m}^3$ ; Salt Lake City; Pope and Kanner, 1993) and in nonsmokers ( $> 60 \mu\text{g}/\text{m}^3$ ; NHANES I data, Chestnut et al., 1991). An increased number of asthma attacks among working age adults was correlated with increases in particulate pollution over a 3-year period (average particle level =  $76 \mu\text{g}/\text{m}^3$ ) in Helsinki (Pönkä, 1991). Thus, the characteristics of health effects on high particle pollution days are mainly cardiopulmonary in nature and are the types of effects that can be considered plausibly related to airborne toxicants.

It is also of interest to consider the health status of the people affected. People with previously existing health conditions (such as COPD, asthma, or other chronic debilitating conditions) are logically likely to be more susceptible to effects from exposure to particulate pollutants than would be healthy persons. Such a situation might result in an increased daily mortality rate on days with higher  $\text{PM}_{10}$ , followed by a decreased daily mortality rate so that the average mortality rate over a longer time period would not be affected.

Data on the relative effect of particle exposures in persons with pre-existing pulmonary disease compared to healthy persons do not yield a clear picture. Pope and Kanner (1993) reported an approximate 2% decline in  $\text{FEV}_1$  in smokers with mild to moderate COPD during an increased concentration in  $\text{PM}_{10}$  of  $100 \mu\text{g}/\text{m}^3$  in Salt Lake City. However, persons with severe COPD (average  $\text{FEV}_1$  equal to 50% of predicted) had no further reduction in pulmonary function upon acute (2 h) exposure to  $90 \mu\text{g}/\text{m}^3$   $\text{H}_2\text{SO}_4$  in clinical

1 studies (Morrow et al., 1994). Exercising asthmatics experienced mild bronchoconstriction  
2 following the same exposures. In a separate study, exercising adolescent asthmatics exposed  
3 to  $68 \mu\text{g}/\text{m}^3$   $\text{H}_2\text{SO}_4$  experienced reduced pulmonary function (average of 6% decrease in  
4  $\text{FEV}_1$ ) (Koenig et al., 1989), but in another study, exercising asthmatics did not respond to  
5 exposures to as high as  $130 \mu\text{g}/\text{m}^3$   $\text{H}_2\text{SO}_4$  (Avol et al., 1990). Using an elastase-induced rat  
6 model of emphysema, Mauderly et al. (1990) found that exposure to diesel exhaust, which  
7 contains aggregates of ultrafine soot particles, resulted in less particle deposition in the lungs  
8 of emphysematous rats than in normal rats, thus sparing the emphysematous rats the health  
9 effects induced by the soot particles in normal animals.

## 11 **Influence of Particle Size, Chemical Composition, and Respiratory Tract** 12 **Deposition/Clearance**

13 The  $\text{PM}_{10}$  standard is the only U.S. national ambient air quality standard that is not  
14 chemical-specific. The chemical composition of a particle will greatly affect its toxicity and,  
15 if possible, should be considered in determining if the observed associations between  
16 atmospheric PM concentrations and increases in morbidity/mortality are causal. For  
17 example, alpha-quartz particles are more toxic than  $\text{TiO}_2$  particles (Driscoll and Maurer,  
18 1991); and acid sulfate aerosols are more likely to cause acute health effects than are neutral  
19 sulfate aerosols (Fine et al., 1987).

20 Size is also important in defining the toxicity of particles. Recent studies indicate that  
21 ultrafine particles ( $<20$  nm) are much more toxic than larger inhalable particles (Oberdörster  
22 et al., 1992; Driscoll and Maurer, 1991). The ultrafine particles have a greater number and  
23 surface area per unit mass than fine or coarse particles, which may account, in part, for their  
24 greater toxicity. Fine particles tend to have a different chemical composition than larger  
25 particles, because their source is often combustion processes. A study of the chemical  
26 composition of  $\text{PM}_{2.5}$  particles versus  $\text{PM}_{10}$  particles in Los Angeles indicated that nitrates,  
27 sulfates, ammonium and organic and elemental carbon were the most abundant species in the  
28  $\text{PM}_{2.5}$  fraction, while the coarser particles contained soil-related species, such as aluminum,  
29 silicon, calcium, and iron (Chow et al., 1994). Chemical composition of  $\text{PM}_{10}$  is discussed  
30 in Chapter 3 and summarized earlier in this chapter (Section 13.2).

1 In a few epidemiology studies, the investigators attempted to determine what size  
2 and/or chemical form of particles had the strongest association with health effects. For  
3 example, in the Harvard 6-cities study (Dockery et al., 1993), the excess chronic mortality  
4 was most strongly associated with the ambient fine particles, including sulfates. However, in  
5 a study of daily air pollution in St. Louis and eastern Tennessee by Dockery et al. (1992),  
6 the strongest association of particulate pollution with daily mortality rates was  $PM_{10}$ , with  
7 progressively weaker associations with  $PM_{2.5}$ , sulfate, and aerosol acidity. This is the  
8 opposite of what one would expect if aerosol acidity were the main cause of increased  
9 mortality, as has been suggested (Lippmann, 1989). The Six Cities study investigators state,  
10 however, that the low daily death counts, the short study period, and the large geographic  
11 areas considered in the St. Louis/Eastern Tennessee study limited the statistical power of the  
12 study, and they could not conclude that the acidity of the aerosol was not associated with  
13 mortality.

14 If the chemical and physical forms of the PM are important in determining the health  
15 effects induced by PM, one would expect different concentration-response curves to be  
16 observed in different epidemiology studies, depending on the type of aerosol present in the  
17 atmosphere. Spurny (1993) in his analysis of studies conducted in the south-western part of  
18 Germany found differences in concentrations, composition, and cell-toxic effects among  
19 urban, residential, and remote areas. The different slopes of the concentration-response  
20 curves for the different cities could be due to several factors, including differences in  
21 physicochemical properties and resultant potency of the PM in the different cities.

22 It is also worth noting that considerations of dosimetry could potentially provide insight  
23 on plausible mechanisms or alter the exposure-dose-response relationships evaluated. To  
24 date, most analyses have used the exposure concentration ( $\mu g/m^3$ ) of particles. Because  
25 deposition of particles in the respiratory tract are determined by particle diameter and  
26 distribution, calculation of the RR estimates based on various internal dose metrics (e.g.,  
27 deposited dose (mass) rate per tracheobronchial or alveolar surface area or deposited particle  
28 number rate per surface area), could alter some of these relationships. Different dose  
29 metrics may be more appropriate to characterize acute effects (e.g., mortality) versus chronic  
30 effects (e.g., morbidity). Certainly dosimetry can provide insight on the variability of  
31 inhaled dose due to differences in airway morphometry and ventilation rates among species,

age, genders, and disease status of the respiratory tract. For example, it has been shown that patients with COPD have increased deposited particle burdens when compared to healthy subjects (Anderson et al., 1992). To the extent that particle composition alters the particle diameter and distribution of a given aerosol, dosimetry will also be effected. Solubility of an aerosol influences clearance rates and subsequent retained dose estimates. The potential for dosimetry to influence the exposure-dose-relationship should be considered to the extent that mathematical modeling and morphometric data allow.

## **Potential Mechanisms of Causality Between Low Levels of Particulate Pollution and Health Effects**

Pathophysiologic mechanisms by which various specific PM constituents can cause health effects are discussed in detail in Chapter 11. Here, the focus is on mechanisms by which airborne particles are known to cause health effects and the extent to which such mechanisms provide plausible evidence or explanations for the reported epidemiologic findings of increases in morbidity and daily mortality rates at low PM concentrations. For purposes of this discussion, health effects of particle inhalation are discussed below in terms of: clinical considerations, acute lung injury, chronic pulmonary toxicity from accumulation of particles in the lung, effects on pulmonary function, effects on pulmonary defense mechanisms, and pathophysiologic mechanisms. Also considered in this section is the potential for interactive mechanisms among air pollutants that might influence the health effects induced by airborne particles. This is an area in which there is little information; most studies have been directed toward determining the toxicity of single compounds.

### ***Clinical Considerations***

Potential mechanisms which might help explain the phenomenon of particle related mortality have been considered by Frampton and Utell (1995). These mechanisms include: (1) "premature" death, that is the hastening of death for individuals already near death (i.e., hastening of an already certain death by hours or days); (2) increased susceptibility to infectious disease; and (3) exacerbation of chronic underlying cardiac or pulmonary disease.

Particulate pollution could contribute to daily mortality rates by affecting those at greatest risk of dying, i.e., those individuals for whom death is already very imminent.

1 Acute exposure to moderately elevated concentrations which might only be a minor irritant to  
2 healthy people could be the “last straw” that tips over the precariously balanced physiology  
3 of a dying patient. Other studies suggest that the full effect of particles on mortality cannot  
4 be explained solely by acute PM exposure death-bed effects (Frampton and Utell, 1995), i.e.,  
5 some studies also indicate an effect on annual mortality rates which cannot be explained  
6 simply by the hastening of death for individuals already near death.

7 Particle exposure could also increase susceptibility to respiratory infection with bacteria  
8 or viruses, leading to an increased incidence of (and death from) pneumonia in susceptible  
9 members of the population. However, pneumonia rarely results in death within 24 h of  
10 onset; serious infections of the lower respiratory tract generally develop and evolve over  
11 weeks, and would not explain effects on daily mortality. If pollutant exposure increased  
12 susceptibility to infectious disease, it should be possible to detect differences in the incidence  
13 of such diseases in communities with low vs. high particle concentrations. Emergency room  
14 visits and hospitalizations for pneumonia caused by the relevant agent should also be  
15 measurably higher on days with elevated ambient particle concentrations. However, no such  
16 relationship has been observed, and laboratory animal data to support such a mechanism are  
17 weak.

18 Particulate air pollution might also aggravate the severity of underlying chronic lung  
19 disease. This mechanism could explain increases in daily mortality (through effects on those  
20 near death from their disease) and longitudinal increases in mortality (if individuals with  
21 chronic airways disease experienced more frequent or severe exacerbation of their disease, or  
22 more rapid loss of function as a result of particulate exposure).

23 What chronic disease processes are most likely to be affected by inhaled particulate  
24 matter? To explain the daily mortality statistics, there must be common conditions that  
25 contribute significantly to overall mortality from respiratory causes. The most likely  
26 candidates are the chronic airways diseases, particularly chronic obstructive pulmonary  
27 disease (COPD). This group of diseases encompasses both emphysema and chronic  
28 bronchitis, however, information on death certificates does not allow differentiation between  
29 these diagnoses. The pathophysiology includes chronic inflammation of the distal airways as  
30 well as destruction of the lung parenchyma. There is loss of supportive elastic tissue, so that  
31 the airways collapse more easily during expiration, obstructing outflow of air. Processes that

1 enhance airway inflammation or edema, increase smooth muscle contraction in the  
2 conducting airways, or slow mucociliary clearance could adversely affect gas exchange and  
3 host defenses. Moreover, the uneven ventilation-perfusion matching characteristics of this  
4 disease, with dependence on fewer functioning airways and alveoli for gas exchange, means  
5 inhaled particles may be directed to the few remaining functioning lung units in higher  
6 concentration than in normal lungs (Bates, 1992)

7       Particulate pollutants have been associated with increases in cardiovascular mortality  
8 both in the major air pollution episodes and in the more recent time-series analyses. Bates  
9 (1992) has postulated three ways in which pollutants could affect cardiovascular mortality  
10 statistics. These include: (1) acute airways disease misdiagnosed as pulmonary edema;  
11 (2) increased lung permeability, leading to pulmonary edema in people with underlying heart  
12 disease and increased left atrial pressure and (3) acute bronchiolitis or pneumonia induced by  
13 air pollutants precipitating congestive heart failure in those with pre-existing heart disease.  
14 Moreover, the pathophysiology of many lung diseases is closely intertwined with cardiac  
15 function. For example, one postulated cause of the increasing mortality rate in asthma is  
16 overuse of adrenergic agonist medications leading to fatal cardiac arrhythmias. Many  
17 individuals with COPD also have cardiovascular disease caused by smoking, aging, or  
18 pulmonary hypertension accompanying COPD. Terminal events in patients with end-stage  
19 COPD are often cardiac complications, and may therefore be misclassified as cardiovascular  
20 deaths. Hypoxemia associated with abnormal gas exchange can precipitate cardiac  
21 arrhythmias and sudden death.

### 23 *Acute Lung Injury*

24       The acute toxicity of particles in the respiratory tract has been the topic of numerous  
25 studies to determine the potential pulmonary toxicity of dusts, particularly those of concern in  
26 industrial processes. Toxic particles that deposit in the lung can induce an inflammatory  
27 response that, if it persists, may lead to pulmonary fibrosis and impaired pulmonary function.  
28 The response of the respiratory tract to such particles includes the release of numerous  
29 cytokines from alveolar macrophages and epithelial lining cells that promote healing and  
30 repair or, if healing does not occur because of the persistence of toxic particles, may  
31 promote development of fibrosis. Although such acute responses are well known, they

typically only occur after several days or weeks of exposure to airborne particle concentrations many fold higher than those that have been shown to be associated with increased mortality and morbidity in epidemiology studies. Recently, however, it has been observed in experimental animal studies that certain types of particles are acutely toxic to the lung at low exposure concentrations. A half-hour exposure of rats to freshly generated ultrafine polytetrafluoroethylene particles at a concentration of  $64 \mu\text{g}/\text{m}^3$  resulted in severe pulmonary inflammation and death (Oberdörster et al, 1995). Warheit et al. (1990) also found that fresh ultrafine aerosols resulted in mortality in rats by causing severe lung injury. The significance for environmental exposures of the highly toxic fresh aerosols formed from pyrolysis of perfluorinated materials is unknown at this time, because of the rapid loss of toxicity of the aerosols with time and the lack of information on the concentration of those specific aerosols in the ambient atmosphere. Although it is known that combustion processes emit ultrafine aerosols into the environment (Cantrell and Whitby, 1978), it is not clear how much ultrafine particulate matter is present as the product of pyrolysis of perfluorinated compounds. Nor is there much information on typical ambient concentrations of other ultrafine particles (e.g., metals from high temperature smelting) or their persistence as ultrafines in urban aerosol mixes.

### ***Toxicity Resulting from Accumulation of Particles in the Lung***

The accumulation of large lung burdens of poorly soluble particles can lead to decreased clearance of subsequently inhaled particles and an enhanced rate of accumulation of particles in the lung (Morrow, 1992). Large lung burdens of particles of even relatively low inherent toxicity have been shown to induce lung cancer in animal models such as the rat (Mauderly et al., 1994). But how much prior exposure to particles is required to accumulate enough particles to impair clearance of subsequently inhaled particles? Rats exposed to  $350 \mu\text{g}/\text{m}^3$  diesel soot (aggregated ultrafine carbon particles) for 24 months did not accumulate enough particles to induce pulmonary inflammation (as measured by both histopathology and analysis of lung lavage fluid) or to impair particle clearance, but rats exposed to  $3500 \mu\text{g}/\text{m}^3$  for the same length of time did. Rats that inhaled carbon black particles at an 8-h time-weighted concentration of  $10,000 \mu\text{g}/\text{m}^3$  5 days a week for 12 weeks also accumulated enough particles to induce an inflammatory response by 6 weeks (Henderson et al., 1992).



1 In general, the toxicity resulting from accumulation of large burdens of particles in the  
2 lung does not likely provide a plausible biological basis for reported associations between  
3 acute exposures to low level PM concentrations (ca, 30 to 200  $\mu\text{g}/\text{m}^3$ ) of inhalable particles  
4 ( $\text{PM}_{10}$ ) and daily mortality/morbidity rates. One possible exception that stands out as a  
5 relatively sizeable segment of the general population would be smokers or former smokers  
6 among the elderly. In such individuals, particle overload from 40 to 60 years of directly  
7 inhaled tobacco smoke particles could make them more vulnerable to the impacts of  
8 relatively small additional acute increments in their lung particle burdens, as would the  
9 preexisting chronic cardiorespiratory diseases caused by smoking.

10 A second possible exception might be elderly persons who experienced notable past  
11 exposures over many years to very high ambient or workplace PM concentrations, as would  
12 be the case for individuals who resided or worked in heavily industrialized cities before  
13 effective occupational and air pollution control measures were introduced in the 1950s to  
14 1970s to reduce such exposures. For example, in the Harvard 6-cities study, an association  
15 was found between daily mortality rates and PM levels across a few rural communities,  
16 lightly industrialized cities, and some heavily industrialized cities. Because the ranking of  
17 the cities in terms of air-pollution levels did not change during the study period, it is not  
18 possible to distinguish completely between effects due to past historical exposures and those  
19 due to recent exposures. Therefore, the elevation in daily mortality rates in industrialized  
20 cities such as Steubenville compared to less industrialized cities (such as Topeka or Portage)  
21 may be in part based on accumulated past exposures to higher particle levels and  
22 consequently larger lung particle burdens in the former.

### 23 24 *Impaired Respiratory Function*

25 Very few of the specific PM constituents discussed in Chapter 11 have acute exposure  
26 effects on respiratory function, except possibly at very high concentrations (in the  $\mu\text{g}/\text{m}^3$   
27 range). One possible exception is acid aerosols, which appear to have acute effects on  
28 pulmonary function among some sensitive individuals at levels below 1,000  $\mu\text{g}/\text{m}^3$ .  
29 Exposures to acid particles are known to induce hyperreactive airways and in some cases,  
30 bronchoconstriction, but at concentrations in the  $\text{mg}/\text{m}^3$  range, well above peak U.S. ambient  
31 acidity levels of 50 to 75  $\mu\text{g}/\text{m}^3$ . In healthy humans, inhalation of 1,000  $\mu\text{g}/\text{m}^3$   $\text{H}_2\text{SO}_4$

aerosol for 3 h did not cause any influx of inflammatory cells into the lung based on analysis of lung lavage fluid obtained 18 h after the exposures (Frampton et al., 1992). However, mild bronchoconstriction has been reported after brief exposures to as low as  $68 \mu\text{g}/\text{m}^3$   $\text{H}_2\text{SO}_4$  in exercising adolescent asthmatics and  $90 \mu\text{g}/\text{m}^3$  in exercising adult asthmatics (Morrow et al., 1994); (Koenig et al., 1989), although this has not always been observed (Avol, et al., 1990). Also of interest is the finding that hyperresponsive airways developed after exposure of healthy rabbits to as little as  $75 \mu\text{g}/\text{m}^3$   $\text{H}_2\text{SO}_4$  for 3 h (El-Fawal and Schlesinger, 1994). Additional studies have also found that acid-coated particles were more potent than the acid or particles alone. Therefore, under some circumstances, one possible mechanism for increased mortality among some elderly persons with a debilitating disease (asthma) on days with moderately high PM pollution might be that acid aerosols place a stress on their cardiopulmonary system, leading to death.

#### ***Impaired Pulmonary Defense Mechanisms***

The ability of particulate exposures to reduce pulmonary defense mechanisms has been documented for aerosols of  $\text{H}_2\text{SO}_4$  and trace metals. Trace metals have been shown to be cytotoxic to alveolar macrophages (AMs) and immunosuppressive, but only at much higher concentrations than encountered in ambient atmospheres (Zelikoff et al., 1993). Sulfuric acid aerosols have also been shown to alter resistance to bacterial infection in mice after acute exposures to  $1,000 \mu\text{g}/\text{m}^3$ ; repeated exposures to  $100 \mu\text{g}/\text{m}^3$  reduced mucociliary transport rates in animals. Even these levels of  $\text{H}_2\text{SO}_4$  are much higher than have been reported in atmospheres of cities evaluated in the recent epidemiology studies. Also, one would expect effects from impaired pulmonary defense mechanisms to develop over an extended period of continuing exposure, not within a few days.

#### ***Synergistic Effects***

An area for which there is little information is the potential interactive effects of mixtures of air pollutants and/or with other factors (e.g., aging). The potential significance of mixtures is illustrated by the studies of Amdur and Chen (1989), in which a repeated daily 3-h exposure for 5 days of guinea pigs to  $20 \mu\text{g}/\text{m}^3$  of  $\text{H}_2\text{SO}_4$  coated on metal particles resulted in decrements in lung volume and pulmonary diffusing capacity and elevations of

lung weight/body weight ratio, protein, and number of neutrophils in pulmonary lavage fluid. For example, A 1-h exposure to 20  $\mu\text{g}/\text{m}^3$   $\text{H}_2\text{SO}_4$  coated on metallic particles increased bronchial reactivity in guinea pigs; a 10-fold higher concentration of  $\text{H}_2\text{SO}_4$  alone was required to produce the same response (Chen et al., 1992b). However, such synergistic effects were not observed by Anderson et al. (1992), who studied the effects on 15 healthy and 15 asthmatic volunteers of 1-hr exposures to 100  $\mu\text{g}/\text{m}^3$   $\text{H}_2\text{SO}_4$  (0.5  $\mu\text{m}$ ) or 250  $\mu\text{g}/\text{m}^3$  carbon black (0.5  $\mu\text{m}$ ) separately or with the  $\text{H}_2\text{SO}_4$  coated on the particles. The exposures did not result in changes in symptoms or pulmonary function, except for an equivocal response in one person.

The population segment most susceptible to elevations in ambient PM are the elderly (> 65 years old) with preexisting respiratory disease. Aging, in the absence of pathology, is an extremely complex biological phenomenon and is described as being a multifactorial process composed of both genetic and environmental components (Cristofalo et al., 1994). While the physiological characteristics of the healthy older population is an area of active research, significant decrements in key physiological parameters including lung volumes, FEV<sub>1</sub>, flow velocity/volume curves, resting cardiac output, and cardiac output reserve with age have been reported (Kenney, 1989). However, there is controversy concerning decrements in physiological function associated with the aging process alone as well as with accompanying disease processes or with other environmental stressors. Moreover, there is little information on the extent to which an older population might be more susceptible to the effects of ambient particulate pollution (Cooper et al., 1991). It is possible that the elderly are more susceptible to ambient particles because of numerous changes in the body's protective mechanisms and protracted exposures to particles over a life time. This could allow time for latent effects from earlier life time exposures to manifest themselves, and for potential cumulative effects to emerge. Virtually nothing is known of the possibilities for interaction among toxicants over a long life time or the possibilities for interaction between medications and ambient pollutants.

## ***Pathophysiologic mechanisms***

The respiratory system may be compromised and become less efficient in older people or as a result of disease, and inhaled particles could, conceivably, further compromise their respiratory function. Because small increases in environmental particle concentrations would not be lethal to most people, the effect must result from initiating or promoting a lethal failing of a critical function, such as ventilation, gas exchange, pulmonary circulation, or cardiorespiratory control in subjects brought to the limits of tolerance by preexisting conditions (Mauderly, 1995).

Inhaled particles or their pathophysiological reaction products could further impair ventilation in the chronically ill individual by further reducing airway caliber. For example, particles may activate airway smooth muscle, constricting airways, or may influence various airway secretions which could add to and thicken the mucous blanket. Inhaled particles or their pathophysiological reaction products could decrease the diffusing capacity of the lungs by decreasing the area of the respiratory membrane available for diffusion, by increasing diffusion distances across the respiratory membrane, and/or by causing abnormal ventilation-perfusion ratios in some parts of the lung. Particles or their products could also act at the level of the pulmonary vasculature to elicit changes in pulmonary vasculature resistance, which could further alter ventilation-perfusion abnormalities in people with respiratory disease. Furthermore, particles could conceivably alter respiratory and cardiovascular control by affecting local control mechanisms located in the endothelial cells or other sites. This could produce changes in peripheral and central control mechanisms and directly affect the respiratory and cardiovascular control centers. Little evidence is currently available that directly addresses the above speculative possibilities.

## **Biological Plausibility Conclusions**

Having considered the characteristics of the particulate exposure atmospheres and the types of morbidity and mortality associated with the polluted atmospheres, what can be concluded about the biological plausibility of the epidemiological results? The types of morbidity and mortality reported to be associated with increased ambient particle concentrations are consistent with the types of health effects that one might expect from exposures to high levels of PM. Therefore, the type of response seems plausible, if one

1 accepts the temporal relationships modeled in the epidemiological studies. The analyses  
2 found associations with 1-day or multi-day (usually 3 to 5 day) lags. The concentrations of  
3 particulate matter reported to be associated with such health responses, however, are much  
4 lower than would be expected based on animal and human clinical studies of responses to  
5 single particulate pollutants. This is true even when one considers that there is evidence that  
6 the people who make up the excess mortality population may be susceptible subpopulations.  
7 Moreover, it is not clear what portion of the inhalable particulate matter constitutes the  
8 delivered dose that is associated with the observed morbidity or mortality. There are  
9 suggestions from both animal toxicology data and epidemiology data that ultrafine acid  
10 aerosols may be of greater health significance than the rest of the particulate mass. Finally,  
11 the potential for interactive effects between PM of different types and PM and other air  
12 pollutants is not known.

13 Thus, although there are several hypotheses as outlined above, little clear or convincing  
14 evidence is available at this time to support the biological plausibility of a causal relationship  
15 for the reported epidemiologic associations between low ambient concentrations of PM and  
16 daily mortality and morbidity rates.

#### 19 **1.14 IDENTIFICATION OF POPULATION GROUPS POTENTIALLY** 20 **SUSCEPTIBLE TO HEALTH EFFECTS FROM PM EXPOSURE**

21 Certain groups within the population may be more susceptible to the effects of PM  
22 exposure, including persons with preexisting respiratory disease, children, and the elderly.  
23 The reasons for paying special attention to these groups is that (1) they may be affected by  
24 lower levels of PM than other subpopulations and (2) the impact of an effect of given  
25 magnitude may be greater. Some potential causes of heightened susceptibility are better  
26 understood than others. Subpopulations that already have reduced ventilatory reserves (e.g.,  
27 the elderly and persons with asthma, emphysema, and chronic bronchitis) would be expected  
28 to be more impacted than other groups by a given decrement in pulmonary function. For  
29 example, a healthy young person may not even notice a small percentage change in  
30 pulmonary function, but a person whose activities are already limited by reduced lung  
31 function may not have the reserve to compensate for the same percentage change.

1       Based on Chapter 12 discussions, it is clear that the bulk of the total mortality effects  
2 suggested by the epidemiology studies discussed earlier are among the elderly. During the  
3 historic London, 1952 pollution episode the greatest increase in the mortality rate was among  
4 older citizens and those having respiratory diseases. An analysis by Schwartz (1994c) of  
5 mortality in Philadelphia, PA found the greatest increase in risk of death in those aged 65 to  
6 74 and those >74 year of age (mortality risk ratios = 1.09 and 1.12, respectively, between  
7 high and low TSP days). Other studies also suggest that the elderly experience a higher  
8 excess risk from exposure to PM air pollution than the population overall.

9       Other potentially susceptible groups include patients with COPD, such as emphysema  
10 and chronic bronchitis. Some of these patients have airway hyperresponsiveness to physical  
11 and chemical stimuli. A major concern with COPD patients is the absence of an adequate  
12 ventilatory reserve, a susceptibility factor described above. In addition, altered distribution  
13 of respiratory tract ventilation in COPD may lead to a greater delivery of PM to the segment  
14 of the lung that is well ventilated, thus resulting in a greater regional tissue dose. Also, PM  
15 exposure may alter already impaired defense mechanisms, making this population potentially  
16 more susceptible to respiratory infection. It is estimated (U.S. Department of Health and  
17 Human Services, 1990; Collins, 1988) that 14 million persons ( $\approx 6\%$ ) suffer from COPD in  
18 the United States. Bronchial mucous transport clearance may be impaired in people with  
19 chronic bronchitis, asthma, and in association with various acute infections. Rates of  
20 alveolar region clearance appear to be reduced in humans with chronic obstructive lung  
21 disease.

22       Throughout the results and discussions presented above and in Chapter 12 regarding the  
23 effects of acute PM exposure on human mortality, a consistent trend was for the effect  
24 estimates to be higher for the respiratory mortality category. This lends support to the  
25 biological plausibility of a PM air pollution effect, as the breathing of toxic particles would  
26 be expected to most directly affect the respiratory tract, and these results are consistent with  
27 this expectation. For example, the estimates of relative risk for PM-induced mortality due to  
28 respiratory causes discussed in Chapter 12 are all higher than the risks for the population as  
29 a whole and for other causes. More specifically, the PM RR for respiratory diseases ranged  
30 from 50 to more than 400% higher for respiratory disease categories than for all causes of  
31 death, indicating that increases in respiratory deaths are a key major contributor to the

1 overall PM-mortality associations noted previously. PM relative risk estimates for  
2 cardiovascular causes were also notably elevated. Moreover, since evidence suggests that an  
3 acute pollution episode is most likely be inducing its primary effects by stressing already  
4 compromised individuals (rather than, for example, inducing chronic respiratory disease from  
5 a single air pollution exposure episode), the above results indicate that persons (especially the  
6 elderly) with pre-existing cardiovascular or respiratory disease constitute a population  
7 segment especially at risk for mortality implications of acute ambient PM exposures.

8       Apropos to the identification of individuals with pre-existing respiratory and  
9 cardiovascular diseases as being at special risk for ambient PM exposure effects, it is  
10 important to highlight smoking as a key etiological agent for such diseases. The U.S.  
11 Environmental Protection Agency (1992) report on environmental tobacco smoke indicates  
12 that smoking is the major cause of chronic obstructive pulmonary disease (COPD), which  
13 includes emphysema, and is thought to be responsible for approximately 61,000 COPD  
14 deaths yearly, i.e., about 82% of U.S. COPD deaths (U.S. DHHS, 1989). Tobacco use is  
15 also a major risk factor for cardiovascular diseases, the leading cause of death in the United  
16 States. It is estimated that each year 156,000 heart disease deaths and 26,000 deaths from  
17 stroke are attributable to smoking (CDC, 1991). Smoking is also a risk factor for various  
18 respiratory infections, such as influenza, bronchitis, and pneumonia. An estimated 20,000  
19 influenza and pneumonia deaths per year are attributable to smoking (CDC, 1991).

20       The U.S. Environmental Protection Agency report also indicates that in children, ETS  
21 exposure is causally associated with an increased risk of lower respiratory tract infections  
22 such as bronchitis and pneumonia. It is estimated that 150,000 to 300,000 cases annually in  
23 infants and young children up to 18 months of age are attributable to ETS. ETS exposure is  
24 also causally associated with additional episodes and increased severity of symptoms in  
25 children with asthma. It is estimated that 200,000 to 1,000,000 asthmatic children have their  
26 condition worsened by exposure to ETS. ETS is also a risk factor for new cases of asthma  
27 in children who have not previously displayed symptoms (U.S. Environmental Protection  
28 Agency).

29       Lastly, the EPA report also indicates that environmental tobacco smoke (ETS) is a  
30 human lung carcinogen, responsible for approximately 3,000 lung cancer deaths annually in  
31 U.S. nonsmokers (U.S. Environmental Protection Agency, 1992).

1 Overall, then, the most susceptible population segment that can be most clearly  
2 identified as being at likely increased risk for low-level ambient PM exposure-induced  
3 mortality or morbidity are elderly individuals with pre-existing cardiovascular respiratory  
4 diseases, the majority of which are likely either current or former smokers. Smoking may  
5 also be a key ancillary contributor to any low-level PM exposure-induced exacerbation of  
6 respiratory infections among other adults and children and to any increased cancer mortality  
7 attributable to chronic ambient PM exposures.

8 Asthmatic subjects appear to be more sensitive than healthy subjects to the effects of  
9 acid aerosols on lung function, but the effective concentration differs widely among studies.  
10 Adolescent asthmatics may be more sensitive than adults, and may experience small  
11 decrements in lung function in response to H<sub>2</sub>SO<sub>4</sub> at exposure levels only slightly above peak  
12 ambient levels. Although the reasons for the inconsistency among studies remain largely  
13 unclear, subject selection may be an important factor. Even in studies reporting an overall  
14 absence of effects on lung function, occasional asthmatic subjects appear to demonstrate  
15 clinically important effects. Studies from different laboratories suggest that responsiveness to  
16 acid aerosols may correlate with degree of baseline airway hyperresponsiveness. On the  
17 other hand, based on very limited studies, elderly and individuals with chronic obstructive  
18 pulmonary disease do not appear to be particularly susceptible to the effects of acid aerosols  
19 on lung function.

20 Alveolar deposition at different flow rates was lower (26% versus 48% thoracic  
21 deposition) in subjects after induced bronchoconstriction. In asthmatics, thoracic deposition  
22 of particles was higher than healthy subjects (83% versus 73% of total deposition).  
23 Trachial/bronchial deposition was also found to be higher in asthmatics. The results are  
24 similar to those found in subjects with obstructive lung disease. The buffering capacity of  
25 mucus may be altered in persons with compromised lungs. For example, sputum from  
26 asthmatics had a lower pH than that from normals and a reduced buffering capacity, and so  
27 may represent a population segment especially sensitive to inhaled acidic particles.

28 The National Institutes of Health (1991) estimates that approximately 10 million persons  
29 in the United States have asthma. In the general population, asthma prevalence rates  
30 increased by 29% from 1980 to 1987. For those under 20 years old, asthma rates increased  
31 from approximately 35 to 50 per 1,000 persons, a 45% increase. The airways of asthmatics



1 may be hyperresponsive to a variety of inhaled materials, including pollens, cold-dry air,  
2 allergens, and air pollutants. The potential addition of an PM-induced increase in airway  
3 response to the already heightened responsiveness to other substances raises the possibility of  
4 exacerbation of this pulmonary disease by PM.

## 7 **1.15 IMPLICATIONS OF RELATIVE RISK ESTIMATES**

8 Preceding sections of this Chapter concluded that the newly emerging epidemiologic  
9 data base on PM-mortality/morbidity effects provides reasonably consistent results indicative  
10 of increased risk of mortality and morbidity effects being associated with exposures of the  
11 general population to ambient air pollutant mixes containing PM concentrations currently  
12 found in many U.S. urban areas. This includes effects associated with ambient air exposures  
13 to pollutant mixes having 24-h  $PM_{10}$  concentrations falling in the range of  $30 \mu g/m^3$  to  $200$   
14  $\mu g/m^3$ , including evidence suggestive of effects below  $150 \mu g/m^3$  (the level of the current 24-  
15 h U.S.  $PM_{10}$  NAAQS).

16 It was also noted in Chapter 12 that the relative risk (RR) estimates for both the  
17 mortality and morbidity effects associated with short-term (ca. 24-h or a few days) exposures  
18 to ambient PM are very small compared to RR values typically viewed in epidemiologic  
19 literature as providing strong evidence for a likely causative association. Section 1.12 further  
20 noted the relatively limited evidence directly demonstrating coherence between the mortality  
21 and morbidity effects findings from epidemiologic studies, with the most compelling evidence  
22 for coherence now being findings of both increased hospital admissions (for cardiopulmonary  
23 endpoints) and increased mortality in relation to increments in 24-h PM concentrations in the  
24 same population group (the elderly) within several U.S. urban areas (Detroit, Birmingham,  
25 Philadelphia) and the Utah Valley. However, only very limited evidence for the biological  
26 plausibility of acute low-level PM exposure effects at the above-stated  $PM_{10}$  concentration  
27 range now appears to exist to support several hypotheses discussed in Section 1.13 with  
28 regard to possible mechanisms of action. A key point emerging from the plausibility  
29 discussion and the ensuing section (1.14) was the identification of elderly individuals (65 yr.  
30 old) with preexisting chronic cardiovascular and respiratory disease conditions (the majority  
31 of whom are likely current or former smokers) as being the most susceptible general

1 population segment most clearly at special risk for mortality and morbidity effects associated  
2 with exposures to ambient air mixes containing moderately elevated PM concentrations.

3 The meaning or interpretation of quantitative estimates of PM-related effects (i.e.,  
4 relative risk estimates) discussed earlier as having been generated by the newly available PM  
5 epidemiology studies remains a subject of controversy, with divided opinions still existing in  
6 the scientific community as noted earlier in this chapter. Thus, in attempting to interpret  
7 such risk estimates, several caveats should be kept in mind. First, caveats analogous to those  
8 made in point (4) at the top of page 1-33 for key conclusions drawn from the last previous  
9 PM criteria review still apply. That is, although new evidence has emerged which points  
10 toward very small, but statistically significant increases in risk of human mortality and  
11 morbidity effects being associated with exposures to ambient air mixes containing moderately  
12 elevated PM (with no evident thresholds being identified in the studied range of PM  
13 concentrations), precise quantitative specification of relative contributions of such low-level  
14 concentrations of ambient PM to reported mortality and morbidity effects is not possible at  
15 this time. Nor can one now separate out with confidence potential relative contributions to  
16 the reported PM effects of several other likely important confounding or interacting  
17 variables.

18 With regard to the latter, it is as of yet very difficult, for example, to sort out with  
19 confidence relative contributions of weather versus PM per se. It is clear that temperature  
20 extremes (very hot or very cold days in relation to typical ranges of temperature for any  
21 given locale) have notable effects on variations in daily mortality, with temperature or other  
22 combinations of variables indexing weather impacts usually being found to be significant  
23 predictors of daily human mortality in modeling of PM effects and to account for distinctly  
24 larger proportions of the variance in daily mortality than do indices of PM pollution. On the  
25 other hand, in most of the newer PM studies, small elevations in relative risk attributable to  
26 PM still remained even after control for temperature extremes and/or other weather indices;  
27 and PM effects were found to be significant in several analyses (e.g., for London) restricted  
28 to days not involving wide variations in temperature that would constitute geographic-specific  
29 extremes. It is also not yet clear to what extent any given relative risk estimate derived from  
30 any of the newer analyses represent actual risk due to an increase in ambient PM or to what  
31 extent the elevations in risk attributed to modeled PM indices more broadly represent

1 increased mortality or morbidity risks due to human exposure to the overall pollutant mix in  
2 the particular airshed evaluated (including not only the ambient PM aerosols present but  
3 other copollutants, such as SO<sub>2</sub>, CO, O<sub>3</sub>, NO<sub>x</sub> or non-particulate organic air toxics).

4 Other caveats bear on the issue of how generalizable the reported PM relative risk  
5 estimates are. It is not yet possible to determine the extent to which the risk estimates for  
6 PM mortality or morbidity effects are generalizable to other geographic areas or are highly  
7 site-specific, i.e., narrowly applicable to the specific cities from which they were derived or,  
8 at least, most credibly confined for use in projecting any estimates of likely PM risk to other  
9 airsheds with fairly similar ambient aerosol mixes in terms of particle size distribution and  
10 chemical composition. Thus, it is not clear, for example, how credible the use of PM-  
11 related relative risk estimates derived from Philadelphia, St. Louis, or other midwestern or  
12 eastern U.S. conurbations (or foreign cities such as Sao Paulo, Santiago, or Athens) with  
13 high percentages of particles from combustion processes might be in attempting to estimate  
14 PM-related risks for other cities, e.g., in the western U.S., with much greater proportions of  
15 crustal materials in the ambient air pollutant mix. Use of presently available PM-related risk  
16 estimates to attempt to quantify potential PM-related risks across various seasons in locales  
17 where widely varying seasonal mixes of particles of different sizes/chemical composition may  
18 also be of dubious scientific credibility at this time.

19 Another issue of much interest and debate has been that of "threshold" for the estimated  
20 PM effects derived from the newly available analyses. As noted earlier and discussed in  
21 Chapter 12, no evident thresholds have yet been demonstrated for reported PM-related  
22 mortality or morbidity effects, based on the presently available published analyses. On the  
23 other hand, as also discussed in Chapter 12, only very limited efforts have been made to date  
24 to undertake statistical analyses by which to more definitively address the issue; and serious  
25 doubt exists as to whether any thresholds, if they do exist, even in the range of the observed  
26 data (i.e., roughly from 30 to 200 µg/m<sup>3</sup> PM<sub>10</sub>) can be demonstrated, given notable  
27 statistical power limitations associated with necessary breaking down of data into more  
28 refined intervals as part of any threshold "search". Nor is there now any scientifically  
29 credible basis by which to make a "no-threshold" argument in support of extrapolating  
30 currently available PM relative risk estimates to ambient PM concentrations below the range  
31 of observed data used in the reported analyses. This is especially true in view of the lack of

1 any well demonstrated evidence for one or another hypothesized potential mechanisms of  
2 action that might plausibly explain the elevated risk of mortality or morbidity at the very low  
3 PM concentrations implied by the results of the newly available epidemiology studies.

4 It is also clear from the available analyses that the occurrence of any increased risk of  
5 mortality or morbidity due to short-term moderate elevations in PM (either alone or in  
6 concert with other copollutants) likely represents the outcome of a combination of risk factors  
7 culminating in relatively rare health events (as clarified further by the ensuing quantitative  
8 discussion below). By far the greatest risk is posed for the elderly over 65 years old and  
9 especially those with preexisting cardiopulmonary diseases, with very distinctively lower risk  
10 estimates having been derived for younger individuals and those without chronic respiratory  
11 or cardiovascular diseases. Thus, in order for notable health effects to occur in association  
12 with short-term exposures to ambient PM (and/or copollutants), it appears that other  
13 predisposing conditions and/or contributing risk factors must be present, as well. That is,  
14 low-level ambient PM exposures alone do not typically appear to be sufficient per se to  
15 induce increased morbidity or mortality, but may contribute to such health outcomes under  
16 conditions when one or more other contributing risk factors also converge. Thus, for  
17 example, short-term low-level exposures to ambient PM at concentrations in the ranges  
18 evaluated in most of the newer epidemiology studies are extremely unlikely alone to cause  
19 lung function decrements or respiratory symptoms of much note (except possibly for some  
20 highly sensitive asthmatic patients), based on currently available epidemiologic and controlled  
21 human exposure study results. Nor are such exposures likely to markedly reduce or impair  
22 respiratory tract defenses (e.g., alveolar macrophage numbers or function, retrociliary  
23 clearance mechanisms, lung immune response, etc.) sufficiently so as to cause increased  
24 susceptibility to respiratory infections, based on available experimental toxicology findings.  
25 On the other hand, once a respiratory infection were to occur due to other causes, then it is  
26 conceivable that added stress due to low-level PM exposure in terms of small further  
27 decrements in pulmonary function or exacerbation of respiratory symptoms could lead to  
28 worsening of the acute illness and, possibly, the need for medical attention and/or hospital  
29 admission in some cases.

30 Still additional converging risk factors appear to be necessary for exposures to ambient  
31 air pollution mixes containing low concentrations of typical outdoor urban aerosols to

1 contribute to increased mortality. By far the most important are the cooccurrence of  
2 advanced age (> 65 yr old) and already compromised cardiopulmonary function. In older  
3 individuals with preexisting COPD, emphysema, chronic heart disease, etc. resulting from  
4 other predisposing risk factors (e.g., long-term earlier high-level particle exposures from  
5 smoking or past occupational or ambient PM exposures before effective control measures  
6 were introduced), it appears conceivable that additional stress from low-level ambient PM  
7 exposures might cause further complications that might lead to terminal consequences in  
8 some cases. Several possibilities were discussed earlier as having been hypothesized, e.g.,  
9 increased air flow to and consequent greater particle deposition/retention in remaining  
10 functioning areas of the compromised lung, possible tipping over by small additional particle  
11 burdens of already saturated lung defenses due to particle overloads from past long-term high  
12 level particle exposures, and/or the induction of cascading inflammatory or other immune  
13 responses (due to particularly toxic specific PM constituents e.g., possibly certain transition  
14 metals) that overwhelm remaining lung reserves and oxygen exchange mechanisms.  
15 However, at this time, no clearly convincing scientific evidence has yet been reported by  
16 which to either compellingly substantiate or refute such hypothesized possibilities. Thus,  
17 considerable uncertainties still exist with regard to what the relative risk estimates from the  
18 newly available epidemiologic studies may imply.

19 In evaluating the potential public health significance of the relative risk increases for  
20 mortality or morbidity effects reported in the newer PM epidemiology studies, much recent  
21 interest has focussed on use of such relative risk estimates to generate projections of numbers  
22 of excess deaths or morbidity events likely to be associated with ambient PM exposures at  
23 concentrations currently found in the United States or other countries. Given the above-  
24 noted caveats and uncertainties pertaining both to the derivation of the relative risk estimates  
25 and their interpretation, there are substantial reasons to caution against attempting such  
26 calculations at this time and to have major reservations about accepting any such projections  
27 as credible quantitative estimates of additional deaths or morbidity events likely to actually  
28 occur with current or future exposures in the United States or elsewhere. At best, such  
29 projections might be associated with exposures to PM-containing ambient air mixes in cities  
30 with closely similar particle size/chemical composition characteristics and population  
31 demographics to those cities from which the relative risk estimates were derived. It is

currently questionable as to whether widely generalizable, broadly applicable projections can be made based on some single "best estimate" of PM-related relative risk and, also, whether such projections can be credibly aggregated across PM exposure variations during different seasons and/or across geographic locales with widely disparate mixes of PM aerosols and/or other copollutants.

Despite the above caveats and reservations, however, it may be useful to provide illustrative examples of possible quantitative implications of relative risk estimates of the type generated by the recent PM epidemiology analyses. Table 1-5 earlier showed that total acute mortality relative risk estimates associated with exposure to ambient air pollution having a 50  $\mu\text{g}/\text{m}^3$  increase in one-day 24-h average  $\text{PM}_{10}$  can range from 1.015 to 1.085, depending upon the site (i.e., the  $\text{PM}_{10}$  composition and population demographics) and also upon whether  $\text{PM}_{10}$  is modeled as the sole index of air pollution or not. Relative Risk estimates with  $\text{PM}_{10}$  as the only pollutant index in the model range from  $\text{RR} = 1.025$  to 1.085, while the  $\text{PM}_{10}$  RR with multiple pollutants in the model range from 1.015 to 0.025. The former range, as noted earlier, might be viewed as approximating an upper bound of the best estimate, as any mortality effects of co-varying pollutants may be "picked up" by the  $\text{PM}_{10}$  index, whereas the latter multiple pollutant model range might be viewed as approximating a lower bound of the best estimate, as the inclusion of highly correlated covariates might weaken the  $\text{PM}_{10}$  estimate. Thus, "typical" total mortality effect estimates (per 50  $\mu\text{g}/\text{m}^3$   $\text{PM}_{10}$  increase) most likely fall within an approximate  $\text{RR} = 1.025$  to 1.06 range, based on the various coefficients reported in the published studies. Formal EPA meta-analyses results discussed in Chapter 12 yielded a best estimate of 1.031 with 95% confidence intervals (CI) of 1.025 to 1.038 for  $\text{PM}_{10}$  studies using models that include 0-1 day lags but no copollutants. For those analyses with longer lag times (3-5 days) and no copollutants in the models, the EPA meta-analyses yielded a best estimate of 1.064 (CI = 1.047 to 1.082). Thus, the very small increased risks of about 3.1 to 6.4% over baseline mortality levels (per 50  $\mu\text{g}/\text{m}^3$  increase in 24-h  $\text{PM}_{10}$  concentration in the 30 to 200  $\mu\text{g}/\text{m}^3$  range) derived from the EPA meta-analyses probably represent currently best available upper bound estimates for reported  $\text{PM}_{10}$ -related total mortality effects. Lower bound estimates, from analyses that included other copollutants in the models for acute PM-mortality effects, could be as much as

1 50% lower than the above upper bound estimates or, possibly, even include zero (i.e.,  
2 represent no increased risk) especially during some seasons in different locales.

3 To help place these findings into a context by which to better understand the potential  
4 implications of such relative risk estimates, Table 1-14 summarizes important information by  
5 which to project potential increases in excess mortality in a city of one million people that  
6 might be associated with exposure to ambient air mixes in which an increment in 24-h  $PM_{10}$   
7 exposure of  $50 \mu g/m^3$  may be a contributing factor. First it is important to note that the  
8 typical general population baseline or background risk of death on any given day in the U.S.  
9 is only about 23.6 in a million ( $23.6 \times 10^{-6}$ ) or 23.6 deaths per day in a city of 1 million  
10 people. If the 24-h  $PM_{10}$  concentration increased by  $50 \mu g/m^3$  on a given day (e.g., from a  
11 usual level of about  $50 \mu g/m^3$  to around  $100 \mu g/m^3$ ) then risk for mortality in the total  
12 general population would be expected to increase by about 3.0 to 6.0% over baseline, i.e., to  
13 increase from 23.6 in a million to about 24 or 25 in a million as an upper bound estimate.  
14 In other words, exposure to the ambient mix of pollutants indexed by the  $50 \mu g/m^3$  increase  
15 in 24-h  $PM_{10}$  levels might contribute to as much as an additional 0.7 to 1.5 deaths per  
16 million people exposed, as shown in the Table 1-14 far right column.

17 Of the 23.6 baseline deaths per day expected in a city of 1 million, about 17 would be  
18 attributable to elderly individuals (aged 65 or over), who only constitute about 12.6% of the  
19 1991 U.S. population but for whom the background risk of dying on a given day is much  
20 higher than for the total general population. For such individuals, the upper bound estimate  
21 for increased numbers of excess deaths possibly contributed to by the  $50 \mu g/m^3$   $PM_{10}$   
22 increase would be projected to be approximately 1.0 (more than half of the higher estimate  
23 for total mortality among the entire population), assuming that the specific city has a typical  
24 demographic distribution of percentages of people in different age brackets. In other cities  
25 or locations with notably higher elderly populations (e.g., some retirement communities or  
26 cities left with higher percentages of the elderly possibly due to outmigration of younger  
27 people), then the overall risk and expected deaths per day would be higher. Conversely, in  
28 other locations with much younger than average populations and lower percentages of elderly  
29 residents, the risk and expected numbers of PM-related excess deaths would be lower.

30 If the increment in  $PM_{10}$  concentration continued to average about  $50 \mu g/m$  above  
31 routine ambient levels for 3-5 days in the given city of 1.0 million people, then relative risk

estimates derived from PM<sub>10</sub>-mortality models using 3-5 d lags might more appropriately apply. Then, the expected number of deaths to which the 3-5 day 50 µg/m<sup>3</sup> PM elevation might be projected to contribute could range up to about 1.5 deaths per day among the total general population per 1 million people exposed; or up to about 4.5 to 7.5 deaths during the full 3-5 days of elevated PM<sub>10</sub>. Of the 1.50 excess death per day attributed to the 3-5 day 50 µg/m<sup>3</sup>-increment in PM<sub>10</sub> 24-h concentrations, an estimated 0.34 would likely be due to respiratory causes and about 0.91 to cardiovascular causes. Obviously, both the increased deaths due to respiratory and cardiovascular causes would mainly occur in elderly persons having preexisting chronic respiratory or cardiovascular disease conditions. Note that small numerical inconsistencies in Table 1-14 and in succeeding tables on morbidity arise from the fact that the excess risk estimates are based on different studies in a number of different populations, with different baseline death or hospital admissions rates.

Table 1-15 simply takes the information from the far right column of Table 1-14 on upper bound estimates of the number of possible PM-contributory deaths per day (for the total population, for the elderly 65+, and for respiratory and cardiovascular causes), and depicts ranges of lower and upper bound estimates for comparable numbers of estimated possible deaths per day contributed to by exposure to ambient air pollution mixes containing 50 µg/m<sup>3</sup> increments in PM<sub>10</sub> concentrations in cities ranging from 10 thousand to 10 million in size. Table 1-14 is extremely informative in showing that no appreciable risk for mortality is expected to occur with exposure to such ambient air mixes for cities less than 1 million population, even if the PM<sub>10</sub> elevation lasts for 3-5 days or occurs several times a year; nor is there much appreciable risk for the elderly in smaller population cities, unless perhaps a particular city with less than 1 million population has an extraordinarily high percentage of elderly residents. This applies even for days when 100 µg/m<sup>3</sup>-increments in PM<sub>10</sub> might occur for 3-5 days in a row. Even for cities of 1 million population, the projected upper bound risk may be of dubious public health significance unless 50-100 µg/m<sup>3</sup> PM<sub>10</sub> elevations were to occur numerous times per year, especially in view of such tiny increased risk likely mainly being posed for elderly individuals with preexisting cardiopulmonary disease conditions that predominantly arise from voluntary smoking. Any risk of excess mortality associated with short-term, acute exposures to ambient air pollutant



**TABLE 1-14. ESTIMATED EXCESS MORTALITY PER DAY IN A POPULATION OF ONE MILLION FOR WHICH AN INCREASE OF 50  $\mu\text{g}/\text{m}^3$   $\text{PM}_{10}$  (24-h) COULD BE A CONTRIBUTING FACTOR**

Health Outcome	Age Group	Population Baseline Annual Mortality	Population Baseline Daily Mortality	$\text{PM}_{10}$ Lag Time	Upper Bound Excess Risk Per $\text{PM}_{10}$ 50 $\mu\text{g}/\text{m}^3$	Possible Number of PM-Related Deaths/Day
Total Mortality	All	8,603 <sup>1</sup>	23.6	< 2d	0.03 <sup>2</sup>	0.7
	65+	6,201 <sup>3</sup>	17.0	2d	0.06 <sup>4</sup>	1.0
Total Mortality	All	8,603	23.6	3-5d	0.06 <sup>2</sup>	1.5
Respiratory Mortality	All	676 <sup>1</sup>	1.85	3-5d	0.19 <sup>5</sup>	0.3
Cardiovascular Mortality	All	3,635	10.0	3-5d	0.09 <sup>5</sup>	0.9

<sup>1</sup>From Monthly Vital Statistics Report for 1991 (U.S. CD 1993).

<sup>2</sup>From EPA meta-analyses, Table 12-25; all models without co-pollutants

<sup>3</sup>Elderly as 12.6% of 1991 U.S. population

<sup>4</sup>From Saldiva and Bohn (1994) and Ostro et al. (1995), variance-weighted average (TWA); Section 12.3.1.3

<sup>5</sup>From Pope, et al. (1991), Schwartz (1993) for Utah Valley and Birmingham TWA, Table 12-4

**TABLE 1-15. ESTIMATED NUMBER OF DEATHS PER DAY IN CITIES OF 10,000 to 10 MILLION<sup>1</sup> FOR WHICH AN INCREASE OF 50  $\mu\text{g}/\text{m}^3$   $\text{PM}_{10}$  COULD BE A CONTRIBUTING FACTOR**

Population of City	Expected Number of PM-Related Excess Deaths Per Day				
	Whole Pop. All Causes < 2d Lag	65+ Pop. All Causes < 2d Lag	Whole Pop. All Causes 3-5 Day Lag	Whole Pop. Respiratory 3-5 Day Lag	Whole Pop. Cardiovascular 3-5 Day Lag
10 Million	~4 - 7	~5 - 10	~7 - 15	~2 - 3	~5 - 9
5 Million	~2 - 4	~2.5 - 5	~4 - 8	~1 - 2	~2 - 5
1 Million	~0.4 - 0.7	~0.5 - 1	~0.8 - 1.5	~0.2 - 0.3	~0.5 - 0.9
500,000	~0.2 - 0.4	~0.3 - 0.5	~0.4 - 0.8	~0.1 - 0.15	~0.2 - 0.5
100,000	~0.05	~0.07	~0.01	~0.03	~0.07
50,000	~0.03	~0.04	~0.05	~0.02	~0.04
10,000	~0.005	~0.01	~0.01	~0.002	~0.008

<sup>1</sup>Upper end of range for each city size calculated from upper bound estimates in Table 13-17 for population of 1 million. Lower end of range derived as lower bound estimate roughly 50% less than the upper bound, as per text.

mixes having 50-100 $\mu\text{g}/\text{m}^3$  increments in 24-h  $\text{PM}_{10}$  levels would most likely be projected as possibly causing meaningful numbers of excess deaths mainly as such exposures occur for large segments of the elderly population (age 65+ yrs) with preexisting cardiopulmonary diseases in rather large cities exceeding 1-2 million population. The level of public concern, however, even in such cases may be tempered by the likelihood that a majority of those at special risk are most probably current or former smokers, given the predominant role attributed (U.S. EPA, 1992) to smoking in the etiology of preexisting cardiopulmonary diseases that distinguish those identified as being at greater risk.

There is some limited direct evidence for an interaction between smoking status and excess mortality attributable to PM exposure. Based on the Six Cities Study, Dockery, et. al. (1993) reported an increased RR for  $\text{PM}_{2.5}$  between the least polluted city (Portage) and the most polluted city (Steubenville) that is substantially (albeit not statistically significantly) higher in individuals who are current or former smokers, compared to never-smokers. This is shown in Table 1-16. Prospective studies that have individual data on smoking status probably offer the best opportunity for detecting differential effects of smoking status on PM-related mortality and morbidity for use in future criteria assessments.

**TABLE 1-16. ASSOCIATION BETWEEN CIGARETTE SMOKING STATUS AND EXCESS MORTALITY RISK FROM AIR POLLUTION IN THE SIX CITIES STUDY**

Smoking Status	Relative Risk for Worst $\text{PM}_{2.5}$ City (Steubenville) Versus Lowest Best $\text{PM}_{2.5}$ City (Portage)					
	M+F	(95 % CI)	M	(95 % CI)	F	(95 % CI)
Never Smoker	1.19	(0.90,1.57)	1.29	(0.80,2.09)	1.15	(0.82,1.62)
Former Smoker	1.35	(1.02,1.77)	1.31	(0.96,1.80)	1.48	(0.82,2.66)
Current Smoker	1.32	(1.04,1.68)	1.42	(1.05,1.92)	1.23	(0.83,1.83)

<sup>1</sup>Based on Table 3 from Dockery, et. al (1993)

The prematurity of the excess deaths is also a matter of considerable importance, but there is as yet little firm evidence from acute mortality studies by which to judge whether PM-related excess deaths generally represent highly compromised elderly individuals dying a

1 few days or weeks sooner than they would have otherwise versus several months or years of  
2 prematurity of death for some.

3 Morbidity effects demonstrated as likely being associated with short-term exposures to  
4 ambient U.S. PM exposures include increased hospital admissions for respiratory and  
5 cardiovascular disease conditions, increased respiratory symptoms (including exacerbation of  
6 asthma), and small pulmonary function decrements (e.g., 2-3% decreases in FEV<sub>1</sub> or FVC).  
7 Probably of most immediate public health concern are the hospital admissions, which are also  
8 more readily quantifiable and understandable as an index of obviously serious health impacts.  
9 Table 13-20 summarizes key types of information by which one might attempt to project  
10 increments in hospital admissions for which exposure to an increment in ambient PM<sub>10</sub>  
11 (24-h) of 50 µg/m<sup>3</sup> might contribute per 1 million people exposed. Table 1-17 can be  
12 interpreted in an analogous fashion to Table 1-14. Note from Table 1-17 that the typical  
13 number of PM<sub>10</sub>-related hospital admissions for cardiovascular causes would be projected to  
14 be only about 2.5 times as high as the number of potential deaths during the same event, and  
15 the number of respiratory admissions about 6 times as high as the possible number of deaths  
16 from respiratory causes shown in Table 1-14. However, many deaths from cardiovascular or  
17 respiratory causes occur without a prior hospital admission. There is, nonetheless, a  
18 reasonable numeric consistency between the rough estimates of potential hospital admissions  
19 or discharges and possible total deaths contributed to by exposure in a community to PM-  
20 containing ambient-air mixes.

21 Table 1-18 then scales expected daily hospital admissions potentially associated with  
22 exposures to ambient air mixes having a 50 µg/m<sup>3</sup> increase in PM<sub>10</sub> (24-h) for towns and  
23 cities with populations of 10 thousand to 10 million (analogous to what was done earlier in  
24 Table 1-15 based on Table 1-14 calculations). However, in this case, both Tables 1-17 and  
25 1-18 provide only upper bound estimates for hospital admissions based on available analyses,  
26 which did not include copollutants in the models. Essentially the same types of statements  
27 as made with regard to the very small increases in excess risk depicted in Tables 1-17 and  
28 1-18 for mortality also generally apply here for hospital admissions, except to note somewhat  
29 larger projected numbers for possible hospital admission cases for which the ambient PM  
30 exposure might be a contributing factor.

**TABLE 1-17. ESTIMATED HOSPITAL ADMISSIONS PER DAY IN A POPULATION OF ONE MILLION FOR WHICH AN INCREASE OF 50  $\mu\text{g}/\text{m}^3$  (24-h)  $\text{PM}_{10}$  COULD BE A CONTRIBUTING FACTOR**

First Listed Diagnosis	Age Group	Population Baseline Annual Discharges	Population Baseline Daily Hospital Discharges	Excess Risk per $\text{PM}_{10}$ 50 $\mu\text{g}/\text{m}^3$ (Lag $\leq 1$ d)	Possible Number of PM-Related Hosp. Admissions Per Day
All conditions	All	124,110 <sup>1</sup>	340.0	--	--
	65+	42,845 <sup>2</sup>	117.4	--	--
Respiratory Conditions (all)	All	12,180 <sup>1</sup>	33.4	0.06 <sup>3</sup>	2.0
	65+	5,101 <sup>1</sup>	14.0	0.08 <sup>3</sup>	1.1
Pneumonia	All	4,340 <sup>1</sup>	11.9	--	--
	65+	2,335 <sup>2</sup>	6.4	0.08 <sup>4</sup>	0.5
COPD	All	3,337 <sup>7</sup>	9.1	0.15 <sup>5</sup>	1.4
	65+	2,560 <sup>7</sup>	7.0	0.16 <sup>3</sup>	1.1
Heart Disease	All	12,310	58.4	0.04 <sup>6</sup>	2.3
	65+	13,502	37.0	0.06 <sup>6</sup>	2.2

<sup>1</sup>From Table 12-7

<sup>2</sup>From Table 12-7, assuming 12.6% age 65+

<sup>3</sup>From Table 12-9, average

<sup>4</sup>From Table 12-11, average

<sup>5</sup>From Table 12-10, average

<sup>6</sup>From Table 12-12

<sup>7</sup>From 1992 detailed Tables; excludes asthma (ICD9 493-493.9)

**TABLE 1-18. ESTIMATED NUMBERS OF HOSPITAL ADMISSIONS FOR RESPIRATORY AND CARDIOVASCULAR CAUSES PER DAY IN CITIES OF 10,000 to 10 MILLION FOR WHICH AN INCREASE OF 50  $\mu\text{g}/\text{m}^3$   $\text{PM}_{10}$  (24-h) COULD BE A CONTRIBUTING FACTOR**

Population of City	All Respiratory Conditions		Pneumonia		COPD		Heart Disease	
	Whole Pop.	65+ Pop.	Whole Pop.	65+ Pop.	Whole Pop.	65+ Pop.	Whole Pop.	65+ Pop.
10 Million	20.0	11.0	--	5.0	14.0	11.0	23.0	22.0
5 Million	10.0	5.5	--	2.5	7.0	5.5	11.5	11.0
1 Million	2.0	1.1	--	0.5	1.4	1.1	2.3	2.2
500,000	1.0	0.55	--	0.25	0.7	0.55	1.15	1.1
100,000	0.2	0.11	--	0.05	0.14	0.11	0.23	0.22
50,000	0.1	0.05	--	0.02	0.07	0.05	0.12	0.11
10,000	0.02	0.01	--	0.01	0.02	0.01	0.02	0.02

1 Overall, based on the foregoing discussions, there appears to exist credible evidence for  
2 a likely very small, but real PM effect on human health in some susceptible subpopulations  
3 (including contributing along with other risk factors to premature deaths among the elderly  
4 with preexisting cardiopulmonary diseases) at PM<sub>10</sub> 24-h concentrations in the range of 30 to  
5 200 µg/m<sup>3</sup>. However, the biological mechanisms by which such effects occur are as yet not  
6 well understood and remain to be delineated, as is the case for clearer characterization and  
7 interpretation of relative risk estimates for PM-related effects and their appropriate use in  
8 projecting potential public health impacts.

## 2. INTRODUCTION

This document is an update revision of "Air Quality Criteria for Particulate Matter and Sulfur Oxides" published by the United States Environmental Protection Agency (EPA) in 1982, an Addendum to that document published in 1986, and an Acid Aerosols Issue Paper published in 1989, and it will serve as the basis for reevaluating the current National Ambient Air Quality Standard (NAAQS) for particulate matter (PM). The present document critically evaluates and assesses the scientific information relative to determining the health and welfare effects associated with exposure to various concentrations of PM in ambient air. Although the document is not intended as a complete and detailed literature review, it is intended to cover pertinent literature through its publication date. The literature through that time is reviewed thoroughly for information relevant to criteria development. Though the emphasis is on the presentation of data on health and welfare effects, other scientific data are also discussed in order to provide a better understanding of the pollutants in the environment.

### 2.1 LEGISLATIVE REQUIREMENTS

Two sections of the CAA (Sections 108 and 109, 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. Section 109(d) of the CAA requires periodic review and, if appropriate, revision of existing criteria and standards.

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. The welfare effects included in the criteria are 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.

## 2.2 REGULATORY BACKGROUND

"Particulate matter" is the generic term for a broad class of chemically and physically diverse substances that exist as discrete particles (liquid droplets or solids) over a wide range of sizes. Particles originate from a variety of stationary and mobile sources. They may be emitted directly or formed in the atmosphere by transformation of gaseous emissions such as sulfur oxides ( $\text{SO}_x$ ), nitrogen oxides ( $\text{NO}_x$ ), and volatile organic substances. The chemical and physical properties of PM vary greatly with time, region, meteorology, and source category, thus complicating the assessment of health and welfare effects. Particles in ambient air usually occur in two somewhat overlapping bimodal size distributions: (1) fine (diameter less than  $2.5\ \mu\text{m}$ ) and (2) coarse (diameter larger than  $2.5\ \mu\text{m}$ ). The two size fractions tend to have different origins and composition.

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, 1986), which collects PM up to a nominal size of 25 to  $45\ \mu\text{m}$  (so-called "total suspended particulate," or "TSP"). Thus, TSP was the original indicator for the PM standards. The primary standards for PM (measured as TSP) were  $260\ \mu\text{g}/\text{m}^3$ , 24-h average not to be exceeded more than once per year, and  $75\ \mu\text{g}/\text{m}^3$ , annual geometric mean. The secondary standard (measured as TSP) was  $150\ \mu\text{g}/\text{m}^3$ , 24-h average not to be exceeded more than once per year.

On October 2, 1979 (Federal Register, 1979a), EPA announced that it was in the process of revising the AQCD and reviewing the existing air quality standards for possible

1 revisions. External review drafts of that revised AQCD were made available for public  
2 comment and peer review by the Clean Air Scientific Advisory Committee (CASAC) of  
3 EPA's Science Advisory Board (SAB). CASAC prepared a "closure" memorandum to the  
4 Administrator indicating its satisfaction with the final draft of the AQCD. After closure,  
5 minor technical and editorial refinements were made to the AQCD (U.S. Environmental  
6 Protection Agency, 1982). The final draft (December 1981) of the document was issued  
7 simultaneously with the proposal of revisions to the PM standards.

8 On March 20, 1984 (Federal Register, 1984), EPA proposed a number of revisions to  
9 the primary and secondary PM standards. Following publication of the proposal, EPA held a  
10 public meeting in Washington, DC, on April 30, 1984, to receive comments on the proposed  
11 standards revisions. After the close of the original public comment period (June 5, 1985),  
12 CASAC met on December 16 and 17, 1985, to review the proposal and to discuss the  
13 relevance of certain new scientific studies on the health effects of PM that had emerged since  
14 CASAC completed its review of the AQCD and staff paper in January 1982. Based on its  
15 preliminary review of these new studies, CASAC recommended that EPA prepare separate  
16 addenda to the AQCD and staff paper for the purpose of evaluating relevant new studies and  
17 discussing their potential implications for standard-setting. The EPA announced its  
18 acceptance of these recommendations on April 1, 1986 (Federal Register, 1986a). On July  
19 3, 1986, EPA announced (Federal Register, 1986b) the availability of the external review  
20 draft document, entitled Second Addendum to Air Quality Criteria for Particulate Matter and  
21 Sulfur Oxides (1982): Assessment of Newly Available Health Effects Information (U.S.  
22 Environmental Protection Agency, 1986). At the same time, on July 3, 1986, EPA  
23 announced a supplementary comment period to provide the public an opportunity to comment  
24 on the implications of the new studies and addenda for the final standards. The CASAC held  
25 a public meeting on October 15 and 16, 1986, to review the AQCD addendum. At this  
26 meeting, CASAC members, as well as representatives of several organizations, provided  
27 critical review of the EPA documents.

28 The CASAC sent a closure letter on the AQCD addendum to the Administrator dated  
29 December 15, 1986, which stated that the 1986 addendum and the 1982 AQCD, previously  
30 reviewed by CASAC, represent a scientifically balanced and defensible summary of the  
31 extensive scientific literature on PM and SO<sub>x</sub> (Lippmann, 1986b).



On July 1, 1987 (Federal Register, 1987), EPA published final revisions to the NAAQS for PM. The principal revisions in 1987 included (1) replacing TSP as the indicator for the ambient standards with a new indicator that includes only particles with an aerodynamic diameter less than or equal to a nominal 10  $\mu\text{m}$  ("PM<sub>10</sub>"), (2) replacing the 24-h primary TSP standard with a 24-h PM<sub>10</sub> standard of 150  $\mu\text{g}/\text{m}^3$ , (3) replacing the annual primary TSP standard with an annual PM<sub>10</sub> standard of 50  $\mu\text{g}/\text{m}^3$ , and (4) replacing the secondary TSP standard with 24-h and annual PM<sub>10</sub> standards identical in all respects to the primary standards.

## **2.3 SCIENTIFIC BASIS FOR THE EXISTING PARTICULATE MATTER STANDARDS<sup>1</sup>**

The following discussion describes the bases for the existing PM NAAQS set in 1987. The discussion includes the rationale for the primary standards, the pollutant indicator for particulate matter, the averaging time and form of the standard, and finally a discussion of EPA's assessment that led to the standard set in 1987.

### **2.3.1 Rationale for the Primary Standards**

In selecting primary standards for PM, the Administrator must specify (1) the particle size fraction that is to be used as an indicator of particulate pollution, (2) the appropriate averaging times and form(s) of the standards, and (3) the numerical levels of the standards. Based on the assessment of relevant scientific and technical information in the earlier 1982 PM AQCD and addenda, the staff paper and staff paper addendum outlined a number of key factors considered in making decisions in each of these areas. The following discussion of the 1987 revisions of the standards focuses mainly on the considerations that were most influential in the Administrator's selection of particular options.

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<sup>1</sup>Adapted from Federal Register (1987) National Ambient Air Quality Standard for Particulate Matter.

### 2.3.2 Pollutant Indicator

Based on the assessment of the available scientific information, EPA concluded in 1987 that (1) a separate PM standard (as opposed to a combination standard for PM and SO<sub>x</sub>) remained a reasonable public health policy choice, and (2) given current scientific knowledge and uncertainties, a size-specific (rather than chemical-specific) indicator should be used. In assessing the information in the AQCD, EPA reached several conclusions summarized here.

- (1) Health risks posed by inhaled particles are influenced by both the penetration and deposition of particles in the various regions of the respiratory tract and the biological responses to these deposited materials. Smaller particles penetrate furthest in the respiratory tract. The largest particles are deposited predominantly in the extrathoracic (head) region, with somewhat smaller particles depositing in the tracheobronchial region; still smaller particles can reach the deepest portion of the lung, the pulmonary region.
- (2) The risks of adverse health effects associated with deposition of typical ambient fine and coarse particles in the thoracic region (tracheobronchial and pulmonary deposition) are markedly greater than those associated with deposition in the extrathoracic region. Maximum particle penetration to the thoracic region occurs during oronasal or mouth breathing.
- (3) The size-specific indicator for primary standards should represent those particles small enough to penetrate to the thoracic region. The risks of adverse health effects from extrathoracic deposition of typical ambient PM are sufficiently low that particles depositing only in that region can safely be excluded from the indicator.

Considering the above conclusions, together with information on air quality composition, the need to provide protection for sensitive individuals who may breathe by mouth or oronasally and the similar convention on particles penetrating the thoracic region adopted by the International Standards Organization (1981), EPA staff recommended that the size-specific indicator include particles of diameters less than or equal to a nominal 10 μm "cut point" generally referred to as "PM<sub>10</sub>". In terms of collection efficiency, this represents a 50% cut point or diameter (D<sub>50</sub>) the aerodynamic particle diameter for which the efficiency of particle collection is 50%. With such a cut point, larger particles are not excluded entirely but are collected with substantially decreasing efficiency, and smaller particles are collected with increasing (up to 100%) efficiency. Ambient samplers with this cut point provide a reliable estimate of the total mass of suspended PM of aerodynamic size less than

1 or equal to 10  $\mu\text{m}$ . Such an indicator ( $\text{PM}_{10}$ ) is conservative with respect to health  
2 protection in that it includes all of the particles small enough to penetrate to the sensitive  
3 pulmonary region and includes approximately the same proportion of the coarse-mode  
4 fraction that would be expected to reach the tracheobronchial region. It places substantially  
5 greater emphasis on controlling smaller particles than does a TSP indicator, but does not  
6 completely exclude larger particles from all control.

7 The assessment of then-available information on respiratory tract deposition in the 1986  
8 AQCD and staff paper addenda reinforced the conclusions reached in the original EPA  
9 assessment. In particular, (1) the data do not provide support for an indicator that excludes  
10 all particles larger than 10  $\mu\text{m}$  in diameter; (2) the analysis used to support an alternative  
11 indicator with a nominal size cut point of 6  $\mu\text{m}$  (Swift and Proctor, 1982) significantly  
12 underestimated thoracic deposition of particles larger than 6  $\mu\text{m}$  in diameter under natural  
13 breathing conditions; (3) the  $\text{PM}_{10}$  indicator generally includes a similar or larger fraction of  
14 the range of particles that can deposit in the tracheobronchial region, although it appears to  
15 be somewhat less conservative in this regard than previously thought with respect to large  
16 ( $> 10 \mu\text{m}$ ) particle deposition under conditions of natural mouthbreathing; and (4) the studies  
17 of tracheobronchial deposition generally involved adult subjects (other information indicating  
18 even greater tracheobronchial deposition of particles in children than in adults provides an  
19 additional reason for an indicator that includes particles capable of penetration to the  
20 tracheobronchial region). Consideration of these and the earlier conclusions led EPA to  
21 reaffirm its recommendation for a  $\text{PM}_{10}$  indicator. The CASAC also restated its support for  
22  $\text{PM}_{10}$  in its review of the proposal and the closure letter to the Administrator (Lippmann,  
23 1986a,c).

24 In 1987 the Administrator accepted the recommendations of the staff and CASAC, as  
25 well as their underlying rationale, and decided to replace TSP as the particle indicator for the  
26 primary standards with a new indicator that includes only those particles less than a nominal  
27 10  $\mu\text{m}$  in diameter ( $\text{PM}_{10}$ ) as specified in the Federal Reference Method.

### 28 29 **2.3.3 Averaging Time and Form of the Standards**

30 The EPA's assessment at that time of scientific information available prior to 1987  
31 confirmed the need for both short- and long-term standards for PM. The alternative of a

1 single averaging time would not provide adequate protection against potential effects from  
2 both long- and short-term exposures without being unduly restrictive. The forms for the  
3 24-h and annual standards are discussed below.

#### 4 5 ***24-Hour Standard***

6 The Environmental Protection Agency proposed in 1987 that the 24-h standard be stated  
7 in a statistical form that uses more than 1 year of data and accounts for variations in  
8 sampling frequency in order to predict the actual number of exceedances to be expected in an  
9 average year. When used with an appropriate standard level, the statistical form can provide  
10 improved health protection that is less sensitive to changes in sampling frequency than the  
11 deterministic form and also can offer a more stable target for control programs. Recognition  
12 of the limitations of the deterministic form also led EPA to promulgate a statistical form for  
13 the ozone standard (Federal Register, 1979b).

#### 14 15 ***Annual Standard***

16 The Administrator decided to change the form of the annual standard in 1987 from the  
17 previous annual geometric mean form to a statistical form expressed as an expected annual  
18 arithmetic mean. The expected annual arithmetic mean is equivalent to the long-term  
19 arithmetic average concentration level, assuming no changes in underlying emissions. The  
20 expected arithmetic mean is more directly related to the available health effects information  
21 than is the annual geometric mean, which was the previous form of the standard. Because  
22 the arithmetic mean concentration is proportional to the sum of the daily means, it reflects  
23 the total cumulative exposure of PM to which an individual is exposed. Therefore, it is an  
24 appropriate indicator to protect against any health effect that depends on chronic, total  
25 exposure. It is also a reasonable indicator for protecting against health effects that depend on  
26 repeated short-term high concentrations (short-term peaks have an influence on the arithmetic  
27 mean that is proportional to their frequency, magnitude, and duration). The geometric mean,  
28 on the other hand, deemphasizes the effect of short-term peak concentrations and is heavily  
29 influenced by days of relatively clean air. For these reasons, EPA staff and CASAC  
30 recommended the change to an arithmetic mean.

Under the statistical form, the expected annual arithmetic average is determined by averaging the annual arithmetic averages from 3 successive years of data. The prior deterministic form of the standard did not adequately take into account the random nature of meteorological variations. In general, annual mean PM concentrations will vary from year to year, even if emissions remain constant, due to the random nature of meteorological conditions that affect the formation and dispersion of particles in the atmosphere. If only 1 year of data is considered, compliance with the standard and, consequently, emission control requirements, may be determined on the basis of a year with unusually adverse or unusually favorable weather conditions. The problem of year-to-year variability is, however, reduced by averaging 3 years of data.

#### **2.3.4 Level of the Standards**

The original Office of Air Quality Planning and Standards (OAQPS) PM Staff Paper and CASAC recommendations set forth a framework for determining the levels for the proposed PM standards that would protect public health with an adequate margin of safety. The discussion that follows relies heavily on that framework and on the supporting material in the staff paper and its addendum, as well as the CASAC closure letters. The essential steps in this framework are summarized here.

#### ***Assessment of the Quantitative Epidemiological Studies***

The 1982 AQCD and its 1986 addendum identified a small number of community epidemiological studies that are useful in determining concentrations at which PM is likely to adversely impact public health. The EPA staff used these quantitative studies to examine concentration-response relationships and to develop numerical "ranges of interest" for possible PM<sub>10</sub> standards.

A number of uncertainties associated with the use of these studies had to be considered in selecting an appropriate margin of safety. As discussed in the staff paper and the AQCD, and the addenda to those documents, epidemiological studies generally are limited in sensitivity and are subject to inherent difficulties involving confounding variables. Moreover, many of the quantitative studies were conducted in times and places where pollutant composition may have varied considerably from current U.S. atmospheres. Also,

1 most of the studies used British Smoke—British Smoke (BS) is a pseudo-mass indicator  
2 related to small particle (aerodynamic diameter less than a nominal 4.5  $\mu\text{m}$ ) darkness—or  
3 TSP as particle indicators. None of the published studies used the proposed  $\text{PM}_{10}$  indicator.  
4 Thus, assumptions had to be used to convert the various results to common ( $\text{PM}_{10}$ ) units.  
5

### 6 *Identification of Margin of Safety Considerations*

7 The 1982 AQCD and its addendum identified an additional substantial body of scientific  
8 literature that, although it did not provide reliable concentration-response relationships for  
9 ambient exposures, did provide important qualitative insights into the health risks associated  
10 with human exposure to particles. This literature included both quantitative and qualitative  
11 epidemiological studies, controlled human exposure experiments, and animal toxicological  
12 studies. The EPA staff assessed this literature to identify additional factors and uncertainties  
13 that should be considered in selecting the most appropriate margin of safety.

14 Experience has shown that it is difficult to identify, with confidence, the lowest  
15 pollution level at which an adverse effect will occur. Moreover, in cases such as the  
16 present one, the evidence suggests that there is a continuum of effects, with the risk,  
17 incidence, or severity of harm decreasing, but not necessarily vanishing, as the level of  
18 pollution is decreased.

19 The requirement for an adequate margin of safety for primary standards addresses  
20 uncertainties associated with inconclusive scientific and technical information available at the  
21 time of standard setting. It also aims to provide a reasonable degree of protection against  
22 hazards that research has not yet identified. Both kinds of uncertainties are components of  
23 the risk associated with pollution at levels below those at which human health effects can be  
24 said to occur with reasonable scientific certainty. Thus, by selecting primary standards that  
25 provide an adequate margin of safety, the Administrator sought not only to prevent pollution  
26 levels that have been demonstrated to be harmful, but also to prevent lower pollutant levels  
27 that may pose an unacceptable risk of harm, even if that risk is not precisely identified as to  
28 nature or degree.

29 In the absence of clearly identified thresholds for health effects, the selection of a  
30 standard that provides an adequate margin of safety requires an exercise of informed  
31 judgment by the Administrator. The level selected will depend on the expected incidence

1 and severity of the potential effects and on the size of the population at risk, as well as on  
2 the degree of scientific certainty that the effects will in fact occur at any given level of  
3 pollution.

4 The 1986 EPA staff paper recommended a range of potential standards for the  
5 Administrator's consideration. The recommended range was below the levels at which EPA  
6 staff, with the concurrence of CASAC, had concluded from the available data that adverse  
7 health effects were "likely", but in the domain where the data suggested that such effects  
8 were "possible". The Administrator proposed refined ranges of standard levels that were  
9 based on the 1984 staff and CASAC recommendations. After consideration of the then new  
10 scientific evidence contained in the AQCD addendum, the staff revised its recommended  
11 range of standards. The Administrator considered the revised assessments and the  
12 recommendations of CASAC (Lippmann, 1986b) in making the final decision on the standard  
13 levels. The rationales for the levels of the 24-h and annual standards are presented below.

#### 14 15 *24-Hour Standard*

16 The 1987 assessment of the short-term epidemiological data expresses PM levels in  
17 both the BS or TSP and PM<sub>10</sub> units. The term "effects likely" denoted concentration ranges  
18 derived from the 1982 AQCD and its addendum at or above which a consensus judgment  
19 suggests the greatest certainty that the effects studied would occur, at least under the  
20 conditions that occurred in the original studies. In the "effects possible" range, EPA found  
21 credible scientific evidence suggesting the existence of adverse health effects in sensitive  
22 populations, but substantial uncertainty exists regarding the conclusions to be drawn from  
23 such evidence.

24 The 1987 review of the data did not provide evidence of clear thresholds in exposed  
25 populations. Instead, they suggested a continuum of response for a given number of exposed  
26 individuals, with both the likelihood (risk) of any effects occurring and the extent (incidence  
27 and severity) of any potential effect decreasing with concentration (this is particularly true for  
28 the statistical analyses of daily mortality in London). Substantial agreement existed that  
29 wintertime pollution episodes produced premature mortality in elderly and ill populations, but  
30 the range and nature of association provide no clear basis for determining lowest  
31 effects-likely levels or for defining a concentration below which no association remained.

1 The lung function studies in children also provided evidence of effects at concentrations over  
2 a range, but the relationships were not certain enough to derive effects-likely levels for  
3  $PM_{10}$ . The lung function studies did, however, suggest levels below which detectable  
4 functional changes were unlikely to occur in exposed populations. Following CASAC  
5 recommendations, EPA used the combined range of effects-possible studies as a starting  
6 point for developing alternative standards.

7 The original range proposed by the Administrator, drawn from the 1984 staff analysis,  
8 was 150 to 250  $\mu g/m^3$   $PM_{10}$  24-h average, with no more than one expected exceedance per  
9 year. The lower bound of this range was derived from the original assessment of the London  
10 mortality studies. As a result of reanalyses of the London mortality data and the findings  
11 from the then current U.S. morbidity studies, the staff reduced the level of the lower bound  
12 of the range of interest to 140  $\mu g/m^3$ , and noted that the difference between it and the  
13 original lower bound (150  $\mu g/m^3$ ) was within the range of uncertainty associated with  
14 converting the morbidity study results from TSP to  $PM_{10}$ .

15 At that time the study of Lawther et al. (1970) was judged to provide evidence that  
16 health effects are likely at PM concentrations above 250  $\mu g/m^3$  (as BS). The effects  
17 observed in this study (related to aggravation of bronchitis) are of concern because of both  
18 their immediate impact and their potential for inducing longer term deterioration of health  
19 status in a significant sensitive group. Based on the uncertain conversion between smoke and  
20  $PM_{10}$ , the lowest effects likely level derived from the Lawther study (250  $\mu g/m^3$  as BS)  
21 should be in the range of 250 to 350  $\mu g/m^3$  in  $PM_{10}$  units.

22 The 1987 assessment of the Lawther et al. (1970) study formed the basis for the upper  
23 bound of the range of  $PM_{10}$  standards proposed by the Administrator in 1984. Considering  
24 this study alone, a  $PM_{10}$  standard of 250  $\mu g/m^3$  might appear to contain some margin of  
25 safety, even for the sensitive bronchitics studied, because it incorporated a conservative  $PM_{10}$   
26 conversion factor and because of differences between exposure conditions in the British study  
27 and current U.S. air quality. Because bronchitics are identified as a group particularly  
28 sensitive to particulate pollution, a standard of 250  $\mu g/m^3$  (as  $PM_{10}$ ) also might provide some  
29 margin of safety for other, less sensitive groups. Nevertheless, this study of bronchitics in  
30 London has inherent limitations in sensitivity that preclude derivation of unequivocal "effects  
31 thresholds" at 250  $\mu g/m^3$  as BS and, by extension,  $PM_{10}$ . The 1982 AQCD noted that



1 associations between pollution and health status persisted at lower BS concentrations in  
2 selected, more sensitive individuals. Although the lead author of the study objected to  
3 attaching any importance to these latter findings (Lawther, 1986), EPA, with CASAC  
4 concurrence, found no basis for asserting that this study demonstrated a population threshold  
5 at 250  $\mu\text{g}/\text{m}^3$ .

6 In evaluating the margin of safety for a 24-h standard, it was also important to consider  
7 the London mortality studies. A standard at the upper portion of the proposed range (250  
8  $\mu\text{g}/\text{m}^3$ ) would be well below the levels (500 to 1,000  $\mu\text{g}/\text{m}^3$  as BS) of the historical London  
9 episodes in which the scientific consensus indicated that pollution was responsible for excess  
10 mortality. The portions of the population at greatest risk of premature mortality associated  
11 with PM exposures in those episodes included the elderly and persons with preexisting  
12 respiratory or cardiac disease. Although the extent of life shortening could not be specified,  
13 the seriousness of the effect strongly justified a margin of safety for it (below the consensus  
14 effects levels) that was larger than that warranted for the effects on bronchitis.

15 The staff assessment at that time of several reanalyses of London mortality suggested,  
16 however, that the risk of premature mortality to sensitive individuals extended to  
17 concentrations substantially lower than those that occurred in the "episodes". Other analyses  
18 (Mazumdar et al., 1982; Ostro, 1984; Shumway et al., 1983) provided no objective support  
19 for a population threshold below which such a risk no longer existed. Although the risk to  
20 individuals may be small at concentrations of 250  $\mu\text{g}/\text{m}^3$  and below, the number of people  
21 exposed to lower concentrations, given U.S. levels, was substantially larger than the number  
22 exposed to higher levels. The increased number of individuals exposed increased the risk  
23 that effects would occur in the total population exposed.

24 Differences in the composition of particles and gases among U.S. cities and between  
25 conditions in the United States and London at the time the mortality and morbidity data were  
26 gathered added to the complexity of assessing the risk associated with PM in the United  
27 States. In the case of the mortality studies, however, the staff found that at least one of the  
28 studies (Özkaynak and Spengler, 1985) provided qualitative support for an association  
29 between daily mortality and particle concentrations in then nearly contemporary U.S.  
30 atmospheres.

1 The 1982 assessment of the mortality studies and related factors prompted the EPA  
2 Administrator to consider standard levels that extended from 250  $\mu\text{g}/\text{m}^3$  to the lower bound  
3 of the original staff range (150  $\mu\text{g}/\text{m}^3$ ) and even lower. Reanalyses of the London mortality  
4 data prior to 1987 provided additional evidence that serious adverse health effects may occur  
5 at PM concentrations below 250  $\mu\text{g}/\text{m}^3$ . These analyses addressed a number of the  
6 uncertainties associated with the earlier studies and reinforced the Administrator's concern  
7 that a 24-h standard at the upper end of the proposed range may not provide an adequate  
8 margin of safety. However, given the uncertainties in converting from BS to PM<sub>10</sub>  
9 measurements, particularly at lower concentrations, and the possible differences in particle  
10 composition between London at the time the data were gathered and the contemporary United  
11 States, it was difficult to use these studies to set a precise level for a PM<sub>10</sub> standard.

12 Given these difficulties, it was important to examine studies contemporary with the  
13 other studies that utilize gravimetric measurements of particulate concentrations. The staff  
14 found the studies of Dockery et al. (1982) and Dassen et al. (1986) to be useful. The  
15 Dockery study observed physiologically small but statistically significant decreases in lung  
16 function in a group of children exposed to peak PM<sub>10</sub> levels of 140 to 250  $\mu\text{g}/\text{m}^3$ . The  
17 decrements persisted for 2 to 3 weeks following the exposures. The study also suggested the  
18 possibility of larger responses in a subset of the children, including those with existing  
19 respiratory symptoms. The Dassen study recorded similar decrements in children in the  
20 Netherlands following exposure to PM<sub>10</sub> levels estimated at 200 to 250  $\mu\text{g}/\text{m}^3$ , but no  
21 observable effects 2 days after exposure to PM<sub>10</sub> levels estimated at 125  $\mu\text{g}/\text{m}^3$ . The particle  
22 composition, at least in the Dockery study, was more representative of contemporary U.S.  
23 cities in that time period, and the associated aerometry provided a more reliable estimate of  
24 PM<sub>10</sub> levels than did the measurements used in the London studies. It was reasonable to  
25 expect the endpoints observed (small reversible reductions in lung function in children) to be,  
26 in most cases, more sensitive to air pollution than those observed in the London studies.  
27 These effects are, of themselves, of uncertain significance to health, but might be associated  
28 with aggravation of respiratory symptoms in children with preexisting illness. Long-term  
29 examination of respiratory health in the same community studied by Dockery et al. (1982)  
30 suggested that the children in that community had a higher incidence of respiratory illness  
31 and symptoms than children in communities with lower particle levels, but the data showed

no evidence for any persistent reduction in lung function (Ware et al., 1986). Uncertainties with respect to the effects of other pollutants (e.g., sulfur dioxide), the consistency of the changes, and exposures precluded specifying unequivocal "effects likely" levels based on this study. The EPA assessment therefore suggested that short-term lung function effects in children were possible across a range of 140 to 250  $\mu\text{g}/\text{m}^3$  or more as  $\text{PM}_{10}$ .

In making a decision on a final standard level, the Administrator also considered information from the more qualitative studies of PM. These studies suggested increased risks for sensitive groups (asthmatics) and risks of potential effects (morbidity in adults) not demonstrated in the more quantitative epidemiological literature. The qualitative studies did not provide clear information on effect levels but did justify consideration of effects of PM that have not been sufficiently investigated.

Based on the 1982 assessment of the available scientific data, in 1984, the Administrator expressed an inclination to select a 24-h level from the lower portion of the proposed range of 150 to 250  $\mu\text{g}/\text{m}^3$ . The addendum to the 1982 assessment supported the original findings and, if anything, suggested an even wider margin of safety was warranted. The Administrator, therefore, decided to set the final standard at the extreme lower bound of the range originally proposed (i.e., 150  $\mu\text{g}/\text{m}^3$ ). This standard provided a substantial margin of safety below the levels at which there was a scientific consensus that PM caused premature mortality and aggravation of bronchitis. Such a margin was necessary because of the seriousness of the effects and because of the analyses of daily mortality studies that suggested that adverse effects may occur at PM levels well below the consensus levels. The standard was in the lower portion of the range where sensitive, reversible physiological responses of uncertain health significance possibly, but not definitely, are observed in children. Using a conservative assessment of the lung function/particle relationship from Dockery et al. (1982), a change in concentration from background levels ( $\approx 20 \mu\text{g}/\text{m}^3$ ) to 150  $\mu\text{g}/\text{m}^3$  would produce lung function changes of at most 10 to 15% in less than 5% of exposed children. Based on the results of Dassen et al. (1986), it appeared unlikely that any functional changes would be detected 1 or 2 days following such exposures. Thus, the maximum likely changes in lung function appeared to present little risk of significant adverse responses. Standards set at a somewhat higher level would, however, present an unacceptable risk of premature mortality and allow the possibility of more significant

functional changes. Furthermore, a standard level of  $150 \mu\text{g}/\text{m}^3$  was fully consistent with the recommendations of CASAC on the 24-h standard (Lippmann, 1986c).

#### *Annual Standard*

The long-term epidemiological studies examined in 1987 were subject to confounding variables that reduce the studies' sensitivity and make their interpretation difficult. No clear thresholds could be identified for the effects-likely levels, and evidence existed for effects at lower levels (the effects-possible levels); however, the evidence was inconclusive, and the effects were difficult to detect.

Based on an EPA assessment of  $\text{PM}_{10}$ /TSP ratios in areas with elevated TSP levels, the effects-likely levels from the Ferris et al. (1973) study were revised to 80 to  $90 \mu\text{g}/\text{m}^3$  as  $\text{PM}_{10}$ . Because of limitations in sampling duration and the conversion to  $\text{PM}_{10}$ , this estimate was particularly uncertain, with effects possible at lower concentrations. Of greatest concern was the possibility of long-term deterioration of the respiratory system in exposed populations, the potential for which is indicated by lung function (mechanical pulmonary) changes and increased incidence of respiratory disease. One set of studies (Ferris et al., 1973, 1976) provided some evidence for a "no-observed-effect level" for those effects at or below  $60$  to  $65 \mu\text{g}/\text{m}^3$  as  $\text{PM}_{10}$  ( $130 \mu\text{g}/\text{m}^3$  as TSP), whereas another study (Bouhuys et al., 1978) suggested some possibility of symptomatic responses in adults at long-term median levels at or below about  $50$  to  $55 \mu\text{g}/\text{m}^3$  as  $\text{PM}_{10}$ . The importance of these symptomatic responses, which were unaccompanied by lung function changes, to long-term respiratory health was unclear.

The most important study of long-term effects at that time was an ongoing examination of six U.S. cities (Ware et al., 1986). The study indicated the possibility of increased respiratory symptoms and illnesses in children at multiyear levels across a range of  $40$  to more than  $58 \mu\text{g}/\text{m}^3$  as  $\text{PM}_{10}$  but found no evidence of reduced lung function at these concentrations. This study did not find similar gradients in symptoms and illness within some of the cities, which had somewhat smaller localized pollution gradients. The results of a separate series of studies of long- and intermediate-term (2- to 6-week) exposures in a number of U.S. metropolitan areas (Ostro, 1987; Hausman et al., 1984) were more supportive of the possibility of effects within cities (respiratory-related activity restrictions in

adults) at comparable U.S. exposure levels. The results of these studies were generally consistent with the earlier U.S. studies. In particular, the finding of symptomatic responses in children with no change in lung function (Ware et al., 1986) was consistent with similar findings in adults (Bouhuys et al., 1978) at estimated long-term  $\text{PM}_{10}$  levels down to  $50 \mu\text{g}/\text{m}^3$ . However, the information available to support the existence of significant adverse effects at annual  $\text{PM}_{10}$  levels below  $50 \mu\text{g}/\text{m}^3$  (especially when 24-h levels are maintained below  $150 \mu\text{g}/\text{m}^3$ ) was quite limited and uncertain.

Because of the uncertainties and the limited scope and number of long-term quantitative studies available for review in 1987, it was important to examine the results of qualitative data from a number of epidemiological, animal, and ambient particle composition studies in determining what constitutes an adequate margin of safety for an annual standard. These studies justified concern for serious effects not directly evaluated in the above studies. Such effects included damage to lung tissues contributing to chronic respiratory disease, cancer, and premature mortality. Substantial segments of the population may be susceptible to one or more of these effects. Although the qualitative data did not provide evidence for major risks of these effects at the annual PM levels in most U.S. cities at that time, the Administrator believed that the seriousness of the potential effects and the large population at risk warranted caution in setting the standard.

Based on the findings discussed in the 1982 AQCD, in 1984, the Administrator proposed to select an annual standard level from a range of  $50$  to  $65 \mu\text{g}/\text{m}^3$ . In the proposal, the Administrator favored a standard in the lower portion of the range. The evidence discussed in the 1986 addendum, although subject to substantial uncertainty, served to reinforce this inclination. In light of the 1986 assessment, and in accordance with the recommendation of CASAC, the Administrator decided to set the level of the annual standard at the lower bound of the original range ( $50 \mu\text{g}/\text{m}^3$ , expected annual arithmetic mean). This standard provided a reasonable margin of safety against long-term degradation in lung function, which was judged likely to occur at estimated  $\text{PM}_{10}$  levels above  $80$  to  $90 \mu\text{g}/\text{m}^3$  and for which there was some evidence at  $\text{PM}_{10}$  levels above  $60$  to  $65 \mu\text{g}/\text{m}^3$ . Such a standard also provided reasonable protection against the less serious symptomatic effects (bronchitis) for which only inconclusive evidence was available. Moreover, the staff and CASAC recommended that the combined protection afforded by both 24-h and annual

standards be considered in selecting the final standard level. In this regard, analyses of air quality data showed that implementation of the 24-h standard would reduce substantially the annual levels in a number of areas to below  $50 \mu\text{g}/\text{m}^3$ , adding to the protection afforded by the annual standard in areas with higher 24-h peak-to-mean ratios. Based on the then available information with respect to risks associated with annual exposures, the Administrator believed that the annual and 24-h standards provided an adequate margin of safety.

### **2.3.5 Welfare Effects**

No convincing evidence existed indicating significant adverse soiling and nuisance at TSP levels below 90 to  $100 \mu\text{g}/\text{m}^3$ , and, on that basis, the Administrator concluded that secondary standards different from the primary standards were not requisite to protect the public welfare against soiling and nuisance. This conclusion was supported by CASAC's determination that there was no scientific support for a TSP-based secondary standard (Lippmann, 1986c). Therefore, the Administrator decided to set 24-h and annual secondary  $\text{PM}_{10}$  standards that are equal in all respects to the primary standards.

The other welfare effects of principal interest were impairment of visibility, potential modification of climate, and contribution to acidic deposition. All three of these effects were believed to be related to regional-scale levels of fine particles, and control programs designed to ameliorate them would likely involve region-wide reductions in emissions of sulfur oxides. The Administrator also concurred with the staff suggestions that a separate secondary particle standard was not needed to protect vegetation or to prevent adverse effects on personal comfort and well-being.

## **2.4 TOPICS/ISSUES OF CONCERN FOR CURRENT CRITERIA DEVELOPMENT**

Based on the available scientific evidence, several critical topics and associated issues are addressed in this document, as part of the current CAA-mandated periodic review of criteria and NAAQS for PM. Some of the most critical topics and issues addressed are as follows.

## 2.4.1 Air Quality and Exposure

### *Physics and Chemistry of Atmospheric Aerosols*

The atmospheric aerosols of interest because of their potential health and welfare effects consist of two principal components: a gas phase ("air" in this case) and a solid or liquid particle phase in suspension. Fine particles in the atmosphere consist mainly of (1) sulfate, nitrate, ammonium ions, and water; (2) photochemically formed organic aerosols; and (3) carbon, organic matter, and metallic components emitted directly into the atmosphere. Coarse particles in the atmosphere are composed mainly of silica, calcium carbonate, clay minerals, soot, and, sometimes, organic substances. A general relationship exists between chemical composition and particle diameter, with particles of  $\leq 2.5 \mu\text{m}$  in diameter containing most of the  $\text{SO}_4^{2-}$ ,  $\text{H}^+$ , and  $\text{NH}_4^+$ , as well as a significant fraction of the  $\text{NO}_3^-$  and  $\text{Cl}^-$ . The particle volume (mass) frequency function is often multimodal. The fine-volume fraction may have two or more modes below  $1.0 \mu\text{m}$ . The coarse fraction generally has one mode within the range  $\approx 5$  to  $50 \mu\text{m}$ . The particle volume frequency functions for the fine and coarse fractions often behave independently, (i.e., vary in relative proportion of the total ambient particle mix from location to location or from one time or season to another at the same location).

Previous documentation has shown that hydroxy, hydroperoxy, and alkoxy radicals are probably important in the oxidation of  $\text{SO}_2$  to  $\text{SO}_3^-$ , although the rate constants for some of these reactions are not well established. The hydroxy radical dominates the gas-phase oxidation of  $\text{SO}_2$  in the clean troposphere, and  $\text{H}_2\text{O}_2$  is effective in the formation of  $\text{SO}_4^{2-}$  in particles, mists, fogs, and rain. Transition metals and soot have been shown to be effective catalysts for atmospheric oxidation of  $\text{SO}_2$ . Oxidation rates for NO and  $\text{NO}_3^-$  are known but have been considered too low to be important. The oxidation rate for  $\text{NO}_2^-$  is known, but the tropospheric concentration of  $\text{HNO}_2$  is probably too low for this reaction to be important. Except for reactions of carbon (soot), solid surface reactions do not appear to be effective pathways for  $\text{H}_2\text{SO}_4$  formation in the troposphere.

The physical properties of particles are physical configuration, bulk material properties, and surface properties. The bulk material properties that affect aerosol behavior include chemical composition, vapor pressure, hygroscopicity and deliquescence, and index of refraction. These properties control the physical state and growth of particles and result in

1 scattering and absorption of light by tropospheric particles. Hygroscopicity, deliquescence,  
2 and efflorescence are critical properties in the growth of particles, but there is a paucity of  
3 thermodynamic data to permit prediction of deliquescence and hygroscopic behavior and  
4 vapor pressures of multicomponent systems, especially for relative humidities below about  
5 90%. Few studies of desorption under atmospheric conditions have been reported. Of  
6 greater concern, desorption may prove to be important in biological systems. Shape,  
7 structure, and density are physical configuration properties that are important parameters in  
8 the equations of motion for particles. Because of irregularities in particle geometry or  
9 because the particles are agglomerates, the three configuration properties are usually defined  
10 in terms of an aerodynamic diameter. Surface properties of importance include electrostatic  
11 charging, adhesion, and the influence of surface films.

12 The physical properties of particles and their modal distributions are important  
13 considerations (1) in the sampling and analysis of atmospheric particles and (2) in predicting  
14 or determining the flux to biological and nonbiological materials and deposition in the human  
15 and experimental animal respiratory tracts.

16 Advances in understanding the properties and behavior of atmospheric particulate matter  
17 have been made since publication of the previous criteria document (U.S. Environmental  
18 Protection Agency, 1982). In the current revision of the document, newer literature and data  
19 on the above topics are reviewed and discussed. For example, chemical pathways and rates  
20 of atmospheric particle formation and of removal from the atmosphere, by dry deposition and  
21 by precipitation scavenging, are examined. Likewise, the physical processes of nucleation,  
22 condensation, and coagulation by which condensible material is converted into particles are  
23 discussed, along with the size distribution of the resulting particles. The physical properties  
24 relevant to sampling considerations and deposition on surfaces, including those of the  
25 respiratory tract, are also discussed, including coverage of several newer areas of expanded  
26 research: aerosol equilibria, the unique properties of semi-volatile aerosols, and the role of  
27 particle-bound water.

## 28 *Measurement Methodology*

29 Techniques available for measurement of mass and specific components of aerosols are  
30 examined. Special attention is given to the suitability of current technology for the  
31



measurement of aerosol mass with sufficient accuracy and precision to determine compliance with one or another possible type of a new PM standard (i.e., a PM<sub>10</sub> standard with a lower level or a fine-particle standard). The need for continuous or at least daily PM measurements, the difficulty of removing particle-bound water without losing NH<sub>4</sub>NO<sub>3</sub> or semivolatile organic matter, problems in defining and maintaining a precise cut at 10 μm or lower (e.g., at 2.5 μm), and techniques for maintaining good quality control in monitoring networks are also addressed.

### *Ambient Levels*

The present draft of the revised PM AQCD describes ambient PM data for the United States, with characterization as available by size (fine/coarse) and chemical composition. Data that focus on the current U.S. PM<sub>10</sub> standard are emphasized, but information is also provided on PM<sub>2.5</sub>, PM<sub>2.5-10</sub>, and other similar cut points, as data are available. Ambient patterns are discussed, to include daily, seasonal, regional, etc. Acid aerosol data are also described as above as a separate aspect of PM. Key questions addressed include: What information is available on the distribution of PM in regard to: geographic, seasonal, diurnal, size, composition, sources, and trends? How important are uncertainties introduced by variations in the position and shape of the 10-μm cut point in various PM<sub>10</sub> monitors? How important are measurement uncertainties due to volatilizable/condensable components (e.g., loss of ammonium nitrate and, possibly, other ammonium salts) and loss of semivolatile organics or retention of particle-bound water? How do these uncertainties vary geographically and seasonally? How do these uncertainties differ for filter collection and subsequent weighing as compared to continuous indicators?

### *Cut Points*

Information helpful in evaluating the possible need for a new particle standard (PM-Fine) in addition to or instead of a PM<sub>10</sub> NAAQS is presented. This information includes discussion of sources, composition, lung deposition, sampling problems, epidemiology, biochemistry, and toxicology of fine and coarse particles. Other considerations include techniques for separating fine particles from coarse particles. Can fine and coarse particles be separated adequately by a single size cut-point in all areas of the country or will the

1 optimal cut point differ in time and space, especially between very dry areas where coarse  
2 particles may be found below 2.5  $\mu\text{m}$  and very humid areas where fine particles may be  
3 found above 1.0  $\mu\text{m}$ ? If a single fine-particle cut point is chosen, which is best: 2.5, 1.0, or  
4 something in between? Is size an adequate separation or will chemical composition  
5 measurements also be needed?

## 6 7 *Exposure*

8 Particulate matter exposure estimates for most epidemiology studies are based on data  
9 from ambient monitoring sites. Relationships between such measurements and personal  
10 exposure are important in evaluating epidemiology studies. Aspects evaluated and discussed  
11 in the present draft document include: urban scale PM exposure models, indoor/outdoor  
12 characteristics and relationships, and the validity of ambient measurements to provide  
13 appropriate estimates to relate to health effect endpoints. Two exposure estimates are of  
14 concern, individual and population estimates of PM exposure. The type of epidemiology  
15 study determines which estimate is appropriate. Additionally, other factors (such as exposure  
16 durations) that may determine health effects are considered. Human exposure patterns to  
17 ambient and indoor air particles, including consideration of activity patterns and various  
18 microenvironments, are characterized.

19 Actual human exposure differs from outdoor concentrations due to infiltration of  
20 ambient aerosols indoors, indoor sources, and human activity patterns. Human exposure can  
21 be determined through measurements and models. For PM the indoor and personal  
22 monitoring data show both higher than ambient and lower than ambient PM concentrations in  
23 indoor settings as a function of varying particle size and human activity patterns.

24 Coarse-mode particles ( $>2.5 \mu\text{m}$ ), which are generally of nonanthropogenic origin  
25 (windblown dust, etc.), require turbulence to provide vertical velocity components greater  
26 than their settling velocity to allow them to remain suspended in the air. Outdoor particles  
27 enter into an indoor setting either by bulk flow (e.g., through an open window) in which all  
28 particles can enter at the inlet condition, or by diffusional flow (e.g., through cracks and  
29 fissures in the barrier of the building envelope) in which velocities are relatively lower and  
30 therefore capable of settling out the coarser particles in the passage through the barrier. Fine

particles, however, are not easily removed by settling or impaction and penetrate indoors with high efficiency.

Indoor settings are usually quiescent, and the larger ambient particles that do enter indoors quickly settle out, leading to the presence of the familiar dust layers that require indoor settings to be cleaned constantly. However, human activity in indoor settings does generate fine particles ( $<2.5\ \mu\text{m}$ ) from smoking, vacuuming, cooking, etc., and resuspends coarse particles that previously had settled out.

Two major factors influencing the relationship of ambient to indoor PM air quality are (1) the variability of indoor concentrations of PM compared to outdoor concentrations as a function of particle size (e.g., fine indoor  $\geq$  fine outdoor and coarse indoor  $<$  coarse outdoor) and (2) the variation of exposures of individuals related to the different activities that are involved with the local generation of particles in their immediate surroundings (smoking, traffic, dusting and vacuuming at home, etc.).

Long-term personal exposures to coarse-fraction PM ( $>2.5\ \mu\text{m}$ ) can be less than half the ambient concentrations. Long-term personal exposures to fine-fraction PM ( $<2.5\ \mu\text{m}$ ) of ambient origin may be estimated by ambient measurements of the  $<2.5\text{-}\mu\text{m}$  PM fraction. However, personal activities and indoor concentrations cause personal exposures to PM to vary substantially raising the issue of how well ambient measurements can serve as predictors of human exposures, either on an individual personal level or on a community-wide level.

## **2.4.2 Health Effects**

A rapidly growing body of epidemiologic data examines relationships between PM concentrations and human health effects, ranging from respiratory function changes and symptoms to exacerbation of respiratory disease and excess mortality associated with premature death. These effects appear to lie along an increasing gradient of severity of effects in different subpopulations. Although the exact biological mechanisms underlying such effects are poorly understood, there seems to be an emerging pattern of findings that increases the plausibility that the observed relationships may reflect a real, causal relationship between particulate matter and human health. This revised PM criteria document assesses evidence suggesting that this overall pattern of effects may extend to concentrations of  $\text{PM}_{10}$  below the current NAAQS or may be associated with other PM size fractions (e.g., fine

particles < 2.5  $\mu\text{m}$ ). Controlled human exposure and animal toxicologic studies are also evaluated, and the overall coherence/consistency of findings in relationship to the epidemiologic database is assessed. These include, for example: (1) studies of respiratory tract disposition and clearance of particles, (2) experimental studies (animal and human) evaluating mechanisms of action of various particles (by size, chemical composition, etc.) in order to evaluate biological plausibility of effects reported by epidemiology studies, and (3) other experimental studies that demonstrate various toxic effects of PM in humans or in animal models.

### *Respiratory Tract Dosimetry*

The biological endpoint or health effect of an aerosol exposure is likely more directly related to the quantitative pattern of deposition within the respiratory tract than just to the external exposure concentration. The regional deposition pattern determines not only the initial respiratory tract dose but also the specific pathways and rates by which the inhaled material is cleared and redistributed. Thus, in order to evaluate different toxic responses to inhaled particles across species and to accurately extrapolate such laboratory animal data to humans, or to evaluate differences that sex, age, or disease may have on human variability, the various physicochemical, anatomic, and physiologic factors described must be integrated to estimate a deposited dose or perhaps a retained dose (deposition – clearance = retention). Delineation of the dose to each respiratory tract region (extrathoracic, tracheobronchial, and pulmonary) is desired because each region has different dominant factors controlling deposition and clearance, and different defense mechanisms. A theoretical model to describe particle deposition and clearance would require detailed information on all the influential parameters mentioned above (e.g., respiratory rates, exact airflow patterns, complete measurements of the branching structure of the respiratory tract, pulmonary region mechanics) for men, women, children, and across the various species used in toxicity studies. An empirical model (i.e., equations fit to experimental data) may adequately describe regional deposition and require much less data to develop the model structure.

Within the dosimetry chapter (Chapter 10) of this document, the anatomy of the respiratory tract and the physicochemical, anatomical, and physiological factors controlling particle deposition, clearance, and retention are reviewed. Other factors that modify

deposition, including sex, age, disease state, and exposure to irritants also are discussed. The available human and laboratory data on deposition and clearance and their positive and negative attributes for use in quantitative model development are discussed. Available validated model structures to estimate deposition and clearance in humans and laboratory animals are described and evaluated. The application of these models to quantitative extrapolation of the human and animal toxicity data also are discussed. Consideration is given to uncertainties in input parameters and the variability of model predictions when evaluating the usefulness of models for quantitative dose extrapolation.

### *Epidemiology Studies*

Epidemiologic analyses are expected to provide some of the most crucial information useful in deriving health criteria upon which to base Agency decisions regarding possible revision of the current PM standards, and such studies are accorded extensive attention in this PM criteria document as evaluated in Chapter 12 and elsewhere.

One useful distinction is to separate short- and long-term effects. The short-term effects include changes in respiratory function, symptom indicators, hospital admissions associated with exacerbation of respiratory or cardiovascular disease, and excesses of daily death rates in urban areas associated with concurrent 24-h PM measurements on the same or preceding few days. The short-term effects studies are typically longitudinal in nature and are specific to a community or metropolitan area with reasonably homogeneous PM exposures. The analyses of data in short-term studies use time-series analysis methods. The long-term or chronic exposure effects studies typically use annual PM concentrations and annual symptom or death rates and are more likely to involve comparisons across several communities rather than within a single community. Although both kinds of epidemiologic analysis are useful, it is important to assess the consistency of conclusions based on different kinds of studies. Coherence of effects at lower concentrations is a useful criterion for assessing diverse studies with different endpoints or effects, different populations, and different exposure metrics (Bates et al., 1990) and is considered as part of the evaluation of the available epidemiology literature.

1 ***Mortality Studies.*** Studies examining the relationship between ambient measures of PM and  
2 mortality were examined during the last review process (U.S. Environmental Protection  
3 Agency, 1982, 1986) and contributed to the key scientific bases underlying the current PM<sub>10</sub>  
4 NAAQS. However, given the uncertainties in converting from British Smoke to PM<sub>10</sub>  
5 measurements, particularly at lower concentrations, and the possible differences in particulate  
6 composition between London at the time the data were gathered and the contemporary United  
7 States, it was difficult to determine a precise level for a relationship between PM<sub>10</sub> and  
8 mortality. Since that time, numerous contemporary U.S. mortality studies using either PM<sub>10</sub>  
9 or TSP measurements have been published that examine short-term measurements. Also,  
10 long-term PM ambient measurements and mortality have been examined in some recent  
11 studies. These and other newly emerging PM-mortality studies are summarized and critically  
12 evaluated.

13 Issues of greatest concern so far relate primarily to the use and interpretation of the  
14 short-term mortality studies. Almost all analyses of the relationship between PM and excess  
15 mortality require statistical adjustment for mortality excesses associated with other potential  
16 confounding factors, including other environmental stressors such as temperature and relative  
17 humidity or other pollutants (co-pollutants) associated with PM and with mortality. For  
18 example, weather-related effects may be directly related to excess mortality, but may also be  
19 indirectly related when weather affects PM emissions and atmospheric concentrations.  
20 Statistical and conceptual approaches to estimating the direct and indirect effects of  
21 confounding variables, and specification of the form of the statistical adjustment for  
22 confounding factors are evaluated in interpreting the PM effects on mortality calculated from  
23 each study. Comparison of studies using different exposure metrics is considered. In  
24 characterizing the relationship between excess mortality and PM in different cities, evaluation  
25 of differences in particle size distribution or particle composition between cities, is done as  
26 the data allow.

27 Specification of "exposure-effect" relationship(s) between mortality and PM is also  
28 important. A number of studies have reported no evident threshold for effects, even at  
29 relatively low concentrations, but the ability to carry out meaningful threshold evaluations  
30 may be greatly limited by the power of the various available studies. Estimates of the  
31 relationship between PM and mortality may depend on differences in model specification.

Even with similar model specifications (exposure-response relationship, adjustment for weather, copollutants, and other factors) there may be differences in the effects of PM at a given concentration, possibly related to particle size/composition and/or differences in climate or demographics among different cities. An important component of the health effects assessment in the criteria document is identification of susceptible subpopulations and other variables such as weather, climate, or other pollutants, potentially contributing to increased mortality risk.

***Morbidity Studies.*** Decreased pulmonary function in predominantly healthy children has been reported in some earlier epidemiology studies. More recent studies add to this database. Earlier long-term exposure studies provided no evidence for an effect from PM exposure on level of pulmonary function, whereas some recent studies report reductions in pulmonary function associated with chronic exposure to particulate pollution. An evaluation of the epidemiologic database relating short-term (24-h) and long-term (annual) ambient measurement of PM<sub>10</sub> and other measures of PM to changes in pulmonary function test results in children and adults is presented. The strength and consistency of epidemiologic databases that relate short-term (24-h) and long-term (annual) PM<sub>10</sub> and other ambient PM indicator measurements to changes in the rate and/or severity of respiratory symptoms and disease are also critically reviewed. Studies examining exacerbation of respiratory (i.e., COPD and asthma) and cardiovascular diseases that lead to increased medical care utilization (such as emergency room visits and hospital admissions) in relation to ambient PM exposure are also evaluated. As appropriate, other factors and copollutants are also examined in relation to findings on each of the above types of health endpoints.

### ***Toxicology of PM Constituents***

In addition to the chapter evaluating epidemiologic studies of PM differentiated mainly in terms of various size indicators (TSP, PM<sub>10</sub>, etc.), the toxicology of various major subclasses of PM constituents is also summarized and discussed in a separate chapter. That toxicology chapter focuses on acid aerosols, metals, ultrafine particles, diesel particles, silica, and other types of particles that make up ambient air mixes of particles in the broad class designated in toto as "particulate matter". Animal inhalation toxicology and other types

of studies reviewed are useful in improving understanding of several key overall health issues, especially: (1) the influence of particle size, number, and mass on health responses; (2) the differential influence of varying particle chemistry on the health effects observed; (3) the array of health effects that can be caused by specific PM constituent; (4) exposure-response relationships for various exposure durations (acute and chronic); (5) mechanisms of toxicity; and (6) pollutant interactions. Some of the information from these studies provides a background for evaluating the biological plausibility of the mortality and morbidity associations reported in epidemiological studies. For example, whether chronic bronchitis can be caused by sulfuric acid exposure, as hypothesized from animal studies, is a significant issue. The data on the relationship between particle size, mass, and number elucidates the appropriateness of various exposure indicators of potential human effects. The document reviews toxicological studies examining hypotheses related to health outcome and the physical and chemical characterizations of PM. For chemistry, this includes acidity, surface coatings (i.e., soluble metals), and particle-bound organics. Particle size is examined (PM<sub>10</sub>, PM<sub>2.5</sub>, other [fine versus ultrafine]). Aerosol concentration examines particle number and mass.

Evaluation of the controlled human exposure (clinical) studies database concerning PM and health outcomes is presented as a subsection of the overall PM constituent toxicology chapter. This includes critical review of PM effects on pulmonary function in healthy and asthmatic individuals, pulmonary clearance mechanisms, airway reactivity, and immunologic defense especially in relation to particle size but only to a limited extent in relation to chemical composition. There remains an almost complete absence of controlled experiment data on exposure of humans to particles other than acid aerosols.

Human clinical studies of PM constituents have been almost completely limited to measuring effects on symptoms, lung function, and airway reactivity, in addition to a few studies of effects on mucociliary clearance. Few have used bronchoalveolar lavage to study effects on airway inflammation and host defense; nor have many, if any, examined effects of acid aerosols or other particle exposures on airway inflammation in asthmatic subjects or on exacerbation of effects of antigen challenge in allergic or asthmatic subjects.



## *Sensitive Groups*

Available data are also evaluated for insight concerning human population groups potentially having increased susceptibility to 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 asthmatic individuals potentially may display increased sensitivity to PM exposure, and, as such, this topic is discussed.

## **2.4.3 Welfare Effects**

### *Effects on Materials*

All manmade materials exposed to the outdoor environment undergo degradation by heat, moisture, and some bacteria and fungi. For many years, air pollution has been suspected of accelerating the natural degradation processes. For example, acidic pollutants have been associated with accelerated degradation of paints such as water-based paint and alkyd coatings containing titanium dioxide, lead minium, or ferric oxide red. Other researchers have reported acidic pollution-related effects on automotive paint and steel coating. Particulate matter has also been reported to produce paint soiling. Also, acid aerosols and other particles containing acids also have been reported to affect building stones, cement, and concrete. Acidic aerosols change the physical characteristics of some stones, cement, and concrete by changing the chemical composition. Studies examining the effects on materials of PM pollution (primary and secondary particles and aerosol precursor gases) are reviewed and summarized; where possible, changes in material damage are correlated with changes in PM concentrations.

### *Visibility Effects*

Airborne PM in the form of varying amounts of sulfates, ammonium and nitrate ions, elemental carbon and organic carbon compounds, water and smaller amounts of soil dust, lead compounds, and other trace species reduce visibility, thereby affecting transportation safety and creating a loss in aesthetic appeal. The natural background visibility range is  $150 \pm 45$  kilometers for the east and  $230 \pm 35$  kilometers for the west. When current visibility data are compared to background visibility data, manmade contributions account for

1 approximately one-third of the average extinction coefficient in the rural west and over 80%  
2 of the average extinction coefficient in the rural east. The effects of aerosol concentration,  
3 composition, and size and pollutant emission trends on visibility are evaluated. Existing PM  
4 models are discussed in relation to how well such models can be used to predict changes in  
5 visibility.

## 6 7 *Climate Change*

8 It has been suggested that fine particles released into the atmosphere may alter the  
9 climate through a reduction in the amount of solar radiation reaching the earth's surface, thus  
10 cooling the surface while heating the aerosol layer. The scattering and absorbing properties  
11 of aerosols and their vertical distribution are briefly reviewed and reference made to other  
12 assessments of their effects on radiative balance and how changes in radiative balance may  
13 affect weather and climate. Aerosols also affect weather and climate through their role as  
14 cloud condensation nuclei. The concentration, composition, size, and number of aerosols can  
15 influence the structure, stability, and albedo of clouds, possibly changing the location and  
16 amount of rainfall and the rate of global and regional warming due to greenhouse gases.

## 17 18 19 **2.5 DOCUMENT CONTENT AND ORGANIZATION**

20 The present document includes review and critical evaluation of relevant scientific  
21 literature on PM through early 1995. The material selected for review and comment in the  
22 text generally comes from the more recent literature published since 1982, with emphasis on  
23 studies conducted at or near PM pollutant concentrations found in ambient air. Older  
24 literature cited in the previous criteria document for PM and Addendum (U.S. Environmental  
25 Protection Agency, 1982, 1986) is generally not discussed. However, as appropriate, some  
26 limited discussion is included of older studies judged to be significant because of their  
27 potential usefulness in deriving a NAAQS. An attempt has been made to discuss key  
28 literature in the text and present it in tables as well. Reports of lesser importance for the  
29 purposes of this document are typically only summarized in tables.

30 Generally, main emphasis is placed on consideration of published material that has  
31 undergone scientific peer review. In the interest of admitting new and important

1 information, however, some material not yet published in the open literature but meeting  
2 other standards of scientific reporting may be included as reviewed by CASAC. Emphasis  
3 has been placed on studies in the range of current ambient levels. On this basis, studies in  
4 which the lowest concentration employed exceeded this level have been included if they  
5 contain unique data, such as documentation of a previously unreported effect or of  
6 mechanisms of effects, or if they were multiple-concentration studies designed to provide  
7 information on concentration-response relationships. Results of studies conducted at higher  
8 levels have been included because of the potential importance of these effects to public  
9 health. In reviewing and summarizing the literature, an attempt is made to present  
10 alternative points of view where scientific controversy exists. As warranted, considerations  
11 bearing on the quality of studies are noted.

12 The present document consists of 13 chapters. The Executive Summary for the entire  
13 document is contained in Chapter 1, followed by this general introduction in Chapter 2.  
14 Chapters 3 through 7 provide background information on physical and chemical properties of  
15 PM and related compounds; sources and emissions; atmospheric transport, transformation,  
16 and fate of PM; methods for the collection and measurement of PM; and ambient air  
17 concentrations and factors affecting exposure of the general population. Chapter 8 describes  
18 effects on visibility, and Chapter 9 describes damage to materials attributable to PM.  
19 Chapters 10 through 13 evaluate information concerning the health effects of PM. More  
20 specifically, Chapter 10 discusses dosimetry of inhaled particles in the respiratory tract and  
21 Chapter 11 summarizes information on the toxicology of specific types of PM constituents,  
22 including experimental toxicological studies of animals and human clinical studies.  
23 Chapter 12 discusses epidemiological studies and Chapter 13 characterizes information on  
24 critical health issues derived from studies reviewed in the prior chapters.

25 Neither control techniques nor control strategies for the abatement of PM are discussed  
26 in this document, although some topics covered may be incidentally relevant to abatement  
27 strategies. Technologies for controlling PM emissions are discussed in other documents  
28 issued by EPA's Office of Air Quality Policy and Standards (OAQPS). Likewise, issues  
29 germane to the scientific basis for control strategies, but not pertinent to the development of  
30 criteria, are addressed in numerous other documents issued by OAQPS.

1 In addition, certain issues of direct relevance to standard setting are not explicitly  
2 addressed in this document, but are instead analyzed in documentation prepared by OAQPS  
3 as part of its regulatory analyses materials. Such analyses include (1) discussion of what  
4 constitutes an "adverse effect" and delineation of particular adverse effects that the primary  
5 and secondary NAAQS are intended to protect against, (2) exposure analyses and assessment  
6 of consequent risk, and (3) discussion of factors to be considered in determining an adequate  
7 margin of safety. Key points and conclusions from such analyses are summarized in a Staff  
8 Paper prepared by OAQPS and reviewed by CASAC. Although scientific data contribute  
9 significantly to decisions regarding the above issues, their resolution cannot be achieved  
10 solely on the basis of experimentally acquired information. Final decisions on items (1) and  
11 (3) are made by the Administrator, as mandated by the CAA.

12 A fourth issue directly pertinent to standard setting is identification of populations at  
13 risk, which is basically a selection by EPA of the subpopulation(s) to be protected by the  
14 promulgation of a given standard. This issue is addressed only partially in this document.  
15 For example, information is presented on factors, such as preexisting disease, that may  
16 biologically predispose individuals and subpopulations to adverse effects from exposures to  
17 PM. The identification of a population at risk, however, requires information above and  
18 beyond data on biological predisposition, such as information on levels of exposure, activity  
19 patterns, and personal habits. Such information is included in the Staff Paper developed by  
20 OAQPS and reviewed by CASAC as a separate item from this document.

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### 3. PHYSICS AND CHEMISTRY OF PARTICULATE MATTER

#### 3.1 INTRODUCTION

##### 3.1.1 Overview

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 and elements, elemental carbon, organics compounds, and crustal compounds. Some atmospheric particles are hygroscopic and contain particle-bound water. The organic fraction is especially complex. Hundreds of organic compounds have been identified in atmospheric aerosols, including alkanes, alkanolic and carboxylic acids, polycyclic aromatic hydrocarbons, and nitrated organic compounds (Rogge et al., 1993; Kaplan and Gordon, 1994; Mazurek et al., 1989; Standley and Simoneit, 1987; Ip et al., 1984; Simoneit and Mazurek, 1982; Schuetzle et al., 1975).

Particle diameters span more than four orders of magnitude, from a few nanometers to one hundred micrometers. Combustion-generated particles, such as those from power generation, from automobiles, and in tobacco smoke, can be as small as  $0.01\ \mu\text{m}$  and as large as  $1\ \mu\text{m}$ . Particles produced in the atmosphere by photochemical processes range in diameter from  $0.05$  to  $2\ \mu\text{m}$ . Fly ash produced by coal combustion ranges from  $0.1$  to  $50\ \mu\text{m}$  or more. Wind-blown dust, pollens, plant fragments, and cement dusts are generally above  $2\ \mu\text{m}$  in diameter. Particles as small as a few nanometers (Covert et al., 1992; Clarke, 1992) and as large as  $100\ \mu\text{m}$  have been measured in the atmosphere (Lin et al., 1993).

Particles are ubiquitous in the atmosphere. The lowest concentrations are found in background marine environments, where particle number concentrations range from  $100/\text{cm}^3$  to  $400/\text{cm}^3$ . In background continental environments, particle concentrations vary from

1 100/cm<sup>3</sup> to 5,000/cm<sup>3</sup>; while in urban areas of the United States concentrations may be as  
2 high as 4,000,000/cm<sup>3</sup> (Willeke and Whitby, 1975; Whitby and Sverdrup, 1980). Particles  
3 account for a mass of a few  $\mu\text{g}/\text{m}^3$  near the surface over dry continental areas to several  
4 hundred  $\mu\text{g}/\text{m}^3$  in polluted urban areas.

5 The composition and behavior of airborne particles are fundamentally linked with those  
6 of the surrounding gas. Although the term aerosol is often used to refer to suspended  
7 particles, aerosol is defined as a dilute suspension of solid or liquid particles in gas.  
8 Particulate material can be primary or secondary.

9 Primary particles are those emitted in particulate form and include wind-blown dust, sea  
10 salt, road dust, mechanically generated particles and combustion-generated particles such as  
11 fly ash and soot. The concentration of primary particles depends on their emission rate,  
12 transport and dispersion, and removal rate from the atmosphere.

13 Secondary particulate material may form from condensation of high temperature vapor  
14 or from vapors generated at as a result of chemical reactions involving gas-phase precursors.  
15 Secondary formation processes can result in either the formation of new particles  
16 (Wiedensohler et al., 1994; Covert et al., 1992; Clarke et al., 1991, 1993; Frick and  
17 Hoppel, 1993; Hoppel et al., 1994; Weber et al., 1994) or the addition of particulate  
18 material to preexisting particles (Andreae et al., 1986; Wall et al., 1988; Wu and Okada,  
19 1994). Most atmospheric sulfate is formed from atmospheric oxidation of sulfur dioxide.  
20 Atmospheric nitrate is also essentially secondary, formed from reactions involving oxide of  
21 nitrogen to form nitric acid. A portion of the organic aerosol is also attributed to secondary  
22 processes (Hildemann et al., 1994; Turpin and Huntzicker, 1991; Mylonas et al., 1991;  
23 Pickle et al., 1990; Gray et al., 1986). Secondary aerosol formation can depend on  
24 concentrations of other gaseous reactive species such as ozone or hydrogen peroxide,  
25 atmospheric conditions including solar radiation and relative humidity, and the interactions of  
26 precursors and preexisting particles with cloud or fog droplets (Meng and Seinfeld, 1993;  
27 McMurry and Wilson, 1983; Hoppel and Frick, 1990). As a result, it is considerably more  
28 difficult to relate ambient concentrations of secondary species to sources of precursor  
29 emissions than it is to identify the sources of primary particles.

30 Airborne particulate matter can be anthropogenic or biogenic in origin. Both  
31 anthropogenic and biogenic particulate material can occur from either primary or secondary

1 processes. Anthropogenic refers to particulate matter which is directly emitted or formed  
2 from precursors which are emitted as a result of human activity. Primary anthropogenic  
3 sources include fossil fuel combustion, fireplace emissions, and road dust. Secondary  
4 anthropogenic particulate material can be generated photochemically from anthropogenic  
5 SO<sub>2</sub>, NO<sub>x</sub>, or organic gases. Primary biogenic sources include leaf waxes and other plant  
6 fragments from plants (Simoneit and Mazurek, 1982). In addition, plants emit gaseous  
7 species such as terpenes (Lamb et al., 1987). Terpenes are photochemically reactive, and in  
8 the presence of nitrogen oxides can form secondary organic particles (Kamens et al., 1981;  
9 Pondis et al., 1991, 1993). Other types of primary particulate material such as sea salt and  
10 wind-generated dust from soil undisturbed by man also are of non-anthropogenic origin.

11 In addition to secondary formation, volatilization and sorption processes also affect  
12 concentrations and compositions of airborne particles. Some aerosol constituents are  
13 semivolatile and exist in both gas and particle phases. Their gas-particle distribution depends  
14 on atmospheric conditions such as temperature, the concentrations of other aerosol species  
15 including water vapor, and the vapor pressure of the constituent. Some inorganic compounds  
16 such as ammonium nitrate (Stelson and Seinfeld, 1982; Bassett and Seinfeld, 1983, 1984) and  
17 organic compounds, including many polycyclic aromatic hydrocarbons (Yamasaki et al.,  
18 1982; Ligocki and Pankow, 1989; Pankow, 1987, 1994a,b) are semivolatile. Diurnal  
19 temperature fluctuations can cause substantial changes in the particle-phase concentrations of  
20 semivolatile constituents as a result of gas-particle redistribution. Evidence exists suggesting  
21 that this volatilization-sorption cycle results in the redistribution of semivolatile material  
22 among particles of differing origins (Venkataraman and Hildemann, 1994).

23 Sampling semi-volatile species requires special techniques, such as the use of denuder  
24 systems (Kautrukis et al., 1988). The processing of atmospheric particles also occurs in  
25 clouds. For example, in-cloud processes can lead to the combination of many small particles  
26 (Andreae et al., 1986).

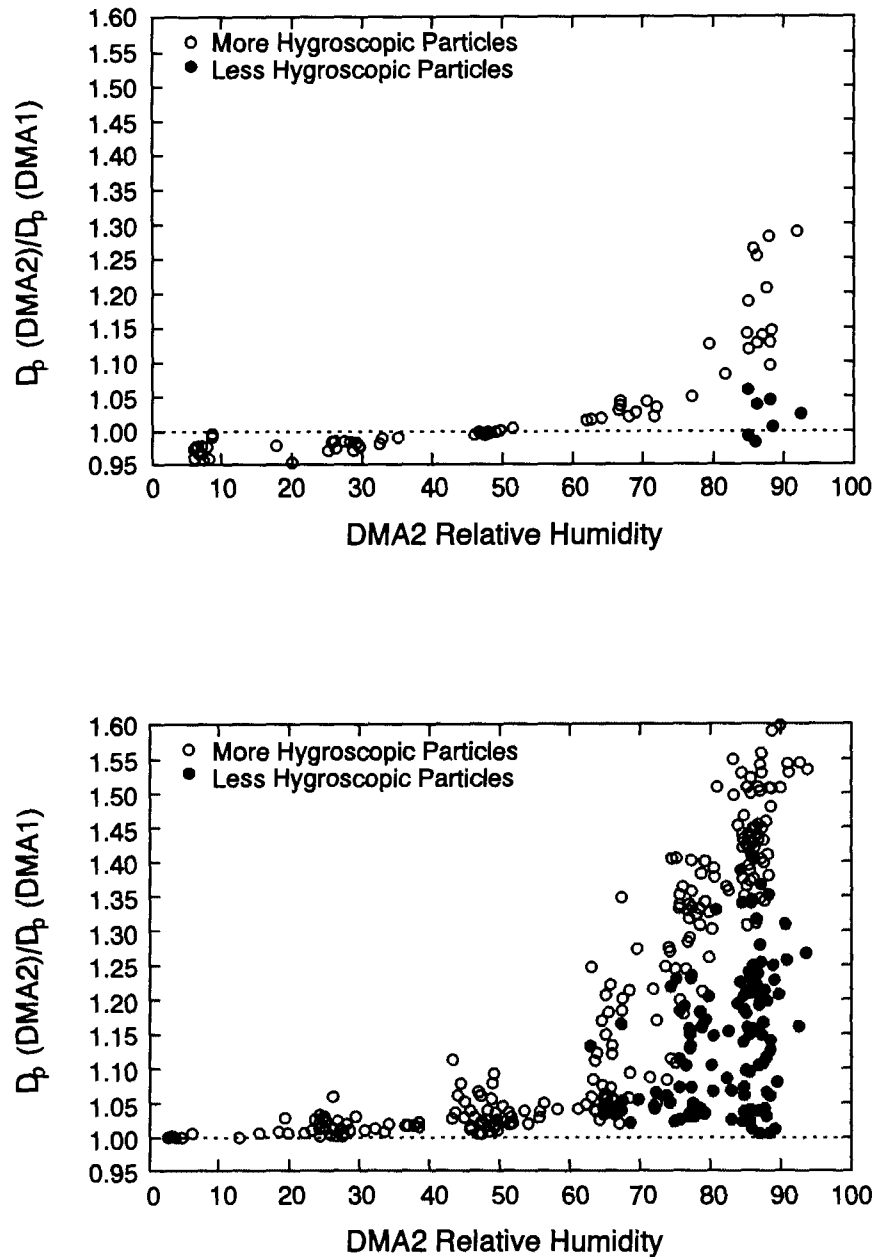
27 A complete description of the atmospheric aerosol would include an accounting of the  
28 chemical composition, morphology, and size of each particle and the relative abundance of  
29 each particle type as a function of particle size (Friedlander, 1970). However, most often  
30 the physical and chemical characteristics of particles are measured separately. Number size  
31 distributions are often determined by physical means, such as electrical mobility or light-

scattering. Chemical composition is determined by analysis of collected samples. The mass size distribution and the average chemical composition of the aerosol as a function of size can be determined by collection of size-segregated samples (Countess et al., 1980; Hering and Friedlander, 1982; John et al., 1990; Sloane et al., 1991). Recent developments in single particle analysis techniques coupled with multivariate classification methods (Van Grieken and Xhoffer, 1992; Germani and Buseck, 1991; Mansoori et al., 1994) are bringing the description envisioned by Friedlander closer to reality. This introductory section describes some of the measurements that have been made on atmospheric particles, and the insights thus provided on the nature, origins, and atmospheric processes that affect particle composition.

### 3.1.2 Major Chemical Constituents

The major constituents of atmospheric aerosol are sulfates, nitrates, carbonaceous compounds, water, ammonium ions and materials of crustal origin. Inorganic ions, including sulfate and nitrate, are typically analyzed by ion chromatography. Crustal elements are analyzed by x-ray fluorescence and/or proton-induced x-ray emission. Average compositions vary with particle size, by location and season. The equilibrium models for inorganic ions predict that water is an important constituent of atmospheric particles, but measurements are limited. McMurry and coworkers (McMurry and Stolzenburg, 1989; Zhang et al., 1993) measured the sensitivity of particle size to relative humidity (RH) for Los Angeles and Grand Canyon aerosols. They found that atmospheric particles of a single size exhibited two distinct hygroscopicities. These were described as "more" and "less" hygroscopic, as shown in Figure 3-1. For example, the diameters of more hygroscopic  $0.2\ \mu\text{m}$  particles humidified to approximately 90% RH increased by factors of  $1.23 \pm 0.08$  and  $1.49 \pm 0.11$  for Los Angeles and Grand Canyon particles, respectively. For relative humidities above 85 or 90%, water was the most abundant particulate species both in Los Angeles and at the Grand Canyon.

Because of the multitude of carbonaceous compounds present in atmospheric aerosols, carbonaceous material is often categorized as organic or elemental carbon (OC or EC). Most measurements of aerosol carbon are made using one of a variety of thermal techniques that



**Figure 3-1. Particle size related to RH.**

1 report particulate organic and elemental carbon concentrations (Huntzicker et al., 1982;  
 2 Mueller, 1982; Turpin et al., 1990). The split between organic and elemental carbon is  
 3 somewhat operationally defined, but the term elemental generally refers to the nonvolatile,  
 4 optically absorbing (black) portion of the carbon aerosol. Elemental carbon is associated  
 5 with soot emissions from combustion. The remaining, more volatile portion is termed  
 6 organic. Various methods of further classifying the organic fraction include: selective

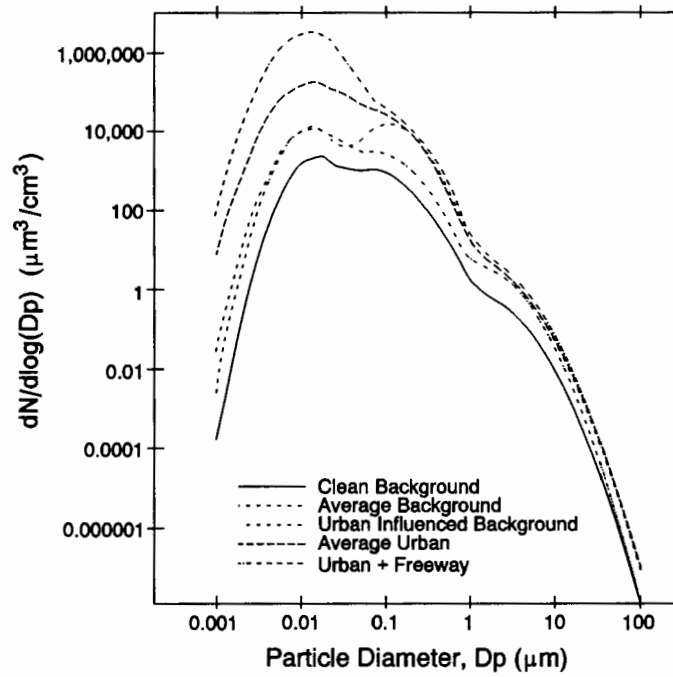
1 solvent extraction (Lioy and Daisey, 1986), functional group identification (Allen et al.,  
2 1994; Gordon et al., 1988), and division into neutral and acidic fractions (Hildemann et al.,  
3 1994a). Radiocarbon dating techniques have been used to distinguish fossil and  
4 contemporary carbon (Currie et al., 1994; Kaplan and Gordon, 1994; Hildemann et al.,  
5 1994b).

### 7 **3.1.3 Atmospheric Aerosol Size Distributions**

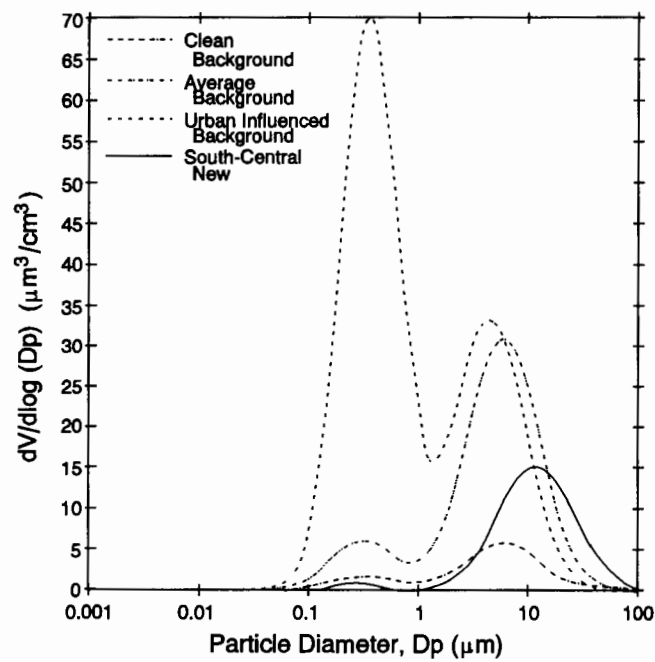
8 Size is one of the most important parameters in determining the atmospheric lifetime  
9 and deposition of particles. As a result, the environmental, visual, and health effects of  
10 atmospheric aerosols and the fate of the compounds that they contain are strongly dependent  
11 on the particle size distribution. Particle size largely determines deposition patterns of  
12 particle-phase compounds within the lung. Light scattering is also strongly dependent on  
13 particle size, and thus particle size distributions have a strong influence on atmospheric  
14 visibility and radiative balance (i.e., climate).

15 Atmospheric size distributions for averaged continental background, urban-influenced  
16 background, averaged urban, and freeway-influenced urban aerosols are shown in  
17 Figures 3-2 to 3-4 (Whitby and Sverdrup, 1980). Figure 3-2 describes the number of  
18 particles as a function of particle diameter. For the same data, the particle volume  
19 distribution with respect to size is shown in Figures 3-3 and 3-4. Number and volume  
20 distributions are defined such that the number (or volume) of particles in a specified size  
21 range is proportional to the corresponding area under the curve. These distributions show  
22 that most of the particles are quite small, below  $0.1\ \mu\text{m}$ , while most of the particle volume  
23 (and therefore most of the mass) is found in particles  $> 0.1$ .

24 An important feature of atmospheric aerosol size distributions is their multimodal  
25 nature. Volume distributions in ambient air are almost always bimodal, with a minimum  
26 between  $1$  and  $3\ \mu\text{m}$ . Particles in the larger mode are termed "coarse" and those in the  
27 smaller mode, "fine". Whitby and Sverdrup (1980) and Willeke and Whitby (1975)  
28 identified three modes: nuclei, accumulation, and coarse. The three modes are most  
29 apparent in the freeway-influenced size distribution of Figure 3-4. The smallest mode,  
30 corresponding to particles below about  $0.08\ \mu\text{m}$ , is the nuclei mode. The middle mode,

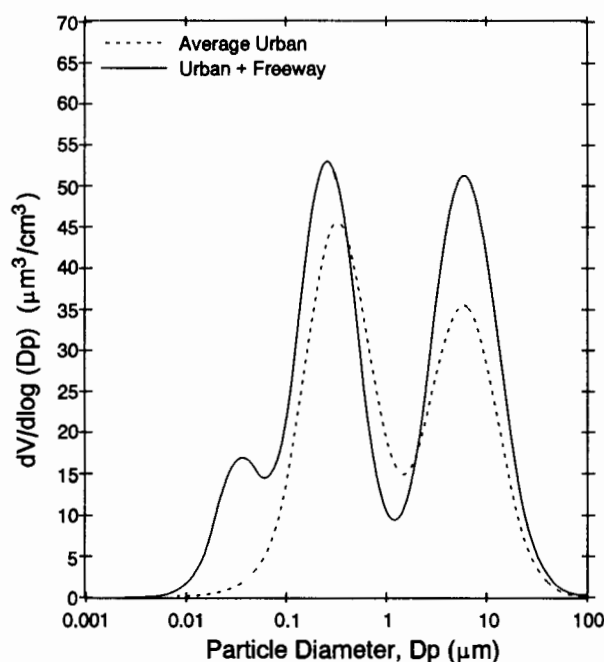


**Figure 3-2. Number of particles as a function of particle diameter.**



**Figure 3-3. Particle volume distribution as a function of particle diameter.**





**Figure 3-4. Particle volume distribution as a function of particle diameter in a freeway-influenced area.**

Source: Whitby and Sverdrup (1980).

from 0.08 to 1 or 2  $\mu\text{m}$ , is the accumulation mode. The largest particles ( $> 1$  or 2  $\mu\text{m}$ ) comprise the coarse mode. Formal delineation of these modes arises from the fitting of a trimodal, lognormal distribution function to the data.

Whitby and coworkers observed that continental background aerosols not influenced by sources have a small accumulation mode and no nuclei mode. For urban aerosols, the accumulation and coarse particles modes are comparable in volume. The nuclei mode is small in volume but dominates the number distributions of urban aerosols. More recent measurements of fine-particle size distributions (Eldering and Cass, 1994) and species-size distributions for sulfates, nitrates, and ammonium ion, as discussed below, indicate that the accumulation mode can be further divided into a "condensation" and "droplet" mode (John et al., 1990). Measurements over remote areas (Hoppel et al., 1986, 1990) indicate that the nuclei mode can also be divided into two separate modes.

Many measurements indicate that the chemical compositions of coarse and fine particles are distinct. The processes that affect the formation and removal of these two size fractions

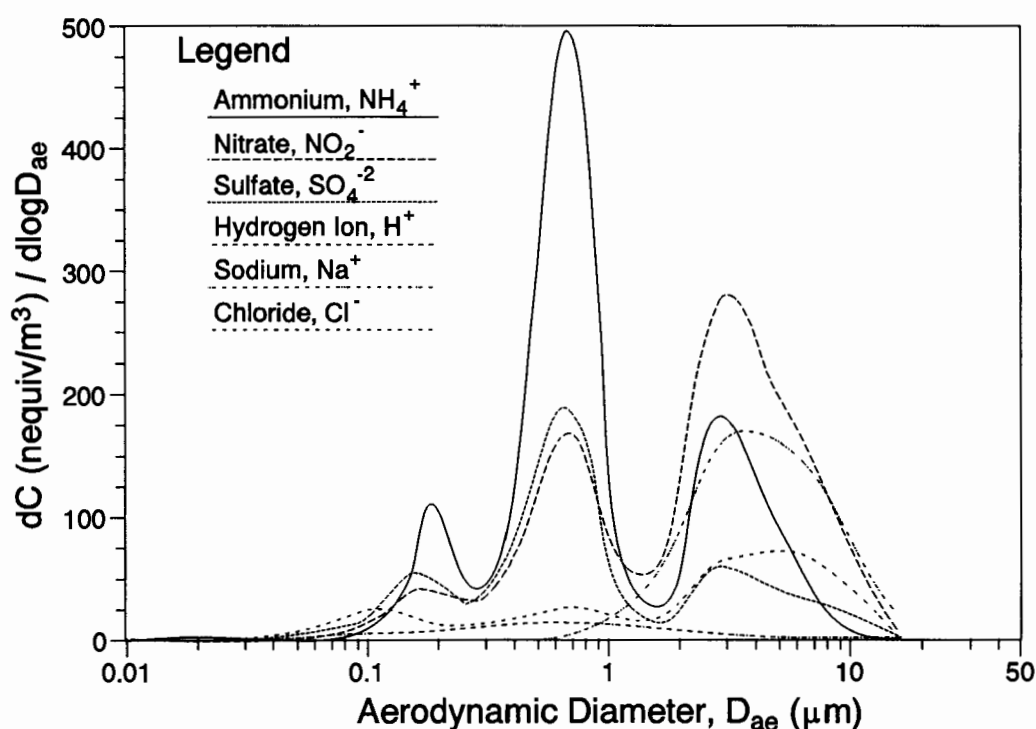
of atmospheric aerosols are also distinct. Coarse particles are generated by mechanical processes and consist of soil dust, sea spray, plant fragments, particles from tire wear, and emissions from rock-crushing operations. These particles are removed primarily by impaction and settling. Nuclei and accumulation mode particles contain primary particles from combustion sources and secondary particles that result from condensation of low-volatility vapors formed from chemical reactions. Particles in the nuclei mode may be transferred into the accumulation mode by coagulation, but cloud coalescence and liquid phase cloud droplet transformations may be more important in atmosphere. In contrast, accumulation mode particles do not ordinarily grow into the coarse mode, because number concentrations are too low for coagulation to be effective. Nuclei are readily removed by diffusion to surfaces. However, accumulation mode particles are not easily removed from the airstream. They have long atmospheric lifetimes and are able to penetrate deep into the lungs. The nuclei and accumulation modes are fairly independent of the coarse mode, both in formation and removal (Willeke and Whitby, 1975; Whitby and Sverdrup, 1980).

Fine and coarse particles are best differentiated by their formation mechanism (Wilson, 1995). Fine particles are formed by nucleation with gases while coarse particles are formed by mechanical processes from larger particles or bulk materials. The most appropriate size cut for separating fine from coarse particles is still under consideration.

#### **3.1.4 Chemical Composition and Its Dependence on Particle Size**

Since the work of Whitby, several studies have been conducted that provide chemical or elemental composition data on the coarse and fine fractions of the atmospheric aerosol. Generally this is done by separate collection of particles less than  $2.5\ \mu\text{m}$  in diameter (fine or  $\text{PM}_{2.5}$ ) and particles less than  $10\ \mu\text{m}$  ( $\text{PM}_{10}$ ). Coarse-particle concentrations are obtained by difference. Alternatively, particles can be collected in two or more size fractions, using impactor methods.

Detailed size distributions of the inorganic ions in Los Angeles are shown in Figure 3-5 (Wall et al., 1988; John et al., 1990). These data show two modes for sulfate and nitrate aerosols between  $0.1$  and  $1\ \mu\text{m}$ . Similar results for sulfate aerosols were reported by Hering and Freidlander (1982). The smaller mode, corresponding to particles near  $0.2\ \mu\text{m}$  in diameter, is attributed to gas-phase formation of condensible species and is referred to as the



**Figure 3-5. Ion concentration as a function of particle size.**

condensation mode. The larger mode has a peak near  $0.6 \mu\text{m}$  and is called the droplet mode. Its existence is attributed to secondary formation through heterogeneous, aqueous-phase transformations. McMurry and Wilson (1983) found  $0.6 \mu\text{m}$  sulfate particles in power plant plumes and attributed their existence to formation by heterogeneous processes. Further analysis of the data by Meng and Seinfeld (1994) indicate that these aqueous reactions most likely occur in cloud or fog droplets.

The data of Figure 3-5 in Los Angeles show that particulate nitrate is found in both coarse and fine particles. Nitrate near the coast was predominantly in the coarse mode. Coarse mode nitrate was less prominent for inland sites. Several investigators (Wall et al., 1988; John et al., 1990; Andreae et al., 1986) proposed that the coarse particle nitrate results from the heterogeneous reaction of nitric acid with sea salt. On the basis of single particle analysis by electron microscopy-energy dispersive spectroscopy, Wu and Okada (1994) concluded that coarse-particle nitrate in a coastal region of Japan formed on sea salt. Course nitrate collected at an inland site was associated with soil dust. These data suggest that a heterogeneous chemical reaction on the surface of a mechanically generated, primary particle

may provide a mechanism for adding secondary material to the coarse particle mode. They also show that secondary particulate material can be formed by the interaction of a natural constituent (sea salt) with a species derived from anthropogenic emissions (nitric acid).

### 3.1.5 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. The gas-particle distribution of semivolatile organic compounds depends on compound vapor pressure, total particulate surface area and composition, and atmospheric temperature (Pankow, 1987; Junge, 1977; Bidleman, 1988). Junge (1977) modeled this relationship using a linear form of a Langmuir adsorption isotherm. Measurements of semivolatile organic compounds show that gas-particle distributions are highly correlated with total suspended particulate matter, temperature, and the sub-cooled liquid vapor pressure of the pure compound (Foreman and Bidleman, 1990; Ligocki and Pankow, 1989; Yamasaki et al., 1982). Yamasaki et al. (1982) used this information to model an empirical relationship between the gas-particle distribution, total suspended particulate matter and temperature. Pankow showed that the expressions of Junge (1977) and Yamasaki et al. (1982) are consistent and continued the theoretical development of equilibrium gas-particle partitioning (Pankow, 1987; 1991; 1994a,b).

Although it is generally assumed that the gas-particle partitioning of semivolatile organics is in equilibrium in the atmosphere, the kinetics of redistribution are not well understood. Gerde and Scholander (1989) and Rounds and Pankow (1993) predicted that redistribution in the ambient air could take minutes to hours. Since changes in atmospheric conditions (i.e., temperature) will drive redistribution, it is not clear whether equilibrium conditions are maintained. However, the gas and particle data agree reasonably well with equilibrium theories. The development of an understanding of gas-particle partitioning of semivolatile organic compounds is hampered by the difficulty associated with measuring the multitude of compounds, all present in small concentrations, for which diurnal temperature fluctuations cause gas-particle partitioning to be dynamic on a time scale of a few hours.

Stelson and Seinfeld (1982) developed a thermodynamic model to predict the temperature and relative humidity dependence of the ammonium nitrate equilibrium dissociation constant, which has been supported by ambient data at inland sites in the Los

Angeles Basin (Hildemann et al., 1984; Doyle et al., 1979). Bassett and Seinfeld extended the equilibrium model to include sulfates (1983) and the effect of particle size (1984). With the inclusion of sodium chloride in the equilibrium model, Pilinis and Seinfeld (1987) were able to predict observations at coastal sites. Atmospheric models based on equilibrium considerations have been successful in accounting for the gas-particle partitioning of inorganic species measured in Phoenix, Arizona (Watson et al., 1994b), and Uniontown, Pennsylvania (Saxena et al., 1994). Wexler and Seinfeld (1992) found that under some atmospheric conditions the size distributions of ammonium ion and nitrate are not accurately predicted by equilibrium considerations alone, and that transport kinetics can be important.

### 3.1.6 Single Particle Characteristics

The "mixing characteristics" of the aerosol describes the distribution of chemical species among particles. An aerosol in which all particles contain the same homogeneous blend of chemical species is internally mixed. In an externally mixed aerosol each chemical species is found in a distinct set of particles. Experiments measuring atmospheric aerosol properties for single-particle size ranges (Hering and McMurry, 1991; Covert et al., 1990; Zhang et al., 1993) and single-particle analyses (Bock et al., 1994; Sheridan et al., 1993; Van Borm et al., 1989; Anderson et al., 1988) indicate that atmospheric aerosols are to some degree both internally and externally mixed. Single particle analyses provide descriptions of individual particle compositions. These are then categorized either manually or through multivariate methods such as cluster analysis (Kim and Hopke, 1988) to give an accounting of the relative number of particles of each chemically defined particle type. Morphological information can also be included in particle type definitions.

Single-particle composition and morphology provide insights into the sources and atmospheric processes affecting airborne particles. For example, a priori one expects that particles emitted from different sources would in fact be distinct. However, Andreae et al. (1986) observed that over remote ocean areas between 80 and 90% of silicon-rich particles (presumably originating from silicate mineral particles) were also rich in sodium, chlorine, and variable amounts of potassium, magnesium, calcium, and sulfur (attributed to sea salt particles). The internal mixing of silicates with sea salt, particles originating from different sources and externally mixed when emitted into the atmosphere, suggests the processing of

aerosol particles within clouds (see Section 3.2.1.4). The hypothesis is that a single cloud droplet takes up two or more particles and that these particles remain together after droplet evaporation. Other mechanisms of particle coalescence, such as differential settling, Brownian coagulation, and electrostatic attraction, are too slow to account for the large fraction of internal mixing observed. Andreae et al. (1986) also found enrichment of sulfur (presumably sulfate) on sea salt particles. This also was attributed to the interaction of clouds with particles. Gas-to-particle conversion in cloud droplets or by condensation can also lead to mixtures of aerosol species.

Particle morphology has many effects on atmospheric particle properties and processes. Chain agglomerates, for example, have much larger surface areas on which adsorption and chemical reactions can take place than spherical particles of identical volumes. In addition, the atmospheric lifetime is longer, and the optical absorption per unit mass is greater for chain agglomerates than for more compact particles. Combustion-generated soot particles are often chain agglomerates composed of a large number of small primary spherules. Laboratory experiments conducted by Huang et al. (1994) and Colbeck et al. (1990) demonstrated that condensation-evaporation processes can cause chain agglomerates to become more compact. Colbeck et al. (1990) also showed that the collapse of the soot aggregates resulting from humidification results in a decrease in both the optical scattering and extinction of the particles.

### **3.1.7 Definitions**

#### **3.1.7.1 Definitions of Particle Diameter**

The diameter of a 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, its settling velocity, or its aerodynamic behavior. Although atmospheric particles are often not spherical, their diameters are described by an "equivalent" diameter, that of a sphere which would have the same physical behavior. Two parameters that are often used to describe particle diameter are the Stokes and aerodynamic diameters. The Stokes diameter,  $D_p$ , describes particle size based on the aerodynamic drag force imparted on a particle when its velocity differs from that of the surrounding fluid. For a smooth, spherically shaped particle,  $D_p$  exactly equals the physical diameter of the particle. For irregularly shaped

particles,  $D_p$  is the diameter of an equivalent sphere that would have the same aerodynamic resistance. Particles of equal Stokes diameters that carry the same electric charge will have the same electrical mobility. Particles of equal density and equal Stokes diameter have the same settling velocity.

Aerodynamic diameter,  $D_a$ , depends on particle density and is defined as the diameter of a particle with equal settling velocity but a material density of 1 g/cm<sup>3</sup>. Particles with the same physical size and shape but different densities will have the same Stokes diameter but different aerodynamic diameters. For particles greater than about 0.5  $\mu\text{m}$ , the aerodynamic diameter is generally the quantity of interest because it is the parameter that is important to particle transport, collection, and respiratory tract deposition. Respirable, thoracic, and inhalable particle sampling are based on particle aerodynamic diameter.

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

$$D_a = \left[ \frac{\rho C}{C_a} \right]^{1/2} D_p \quad (3-1)$$

where  $\rho$  is the particle density, and  $C$  and  $C_a$  are the Cunningham slip factors evaluated for the particle diameters  $D_p$  and  $D_a$  respectively. The slip factor is a function of the ratio between particle diameter and mean free path of the suspending gas; it is given by the expression (Hinds, 1982):

$$C = 1 + \frac{\lambda}{D_p} \{2.514 + 0.800 \exp(-0.55 \frac{D_p}{\lambda})\} \quad (3-2)$$

where  $\lambda$  is the mean free path of the air.  $C$  is an empirical factor that accounts for the reduction in the drag force on particles due to the "slip" of the gas molecules at the particle surface. It is important for particles less than 1  $\mu\text{m}$  in diameter, for which the surrounding air cannot be modeled by a continuous fluid. At normal atmospheric conditions (temperature = 20 °C, pressure = 1 atmosphere)  $\lambda = 0.066 \mu\text{m}$ . For large particles ( $D_p > 5 \mu\text{m}$ )  $C = 1$ ; while for smaller particles  $C > 1$ .

For particles with diameters greater than the mean free path, the aerodynamic diameter given by equation (3-1) is approximated by:

$$D_a = (\rho)^{1/2} D_p \quad (D_p \gg \lambda) \quad (3-3)$$

This expression, which shows that aerodynamic diameter is directly proportional to the square root of the particle density, is often used for particles as small as 0.5  $\mu\text{m}$ . For particles with diameters much smaller than the mean free path, the slip factor must be taken into account. In this case the aerodynamic diameter is directly proportional to the particle density [ $D_a = (\rho) D_p$  for  $D_p \ll \lambda$ ].

### 3.1.7.2 Definitions of Particle Size Fractions

In the preceding discussion several modes of the aerosol size distribution were identified; they are defined as follows:

Nuclei Mode: that portion of the fine mode particles with diameters below about 0.08  $\mu\text{m}$ ;

Accumulation Mode: particles formed from gases;

Condensation Mode: that portion of the accumulation mode with a volume (mass) median diameter near 0.2  $\mu\text{m}$ ;

Droplet Mode: that portion of the accumulation mode with a volume (mass) median diameter at 0.5 to 0.8  $\mu\text{m}$ ;

Fine Particles: The combination of the modes listed above.

Coarse Mode or Coarse Particles: mechanically generated particles.

There is some overlap between fine and coarse particles in the 1 to 3  $\mu\text{m}$  region. For further discussion see Chapter 4.  $\text{PM}_{2.5}$  refers to particles less than 2.5  $\mu\text{m}$  diameter and is frequently referred to as "fine" PM. A discussion of the best size to differentiate fine from coarse particles is given in Section 3.7.

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 a



specified aerodynamic size cut, and has arisen in an effort to measure the particle size fractions of importance to human health. The  $PM_{10}$  standard set by the U.S. Environmental Protection Agency in 1987 is one example of size-selective sampling criteria, and it was designed to match the penetration of particles into the thoracic region. It is a fairly sharp cutpoint with a 50% efficiency near  $10\ \mu m$  in particle aerodynamic diameter. The exact definition is given by a table of efficiency values (Federal Register, 1988) and is shown in Figure 3-6.

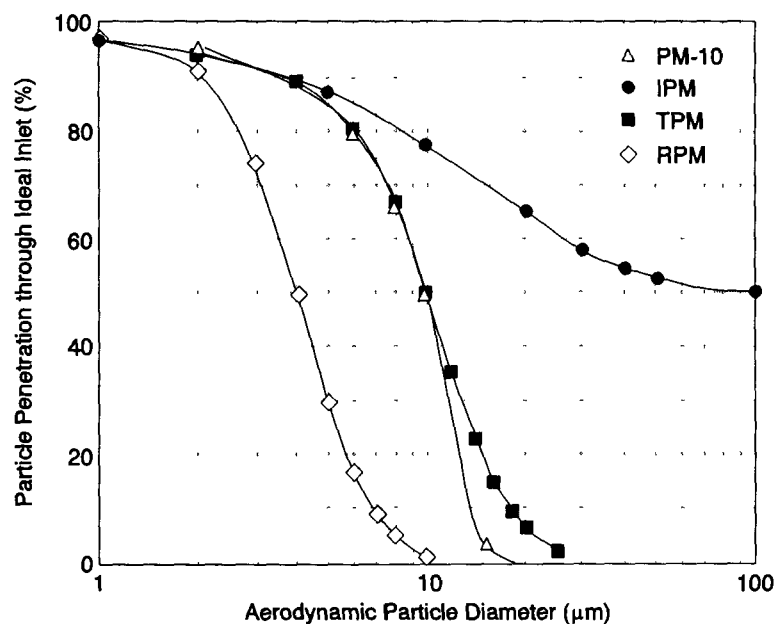


Figure 3-6. Efficiency values for size-selective sampling criteria.

### 3.1.7.3 Other Terminology

Other terminology that has been introduced in this section is summarized below:

**Primary Particles:** those directly emitted to the atmosphere from either natural sources or sources derived from human activity;

**Secondary Particulate Material:** material formed in the atmosphere as the result of chemical and physical conversion of gaseous species;

1 Internal Mixture: an aerosol for which the chemical composition of each individual  
2 particle is the same, that is, equal to the bulk composition;  
3  
4 External Mixture: an aerosol for which different chemical species comprise separate  
5 particles;  
6  
7 Anthropogenic: derived from human activities;  
8  
9 Biogenic: derived from plants;  
10  
11 Bioaerosols: airborne microorganisms and aeroallergens;  
12  
13 Fossil: derived from fossil fuel combustion; and  
14  
15 Contemporary carbon: derived from non-fossil fuel sources such as plants, wood  
16 burning, and cooking oils.  
17

### 18 **3.1.8 Field Studies**

19 Appropriate and reliable field measurements play a central role in shaping our under-  
20 standing of atmospheric processes, in providing key model inputs, and in the evaluation of  
21 models. Real-world observations are all the more important in the case of atmospheric  
22 aerosols, which, on the one hand, are the end product of many complex processes and, on  
23 the other hand, are key precursors of important microphysical cloud processes. Field studies  
24 include short-term, 3-D, high-resolution intensive research campaigns, as well as longer-term  
25 surface and upper-air monitoring programs (in routine mode, or in more comprehensive and  
26 higher-resolution research mode). Research studies are generally mechanistic (targeted at  
27 understanding of process rates and mechanisms), and/or diagnostic (aimed at development  
28 and testing of individual process modules or subgrid-scale parameterizations for use in  
29 complex models). Routine monitoring studies are aimed more at operational evaluation of  
30 overall model performance, or at generation of model input data including those (e.g.,  
31 meteorological) which, through dynamic assimilation into the computations, can improve the  
32 realism of the simulations. Since atmospheric fine particles (FP) are substantially of  
33 secondary origin, measurements of their gaseous precursors and other reactants are also  
34 important. In North America, most of the anthropogenic emissions of FP and their  
35 precursors are from large point sources (power plants and smelters) and from urban-

1 industrial complexes including vehicle emissions. Consequently, special attention is given in  
2 this section to measurements in the plumes of such emissions.

### 3 4 **3.1.9 Dry Deposition**

5 Dry deposition is the process whereby airborne gases and particles are transported  
6 down to the surface of the earth where they are removed. Atmospheric turbulent mixing  
7 continually brings airborne gases and particles into close proximity to the earth's surface,  
8 where they may diffuse across a thin layer of stagnant air to the surface itself. Actual  
9 removal at the surface depends on the affinity between the airborne substance and the surface  
10 element (ground, body of water, vegetation surface, etc.). Dry deposition is a complex  
11 process but it is represented as occurring in three steps: 1) transport down to the vicinity of  
12 the earth by turbulent mixing processes; 2) diffusion across a thin quasi-laminar layer of air;  
13 and 3) attachment to the surface itself.

### 14 15 **3.1.10 Atmospheric Scavenging**

16 Atmospheric gases are scavenged directly by absorption in droplets and by chemical  
17 reactions in clouds. The direct absorption of gases in falling droplets depends on the  
18 solubility of the gas in water, and may be affected by the presence of other species in  
19 solution (Seinfeld, 1986). Particles are scavenged when they serve as cloud condensation  
20 nuclei (CCN) and when they are intercepted by falling hydrometers. The wet removal of  
21 particles depends on the air trajectories through clouds, the supersaturation to which the air  
22 mass is exposed, and the time for which droplets are present before arriving at the ground.

## 23 24 25 **3.2 PHYSICAL PROPERTIES**

### 26 **3.2.1 Aerosol Size Distributions**

#### 27 **3.2.1.1 Particle Size Distribution Functions**

28 The distribution of particles with respect to size is perhaps the most important physical  
29 parameter governing their behavior. The concentration of the number of particles as a  
30 function of their diameter is given by a particle number distribution.

Because the sizes of atmospheric particles cover several orders of magnitude in particle size, and because atmospheric size distributions tend to be log-normally distributed (see Section 3.2.2), size distributions are often expressed in terms of the logarithm of the particle diameter, on the X-axis and differential concentration on the Y-axis:

$$\frac{dn}{d(\log D_p)}$$

= the number of particles per cm<sup>3</sup> of air having diameters in the size range from log  $D_p$  to  $\log(D_p + dD_p)$ .

Formally, it is not proper to take the logarithm of a dimensional quantity, but one can think of the distribution as a function of  $\log(D_p/D_{p0})$  where the reference diameter  $D_{p0} = 1 \mu\text{m}$  is not explicitly stated.

The number of particles is proportional to the area under the curve of  $n(\log D_p)$  versus  $\log D_p$ . Similar considerations apply to distributions of surface, volume, and mass.

### 3.2.1.2 Log-Normal Size Distributions

As presented in Section 3.1, atmospheric aerosols tend to follow a sum of log-normal distributions. A log-normal distribution is a specific functional form of the size distribution function for which the population of particles follows a Gaussian distribution function with respect to the logarithm of the particle diameter. The geometric standard deviation  $\sigma_g$  is the standard deviation of the quantity  $\log D_p$  and defines the width of the distribution. For a monodisperse aerosol, that is, one for which all particles are the same diameter,  $\sigma_g = 1$ . For polydisperse aerosols,  $\sigma_g > 1$ . Typical values for one of the modes of the atmospheric aerosol, such as the accumulation mode discussed above, are  $1.8 < \sigma_g < 2.8$ . For log-normal distributions, 84.1% of the particles are below the size  $\sigma_g \cdot D_{gn}$ , 15.9% lie above the size  $D_{gn}/\sigma_g$ , and 95% of the particles lie within two standard deviations of the mean, that is, the range from  $D_{gn}/2\sigma_g$  to  $D_p \cdot 2\sigma_g$ .

One of the properties of the log-normal distribution is that if the number distribution is log-normal, the surface and volume distributions are also log-normal, and their geometric standard deviation  $\sigma_g$  is the same as for the number distribution.

### **3.2.1.3 Ambient Aerosol Size Distributions**

Ambient aerosol size distributions are completely described by the geometric number mean diameter  $D_{gn}$ , geometric standard deviation  $\sigma_g$ , and number concentration  $N$  for each mode, as listed in Table 3-1. Also given are the parameters of the lognormal volume distributions, geometric mean diameters  $D_{gv}$ , and the corresponding total particle volume for each mode  $V$ . Because the distributions are lognormal, the geometric standard deviation is the same for both number and volume distributions. The results from more recent measurements in a nonurban area of New Mexico, for which the distribution is described by the sum of two lognormal distributions, were obtained with laser light scattering instrumentation, and were fitted to a bimodal lognormal form, corresponding to the accumulation and coarse particle modes. The lognormal fit parameters characterizing these distributions are also listed in Table 3-1. Note that the volume geometric mean diameters for the accumulation mode vary from 0.2  $\mu\text{m}$  to 0.4  $\mu\text{m}$ , those for the coarse mode from 5 to 12  $\mu\text{m}$ . The standard deviations for the coarse particle mode tend to be larger than for the accumulation mode.

### **3.2.1.4 Coagulation of Spherical Particles**

Many processes affect the size distribution of an aerosol, including addition of volume by gas-to-particle conversion, and losses by deposition. Even without these processes, under conditions in which the total volume of an aerosol is conserved the number of particles will decrease by coagulation while the average volume per particle increases. The coalescence of two particles always reduces the total surface area and therefore is favored thermodynamically. Thus, in this sense, aerosols are inherently unstable. In some cases coagulation leads to the formation of chain agglomerates, such as for soot and some metals.

TABLE 3-1. LOGNORMAL PARAMETERS FOR AMBIENT AEROSOLS

A. Parameters of the Number Distribution										
Site of Measurement	Nuclei Model			Accumulation Mode			Coarse Mode			Reference
	Num. (cm <sup>3</sup> )	Dgn (μm)	σ <sub>g</sub>	Num. (cm <sup>3</sup> )	Dgn (μm)	σ <sub>g</sub>	Num. (cm <sup>3</sup> )	Dgn (μm)	σ <sub>g</sub>	
Clean continental background	N: 1,000	0.016	1.6	800.00	0.067	2.1	0.72	0.93	2.2	(1)
Average continental background	N: 6,400	0.015	1.7	2,300.00	0.076	2.0	3.2	1.02	2.16	(1)
Urban influenced background	N: 6,600	0.014	1.6	9,600.00	0.120	1.84	7.2	0.83	2.12	(1)
Urban average	N: 106,000	0.014	1.8	32,000.00	0.054		5.4	0.86	2.25	(1)
Urban and freeway	N: 2,120,000	0.013	1.74	37,000.00	0.032	1.98	4.9	1.08	2.13	(1)
South central NM - February 1989	N:			706.00	0.13	1.72	0.42	2.45	1.91	(2)
South central NM - July 1989	N:			253.00	0.13	1.71	0.72	1.59	2.27	(2)
B. Parameters of the Volume Distribution										
Site of Measurement	Nuclei Model			Accumulation Mode			Coarse Mode			Reference
	Volume (μm <sup>3</sup> cm <sup>3</sup> )	Dgv (μm)	σ <sub>g</sub>	Volume (μm <sup>3</sup> cm <sup>3</sup> )	Dgv (μm)	σ <sub>g</sub>	Volume (μm <sup>3</sup> cm <sup>3</sup> )	Dgv (μm)	σ <sub>g</sub>	
Clean continental background	V: 0.01	0.030	1.6	1.50	0.35	2.1	5.0	6.0	2.0	(1)
Average continental background	V: 0.04	0.034	1.7	4.45	0.32	2.0	25.9	6.04	2.16	(1)
Urban influenced background	V: 0.03	0.028	1.6	44.00	0.36	1.84	27.4	4.51	2.12	(1)
Urban average	V: 0.63	0.038	1.8	38.40	0.32	2.16	30.8	5.7	2.25	(1)
Urban and freeway	V: 9.20	0.032	1.74	37.50	0.25	1.98	42.7	6.0	2.13	(1)

Sources: (1) Whitby and Sverdrup (1980); (2) Kim et al. (1993).

### 3.2.2 Particle Formation and Growth

A significant portion of the fine atmospheric aerosol is secondary, it is material added to the particle phase as the result of gas-to-particle conversion processes. For example, fine-particle sulfate and nitrate particles are mostly formed by secondary processes. One mechanism of gas-to-particle conversion is homogeneous gas-phase chemical reactions to form a condensible species, such as the oxidation of sulfur dioxide to form sulfuric acid. Condensible species can either nucleate to form a new particle (nucleation), or can condense onto the surface of an existing particle (condensation). Another important class of gas-to-particle conversion mechanisms is heterogeneous chemical reactions, which are chemical reactions involving both gas-phase and particle-phase constituents. Transformation on the surface of particles, such as the uptake of nitric acid on the surface of sodium chloride (sea salt) particles to produce nitrate is one type of heterogeneous reaction. Chemical reactions within aerosol and cloud droplets, such as when sulfur dioxide dissolves within an aqueous droplet and is subsequently oxidized to sulfate, are another important heterogeneous gas-to-particle mechanism. Heterogeneous reactions lead to addition of aerosol material to existing particles. Nucleation results in an increase in particle number as well as an increase in particle mass. In this section we consider the physical aspects of these gas-to-particle conversion mechanisms, and their effects on the particle size distribution.

#### 3.2.2.1 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 due to the presence of other compounds.

1 For an aqueous solution of a nonvolatile salt, the presence of the salt decreases the  
2 equilibrium vapor pressure of the drop. This effect is in the opposite direction as the Kelvin  
3 effect, which increases the equilibrium vapor pressure above a droplet because of its  
4 curvature.

#### 6 **3.2.2.2 New Particle Formation**

7 When the vapor concentration of a species exceeds its equilibrium concentration  
8 (expressed as its equilibrium vapor pressure), it is considered condensible. Condensible  
9 species can either condense on the surface of existing particles or can form new particles.  
10 The relative importance of nucleation versus condensation depends on the rate of formation  
11 of the condensible species and on the surface area of existing particles. An analytical  
12 relation for the relative importance of each pathway is dependent on the ratio of the square of  
13 the available surface area to the rate of formation (McMurry and Friedlander, 1979). In  
14 urban environments, it was found that new particle formation is found only near sources of  
15 nuclei such as freeways because the available surface area is sufficient to rapidly scavenge  
16 the newly formed condensible species. Wilson et al. (1977) report observations of nuclei  
17 mode in traffic. New particle formation can also be observed in cleaner, remote regions.  
18 Bursts of new particle formation in the atmosphere under clean conditions correspond to low  
19 aerosol surface area concentrations (Covert et al., 1992). The highest concentration of  
20 volatile ultrafine particles occur in regions corresponding to the lowest particle mass  
21 concentrations, indicating that new particle formation is inversely related to the available  
22 aerosol surface area Clarke (1992). In contrast to continental aerosols where sulfate  
23 formation is the result of conversion of sulfur dioxide, the sulfur particles over the oceans  
24 are formed from the oxidation of dimethylsulfide emitted by phytoplankton (Charlson et al.,  
25 1987).

#### 27 **3.2.2.3 Particle Growth**

28 When material is added to the particle phase by condensation or by heterogeneous  
29 chemical reactions, particles of different sizes may grow at different rates, depending on the  
30 mechanism involved. Condensational growth can have a different effect on the size  
31 distribution of the aerosol than the effect of heterogeneous conversion through chemical



1 reactions within a droplet. The relative rates at which the size of particles change depends  
2 on whether the rate-limiting step in the growth process is transport to the particle, chemical  
3 reactions at the surface of the particle, or chemical reactions within the particle. These are  
4 referred to as transport-limited, surface-reaction rate-limited or volume-reaction rate-limited.  
5 These different physical mechanisms give rise to a different form of the growth law for the  
6 particle. Growth laws are the expressions for  $dv/dt$  or  $dD_p/dt$  as a function of particle size  
7 (where  $v$  is single particle volume and  $D_p$  is particle diameter).

8 For condensational growth, the rate-limiting step relevant to the rate at which particles  
9 of different size grow is transport of condensible species to the particle surface. For  
10 particles much smaller than the mean free path of air, transport is governed by single  
11 molecular bombardment of the surface, and the volume (or mass) of these particles grows in  
12 proportion to their surface area. For particles larger than the mean free path, transport is  
13 governed by diffusion. In this regime the loss of diffusing species at the surface of the  
14 particle causes a gradient in the concentration of the diffusing species near the surface of the  
15 particle such that the volume of the particle grows in proportion to particle diameter rather  
16 than surface area.

#### 17 18 **3.2.2.4 Resuspension**

19 The resuspension of deposited material as well as the suspension of material which has  
20 not been previously airborne can be an important source of particulate contamination. This  
21 discussion will use "resuspension" to include both resuspension and suspension. Surface  
22 contamination may result from the atmospheric deposition of a number of materials; for some  
23 of these (e.g., plutonium), resuspension has been considered to be the most important  
24 exposure pathway. Likewise, resuspended soil particles have the greatest atmospheric mass  
25 over continents of any single particle type (Peterson and Junge, 1971). Despite this  
26 importance, the literature shows relatively few experimental or theoretical studies for the  
27 resuspension mechanism compared to other aerosol generation mechanisms. The following  
28 summarizes work on the physics of resuspension, physical/chemical properties of  
29 resuspension generated particles, and levels of production and transport of resuspended  
30 particles.

## *Resuspension Mechanics*

Resuspension studies may be divided into applied research and detailed studies of mechanisms. Applied studies are usually motivated by atmospheric deposition of hazardous substance (i.e., radionuclides from the Chernobyl 1982 accident [Cambray, 1989]) and the need to predict the spreading of contamination and the lifetime of hazardous air concentrations. Resuspension experiments have been conducted over a wide range of surface types. Many experiments have been conducted in dry or arid regions, simply because many contamination events have occurred in such locations (i.e., the Nevada Test Site). Of the experiments conducted over vegetation, most have been related to short grass. Alternately, applied studies may be motivated by mitigation efforts for soil erosion by wind or by need for measurement of high atmospheric particulate concentrations caused by resuspension, so-called "fugitive dust". Experiments concerning wind erosion have largely occurred in locations where wind erosion is prevalent, i.e., in the "Dust Bowl" area of the central United States).

## *Applied Studies*

Resuspension can occur due to the action of wind or by mechanical stresses. Applied research considers resuspension factors,  $K$  (air concentration divided by surface concentration) (units of  $\text{length}^{-1}$ ) and resuspension rates (flux of contaminant divided by surface concentration) (unit of  $\text{time}^{-1}$ ). Mechanical stresses, such as disturbances by traffic or agricultural operations, might result in large amounts of resuspension over short intervals in specific localities. For example, Sehmel (1984) quotes  $K$  values of  $4 \times 10 \text{ m}^{-1}$  (for beryllium particles by vigorous sweeping in an unventilated room) to  $7 \times 10^{-3} \text{ m}^{-1}$  for plutonium particles in extensive traffic at the Nevada Test Site to  $3 \times 10^{-7} \text{ m}^{-1}$  for gamma-radioactive-fallout by walking on the deposit in an Australian desert.

Wind generated resuspension is considered to be of major importance because it can be relatively continuous and can occur over large regions. Resuspension has been found to increase as a power of wind speed (with the resuspension rate being related to the second or third power of wind speed). Examples of resuspension factors from wind stresses quoted by (Sehmel, 1984) range from  $3 \times 10^{-4} \text{ m}^{-1}$  for uranium at Maralinga trials to  $9 \times 10^{-11} \text{ m}^{-1}$  for yttrium chloride on a cleared, sandy soil. Part of the range of  $K$ 's quoted above might be

caused by the aging of deposits, although a lack of understanding of the mechanisms dominant in the resuspension process has precluded identifying any reasons for the wide range of results.

Nicholson's (1993) data verify previous work, giving an approximate 1/time decrease of the resuspension rate. Makhon'ko's (1986) data for resuspension from grass suggest a relationship between relative resuspension rate  $K'$  versus phytomass  $m$  in grams per square meter,

$$K' = 2.9 \times 10^{-8} m^{-1.4} [\text{sec}^{-1}]. \quad (3-4)$$

### *Aerodynamic Resuspension*

Aerodynamic Models include (1) balance of forces models and (2) statistical mechanisms. Balance of forces models account for forces holding the particles to the surfaces versus those forces acting to remove the particles from the surfaces. Experimental studies of particle motions show that particles being entrained into a turbulent fluid tend to move vertically into the stream with unsteady motions (Sutherland, 1967). Braaten et al. (1990) and Braaten and Paw U (1992) stressed the importance of bursts of a sweeping eddy having the characteristics of large shear stress near the wall where particles are sparsely deposited, breaking up the viscous sublayer and transporting fluid forces to the particles. This mechanism removes particles from a surface in short bursts followed by periods of little resuspension activity. Observations of Lycopodium spores placed on the flat floor of a wind tunnel were used to verify the model.

Reeks et al. (1988) proposed a different aerodynamic mechanism that would account for sudden random injections of particles into the air, the injections taking place more randomly in time than in the above force balance model. Their mechanism calls for the individual particles to accumulate energy from the turbulent stream (most efficiently at a resonant frequency for the particle). Accumulation of energy takes place because energy dissipation is limited by the local fluid and substrate. Once sufficient energy has accumulated to overcome the potential energy well holding it in place, the particle is resuspended. Slow motion movies of saltating sand surfaces showed such a vibrating motion of a particle before it becomes airborne (Willetts, 1992).

## *Mechanical Resuspension*

The importance of mechanical disturbance is seen in the differences of resuspension factors given by Sehmel (1984) for mechanical activities over contaminated soil versus those for wind. Another example of the comparison of resuspension by mechanical disturbance with resuspension by the wind was given by Garland (1979) as a two-order-of-magnitude increase of the resuspension factor for the mechanical disturbance of a full 5-liter bottle dragged along the grass 20 times in 5 minutes in wind compared to the 10 m/s wind alone. Sehmel (1984) conducted experiments to determine the fraction of tracer particles resuspended by driving cars and trucks through the deposited tracer or near the deposited tracer. The fraction increases with speed and size of vehicle. The fraction resuspended per vehicle pass increased as the first power of vehicle speed for the truck driven through the tracer, the fourth power of vehicle speed for a car driven through the tracer, and the third power of the vehicle speed for a car driven near the tracer.

The emission of PM-10 particles in wind erosion is driven by the mechanical process of sandblasting, although Shinn et al. (1983) have pointed out the importance of direct aerodynamic emission for low emission rates below erosion threshold. Threshold velocities for particles smaller than 10 micrometer diameter are several times greater than that for 100 micrometer particles (Bagnold, 1941). Nonetheless, one observes submicrometer to 10-micrometer particles in wind erosion events for winds very much below the threshold velocity for the above mentioned particles. Gillette and Walker (1977) interpreted this to be caused by the mechanical suspension (sandblasting) of fine particles by more-easily-eroded sand particles. Shao et al. (1993) showed that sand-grain bombardment (saltation) is the overwhelmingly dominant mechanism in maintaining fine particle emissions from the surface. To derive an expression for the emission of dust, Shao et al. (1993) assumed that the number of dust particles dislodged from a surface per sand grain impact was proportional to the ratio for the kinetic energy loss of the impacting sand grain to the binding potential energy holding a dust particle to the surface. This assumption led to the prediction that the dust flux is proportional to the sand grain mass flux, which was in turn proportional to the friction velocity cubed. Dust emission is highly sporadic. After the wind stress threshold is surpassed, the vertical flux increases with the third power of friction velocity.

## ***Physical and Chemical Properties of Resuspended Particles***

The physical and chemical properties of resuspended particles depend partly on the properties of the particles that were deposited on the surface in the initial stage of resuspension. But,

"the deposited particles probably lose their individual identity by becoming attached to host (soil) particles. When the pollutant particle is transported downwind, it is usually attached (aggregated) to this host particle" (Sehmel, 1978).

Furthermore, the host particle is most likely an aggregate itself. Studies of the cross section of particles, mineralogy, and scanning electron microscope analysis of dust samples show that particles suspended from the soil are aggregated. For these reasons, this section describes physical properties of the aggregated (host plus pollutant) particles.

The size distribution of resuspended soil particles may be described as lognormal bimodal with one mode at 2 to 5 micrometers and another mode at 30 to 60 micrometers (Sviridenkov et al., 1993; Patterson and Gillette, 1977; Gillette and Nagamoto, 1993; Gillette, 1974). Because the mass mode of the distribution for particles smaller than 10 micrometers is roughly at 2.5 micrometers, a rough approximation is that half the PM10 mass is smaller than 2.5 micrometers and half is larger. The parameter

$$\frac{v_{\text{sed}}}{u_*} < 0.1 \quad (3-5)$$

defines the upper size of suspended dust, where  $v_{\text{sed}}$  is the sedimentation velocity of the upper size limit, and  $u_*$  is friction velocity. Data from Pinnick (1985) shows that very similar size distributions result from resuspension by traffic.

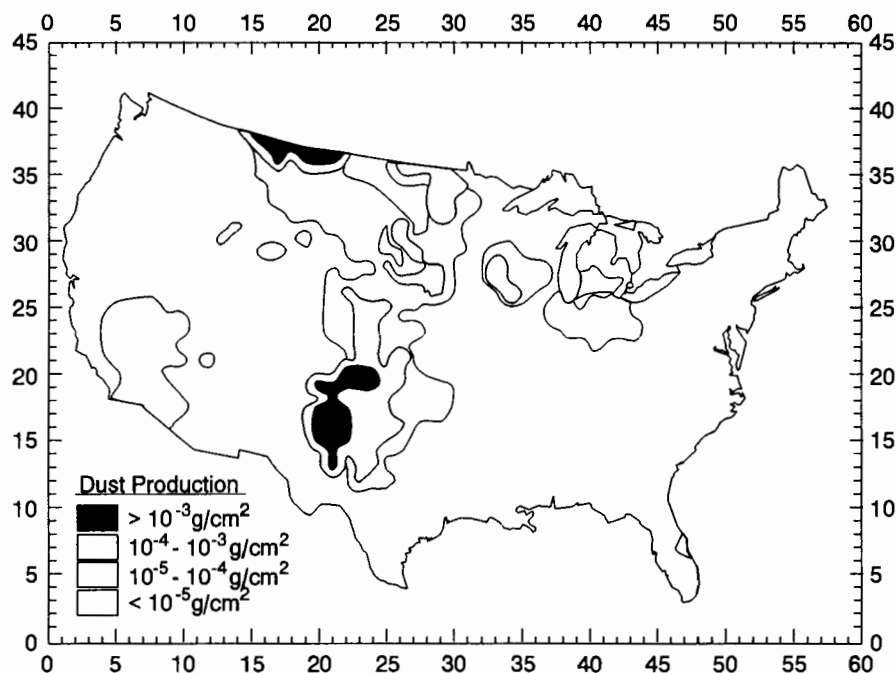
Mineralogically (chemically) the dust consists of (in order of the most abundant) for particles 1 to 10 micrometers: quartz, mica, kaolinite, mixed layer phyllosilicates and feldspars. For particles smaller than 1 micrometers: mica, kaolinite, quartz, and mixed layer phyllosilicates (Gillette et al., 1978). Studies of elemental composition show that composition of the resuspended material compared to that of the total sediment is enriched in

elements associated with the smallest particles (i.e., titanium) and impoverished in elements associated with the coarsest materials (i.e., silicon).

#### *Levels of Production and Transport of Resuspended Aerosols*

Airborne dust measurements in the southern and central Great Plains states of the United States were made in the early 1970's. The total mass of dust produced by individual dust storms was 300,000 to 500,000 million Tg (Gillette et al., 1978). Individual dust storm production rates may be compared to the global production rate estimated by d'Alameida (1989) of 1,800 to 2,000 Tg per year. The Great Plains study, part of a severe storm study, showed that the dust storms were typically associated with vigorous frontal activity, and that the dust travels great distances (many 100's of km) as tracked by jet aircraft. Estimates of transport distance for dust of well over 1,000 km (from West Texas dust storms to deposition sites in northern Minnesota) were supported by isentropic trajectories, positions of rainclouds and elevated concentrations of calcium in collections of rainwater in the National Acid Deposition Program/National Trends Network. Even greater transport distances of resuspended dust are shown by oxygen isotopic 18 to 16 ratios ( $\delta^{18}$ ) in quartz (parts per thousand). By matching the  $\delta^{18}$  value for deposited quartz and source areas for the quartz (wind erodible soils) the following long-range transport paths were found: Asian deserts to Hawaii; Sahara desert to the Caribbean, South America, and Florida; and U.S. sources to Greenland and northern Europe (Jackson et al., 1973).

A model developed for national acid rain and decertification/paleoclimate studies (Gillette and Passi, 1988) expressed the emission of dust for a given study area as an integral over friction velocity (expressing the forcing function), and the threshold friction velocity (expressing the resistance of the soil and environment to ablation). Results from the model for the contiguous United States (Figure 3-7) show a strong agreement of the model dust emissions with known dusty areas (Gillette and Hanson, 1989). Predicted alkaline emissions also agree in many respects with observed wet deposition patterns of alkaline elements (Gillette et al., 1993). A considerable fraction of wind emitted dust is from dust devils (Gillette and Sinclair, 1989).



**Figure 3-7. Model dust emissions for the United States.**

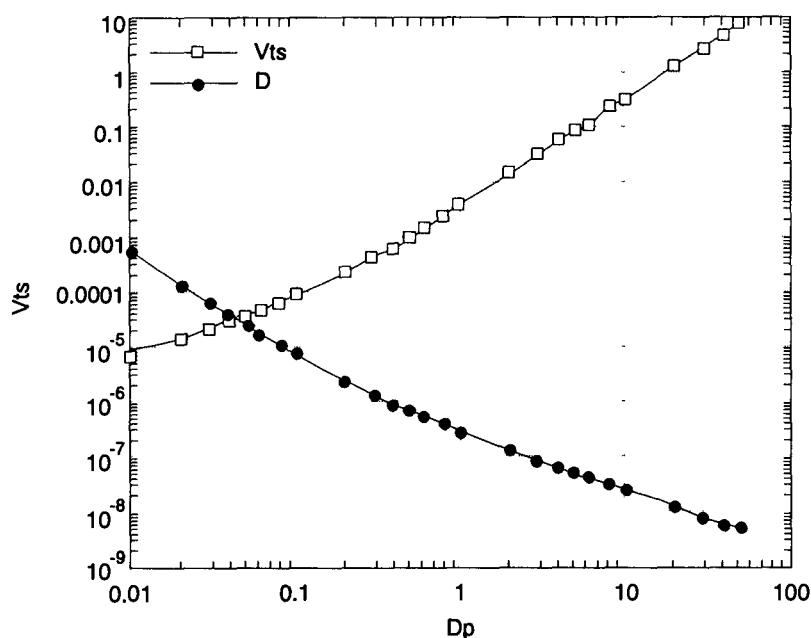
Source: Gillette and Manson, 1989.

### 3.2.3 Particle Removal Mechanisms and Deposition

Particles in the air are in constant motion. They are subject to Brownian motion, which is the constant random movement along an irregular path caused by the bombardment by surrounding air molecules. This process is most important for small particles, and is related to the particle diffusion coefficient. Particles are also subject to the earth's gravitational force, as characterized by a sedimentation velocity. Gravitational settling is most important for larger particles. Both of these processes involve the motion of the particle relative to its surrounding air medium.

Brownian diffusion is important for small particles, whereas gravitational settling is important for large ones. During a time period of 1 s a  $0.1 \mu\text{m}$  particle will travel a distance of about  $40 \mu\text{m}$  from Brownian motion, while it will fall about  $1 \mu\text{m}$  due to gravity. In the same 1 s time period a  $1 \mu\text{m}$  particle will diffuse about  $8 \mu\text{m}$  and will fall  $35 \mu\text{m}$ . Note that the diffusion constant is directly proportional to the particle mobility  $B$ , while the settling

velocity depends on the product of particle mass and mobility,  $mB$ . Diffusion constants and settling velocities are plotted in Figure 3-8.



**Figure 3-8. Diffusion constants and settling velocities for particles.**

The deposition of particles in the atmosphere is not easily modeled, and is characterized by a deposition velocity, which is defined as the ratio of the flux of particles to the surface to the ambient concentration. Results from wind tunnel studies, shown in Figure 3-9, show characteristic minima. Small particles are collected by diffusion, larger particles are collected by impaction and sedimentation. Deposition models which account for these mechanisms are given by Sehmel (1982), Fernandez de la Mora and Friedlander (1982) and Fernandez de la Mora (1986). Atmospheric data from Lin et al. (1994), shown in Figure 3-10 show that inertial mechanisms, as well as sedimentation, are important for the deposition of large particles.



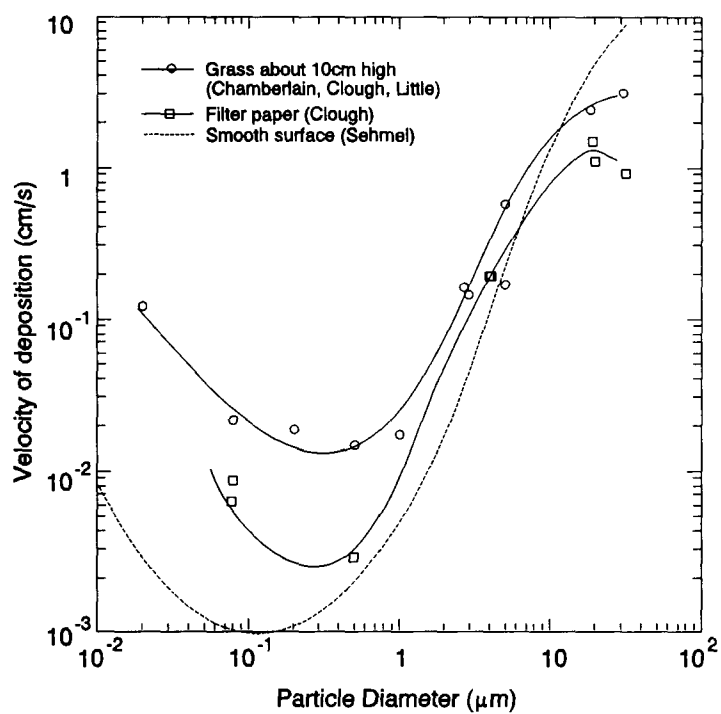


Figure 3-9. Particle deposition from wind tunnel studies.

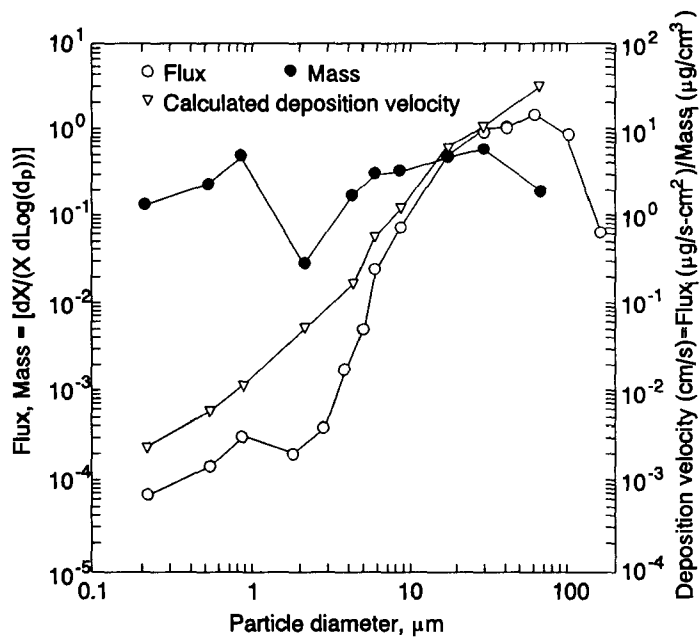


Figure 3-10. Sedimentation and inertia effects on large particle deposition.

1 This section examines the present state of knowledge regarding the loading, size  
2 distribution, and chemical composition of the fine particle component of tropospheric  
3 aerosols and the processes that govern these properties. Reasons why it is necessary to know  
4 the physical properties and composition of these aerosols include the following:

- 5 1. Identification of the processes and sources responsible for the aerosol.
- 6 2. Development of a data base of measurements to be used in setting standards
- 7 3. Relating aerosol loadings and composition to putative deleterious consequences,  
8 e.g. epidemiological studies.
- 9 4. Development of models whose objective is to relate aerosol loading and chemical  
10 and physical properties to sources of the aerosols and their precursors and  
11 evaluation the performance of such models.

### 14 **3.3 CHEMISTRY AND CHEMICAL COMPOSITION**

#### 15 **3.3.1 Fine Particle Chemistry**

##### 16 **3.3.1.1 Acid Aerosols and Particulate Sulfates**

17 Sulfuric acid and its neutralization products with ammonia constitute a major  
18 anthropogenic contribution to fine particle aerosol. This section reviews recent advances in  
19 understanding of the sources, removal processes, loadings and properties of tropospheric  
20 sulfate aerosols. Emphasis is given to properties and processes pertinent to these aerosols in  
21 regions influenced by anthropogenic emissions as distinguished from remote locations  
22 influenced primarily by natural sources.

##### 24 *Sources*

25 Aerosol sulfate in the troposphere consists of particles emitted directly from sources  
26 (primary sulfate) and of sulfate formed by atmospheric oxidation of gaseous sulfur  
27 compounds, mainly SO<sub>2</sub>. Knowledge of the sources of this particulate material is important  
28 to understanding the processes responsible for observed loading, composition, and size  
29 distribution of the material and to developing effective methods to control its concentration.  
30 Principal sources of ambient sulfate may be distinguished into primary emissions (that is  
31 material emitted into the atmosphere as particulate sulfate or as gas-phase SO<sub>3</sub> and/or H<sub>2</sub>SO<sub>4</sub>,

both of which readily form condensed-phase species) and gas-to-particle conversion in the atmosphere that produces SO<sub>3</sub> and/or H<sub>2</sub>SO<sub>4</sub>.

#### *Atmospheric oxidation of SO<sub>2</sub>*

Atmospheric oxidation of SO<sub>2</sub> takes place both by gas-phase reaction and by aqueous-phase reaction. The principal gas-phase mechanism is thought to be the OH-initiated reaction. The principal aqueous-phase reactions are thought to be oxidation by H<sub>2</sub>O<sub>2</sub> and O<sub>3</sub>. Aqueous-phase reactions followed by cloud evaporation can result in formation of clear-air aerosol. Evaporation can be a major production route for atmospheric sulfate aerosols. The relative proportion of sulfate aerosol produced by the aqueous and gas-phase routes is not well established.

*Gas-phase oxidation of SO<sub>2</sub>.* Gas phase oxidation of SO<sub>2</sub> is thought to occur largely, if not entirely, by a sequence of reactions initiated by the reaction of OH with SO<sub>2</sub>.



The gaseous H<sub>2</sub>SO<sub>4</sub> subsequently adds to existing particles or may nucleate to form new particles.

Until recently the evidence for the occurrence of this reaction in the atmosphere has relied on modeled OH concentrations and on laboratory-determined reaction rate coefficient (Gleason et al., 1987) for the OH + SO<sub>2</sub> reaction. However, recent measurements of OH and H<sub>2</sub>SO<sub>4</sub> in the atmosphere provide empirical evidence for this mechanism (Eisele and Bradshaw, 1993; Eisele and Tanner, 1993). Simultaneous measurements of OH and SO<sub>2</sub> allow the gas-phase reaction production rate of H<sub>2</sub>SO<sub>4</sub> to be calculated at the time and location of the measurement. Likewise, measurements of particle size distribution allow the effective first-order rate coefficient for diffusive uptake of H<sub>2</sub>SO<sub>4</sub> monomer by aerosol

particles to be calculated, and measurement of the concentration of H<sub>2</sub>SO<sub>4</sub> monomer allows the loss rate by this mechanism to be calculated. Comparison of the calculated production and loss rates of H<sub>2</sub>SO<sub>4</sub> monomer show them to be equal, consistent with the observed steady state concentration of this species. This study lends substantial confidence to the applicability of the laboratory mechanism and rate to evaluation of the rate of sulfuric acid formation in the ambient atmosphere. At night, however, the calculated loss rate substantially exceeded the apparent production rate. This suggests an additional source of H<sub>2</sub>SO<sub>4</sub> monomer, either from some hitherto unrecognized reaction, or from release of H<sub>2</sub>SO<sub>4</sub> from the particles back to the gas phase. The investigators suggest that the explanation is the latter, in view of correlation of particle concentration and H<sub>2</sub>SO<sub>4</sub> monomer concentration.

The substantial progress made in the past few years in measurement of OH leads to the expectation of increased confidence in models that calculate the concentration of this species from local photolysis rate constants and abundances. This may be expected to lead in turn to enhanced confidence in OH concentrations and sulfuric acid production rates calculated by regional scale transport models.

The reaction of SO<sub>3</sub> has recently been reexamined by Kolb et al. (1994), who find that the reaction is second order in water vapor and propose that the reaction takes place by interaction of SO<sub>3</sub> with water vapor dimer:



The investigators note that it is probable that sufficient water dimer exists in the atmosphere to allow the reaction to efficiently form sulfuric acid vapor. Other processes may involve H<sub>2</sub>SO<sub>3</sub> + H<sub>2</sub>O. The complex H<sub>2</sub>O × SO<sub>3</sub> also may be involved in sulfuric acid formation (Leopold et al., 1985).

### **3.3.2 Formation of Sulfates in Clouds**

#### **3.3.2.1 Particle Formation in Clouds**

##### **3.3.2.1.1 Introduction**

The atmospheric aqueous phase (clouds, fogs) can be viewed as a processor of the aerosol size/composition distribution (Pandis et al., 1990a,b). Precipitating clouds are well

known to be the major removal mechanism of aerosol particles from the atmosphere. At the same time, the liquid droplets provide the reacting medium for aqueous-phase reactions (Graedel and Weschler, 1981; Chameides and Davis, 1982; Graedel and Goldberg, 1983; Jacob and Hoffmann, 1983; Munger and Hoffman, 1983; Chameides, 1984; Seigneur and Saxena, 1984; Hoffman and Jacob, 1984; Fuzzi et al., 1984; Hong and Carmichael, 1986; Hill et al., 1986; Jacob, 1986; Jacob et al., 1986; Johnson et al., 1987; Fuzzi et al., 1988; Dlugi, 1989; Pandis and Seinfeld, 1989; Munger et al., 1990; Forkel et al., 1990; Bott, 1991; Joos and Baltensperger, 1991; Barth, 1994; De Valk, 1994). Several gaseous species dissolve in cloudwater and react giving products that remain in the aerosol phase after the cloud dissipates; for example, the dissolution of SO<sub>2</sub>, its ionization, and subsequent oxidation to sulfate. These species can attract additional gaseous species, such as ammonia and water into the aerosol phase and thereby increase further the aerosol mass. Therefore, aerosol processing by nonprecipitating clouds represents a mechanism by which atmospheric particles can grow during their residence time in the atmosphere. A detailed review of the state of science in 1990 has been presented by United States National Acid Precipitation Assessment Program (U.S. NAPAP) (1991).

A cyclical relationship between the occurrence of smog and fog in polluted areas has been proposed by Munger et al. (1983) and was termed the smog-fog-smog cycle. In a polluted atmosphere with high aerosol concentration, the formation of late night and early morning fogs is augmented enhancing smog production, visibility reduction, and aerosol sulfate the next day (Cass, 1979; Cass and Shair, 1984; Pandis et al., 1990). Processing of aerosol by clouds can result in similar cyclical relationships and enhanced contribution of the aerosol produced in clouds to ground-level particulate concentrations (Altshuller, 1987). This processing cycle accelerates the production of atmospheric acidity through aqueous-phase reactions (Schwartz, 1989).

#### ***3.3.2.1.2 Cloud Effects On Particle Number Concentration***

There has been a series of observations of enhanced aerosol number concentrations in the vicinity of clouds (Saxena and Hendler, 1983; Hegg et al., 1990; Radke and Hobbs, 1991; Hegg et al., 1991). Saxena and Hendler (1983) suggested that the observed high aerosol number concentrations near clouds could be due to the shattering of rapidly

1 evaporating droplets. Hegg et al. (1991) proposed that the high actinic radiation fluxes near  
2 cloud tops could lead to high OH concentrations and nucleation of new  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$  particles.  
3 The high relative humidity areas around clouds often have total particle number  
4 concentrations about twice those in the air at the same level but well removed from the cloud  
5 boundaries (Radke and Hobbs, 1991). Kerminen and Wexler (1994) have demonstrated that  
6 there is high nucleation probability associated with these high relative humidity areas,  
7 especially near relatively clean clouds. All these speculated mechanisms for production of  
8 new particles produce negligible new aerosol mass, but may influence the shape of the  
9 aerosol distribution, especially in remote regions. Aqueous-phase reactions producing sulfate  
10 and nitrate increase the aerosol mass, but do not influence directly the aerosol number  
11 concentration. The removal of gas-phase  $\text{SO}_2$ ,  $\text{H}_2\text{SO}_4$ , and  $\text{NH}_3$ , due to their transfer to  
12 aqueous-phase, indirectly slows down the production of new particles in the vicinity the  
13 cloud.

#### 15 **3.3.2.1.3 Cloud Effects On Aerosol Mass Concentration**

16 Significant production of sulfate has been detected in clouds and fogs in different  
17 environments (Hegg and Hobbs, 1987, 1988; Pandis and Seinfeld, 1989b; Husain et al.,  
18 1991; Swodziazak and Swodziazak, 1992; Pandis et al., 1992; De Valk, 1994; Liu et al.,  
19 1994). The detection of sulfate-producing reactions is often hindered by the variability of  
20 cloud liquid water content and the temporal instability and spatial variability in concentrations  
21 of reagents and product species (Kelly et al., 1989). The production of sulfate has also been  
22 detected and investigated in laboratory clouds (Hansen et al., 1991). Aqueous-phase  
23 oxidation of  $\text{HSO}_3^-$  by  $\text{H}_2\text{O}_2$  is particularly fast, as illustrated by the mutual exclusivity of  
24  $\text{SO}_2$  and  $\text{H}_2\text{O}_2$  observed in clouds (Daum et al., 1984; 1987). Other reactions, including  
25 oxidation of dissolved  $\text{SO}_2$  by ozone and oxidation by  $\text{O}_2$  catalyzed by  $\text{Fe}^{3+}$  and  $\text{Mn}^{2+}$  may  
26 also contribute, significantly in some cases, to sulfate production (Pandis et al., 1989; Barth  
27 et al., 1992; Barth, 1994). During aqueous-phase sulfate production the reactants including  
28  $\text{SO}_2$ ,  $\text{H}_2\text{O}_2$ ,  $\text{O}_3$ , and OH are transferred from the gas-phase to the cloud droplets. This  
29 transport includes a series of steps (gas-phase diffusion, transport across the gas-liquid  
30 interface, dissociation and aqueous-phase diffusion) that ultimately couple the gas and

1 aqueous phases and in some cases control the overall sulfate production rate (Schwartz,  
2 1988).

3 Hydrogen peroxide is the most important oxidant for the conversion of SO<sub>2</sub> in cloud  
4 water at pH 4.5 or lower (Calvert et al., 1985) and dominates the aqueous sulfate formation  
5 pathways (McHenry and Dennis, 1994) in the northeastern United States. The measured  
6 H<sub>2</sub>O<sub>2</sub> gas-phase mixing ratio over the northeastern and central United States has been  
7 reported to vary from 0.2 to 6.7 ppb (Sakugawa et al., 1990) with the highest values during  
8 the summer and the lowest during the winter months. The H<sub>2</sub>O<sub>2</sub> concentrations usually  
9 increase with decreasing latitude and increasing altitude (Sakugawa et al., 1990). The  
10 availability of hydrogen peroxide is often limiting the sulfate formation in clouds. This  
11 limitation is more pronounced near SO<sub>2</sub> sources and during the winter months. The seasonal  
12 contribution of clouds to sulfate levels depends on both the availability of oxidants and on the  
13 cloud cover. In cases where the sulfate cloud production is oxidant limited, changes in  
14 aerosol sulfate levels will be less than proportional to SO<sub>2</sub> emission changes, with the  
15 relationship being more nonlinear in winter than in spring or summer (U.S. NAPAP, 1991).

16 Evaluations of the rate of the SO<sub>2</sub>-H<sub>2</sub>O<sub>2</sub> reaction in cloudwater indicate that the  
17 characteristic time for this reaction is a few minutes to an hour, depending on conditions  
18 (Schwartz, 1984; Meagher et al., 1990). Since such a reaction time is shorter than the  
19 lifetime of stratiform clouds in the troposphere it is anticipated that the reaction of SO<sub>2</sub> and  
20 H<sub>2</sub>O<sub>2</sub> will proceed to completion in liquid water stratiform clouds. Evidence of this  
21 occurring would be that only one or the other of these species would be present in such  
22 clouds, but not both at the same time. This expectation has been borne out in field  
23 measurements supporting the inference of rapid reaction given by the model estimates.  
24 Daum and colleagues (Daum et al, 1984; Daum, 1988) have presented results of  
25 simultaneous aircraft measurements of H<sub>2</sub>O<sub>2</sub> in collected cloudwater samples and SO<sub>2</sub> in air  
26 (filter pack measurements) in nonprecipitating stratiform clouds indicating that in almost all  
27 instances either one or the other species was at very low concentrations, and by inference  
28 that the reaction has proceeded essentially to completion in the clouds. A rather different set  
29 of results was reported by Husain et al. (1991) who conducted measurements of gas-phase  
30 SO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> during cloud events at Whiteface Mountain, NY. Although a general negative

1 correlation between the two species concentrations was exhibited, the data indicated  
2 substantial periods of apparent coexistence of these species.

3 There is the possibility of spatial inhomogeneities in the clouds that are not resolved in  
4 the sampling period (typically 30 min in the Daum studies; an hour or more for the Husain  
5 studies), in which one region was H<sub>2</sub>O<sub>2</sub> rich and another SO<sub>2</sub> rich. In such instances a lack  
6 of coexistence of the two species would be masked by the extended duration of sampling.  
7 Such spatial inhomogeneities might also account for the few instances reported by Daum in  
8 which SO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> apparently coexisted in clouds. Additionally, local patches of  
9 subsaturated air in the clouds during the sampling period might also account for these  
10 observations, although Daum took efforts to exclude such instances from their data base.  
11 Yet another possible explanation of the Husain results is that the cloud was relatively newly  
12 formed, and the material had not had time to react. An obvious improvement in this  
13 approach is to measure the species, as well as cloud liquid water content, with greater time  
14 resolution. Burkhard et al. (1994) have present aircraft measurements of gas-phase SO<sub>2</sub> and  
15 H<sub>2</sub>O<sub>2</sub> during in-cloud flights; traces of liquid water content are also shown. These data  
16 support a strong anticorrelation of SO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> in clouds on various time (location) scales,  
17 with numerous instances of peaks of SO<sub>2</sub> coincident with valleys of H<sub>2</sub>O<sub>2</sub> and vice versa.

18 A quantitative estimate of the amount of cloudwater sulfate that is formed by in-cloud  
19 reaction can be gained by inferring the amount of cloudwater sulfate that derives from  
20 preexisting sulfate aerosol. Husain et al. (1991) has used selenium as a tracer to allow such  
21 inferences to be drawn. By measuring the sulfate to selenium ratio in clear air aerosol that is  
22 representative of the aerosol that is the pre-cloud aerosol of the clouds under investigation,  
23 and by assuming that the fractional incorporation of the sulfate and selenium into cloudwater  
24 is identical (and/or by measuring this ratio), it is possible to infer the amount of cloudwater  
25 sulfate derived from preexisting sulfate aerosol and by difference, the amount formed by in-  
26 cloud reaction. A series of such studies carried out at Whiteface Mountain, NY, indicates  
27 that assumption of identical scavenging of sulfate and selenium is valid ( $1.04 \pm 0.29$ ;  $1.04$   
28  $\pm 0.19$  in two separate cloud systems). Evidence of enhanced sulfate in cloudwater,  
29 attributed to sulfate formed by in-cloud reaction, was found in five of six cloud systems  
30 studied; amounts formed were consistent with ambient SO<sub>2</sub> concentrations. Examination of  
31 the pH dependence of the concentration of in-cloud produced sulfate inferred by this

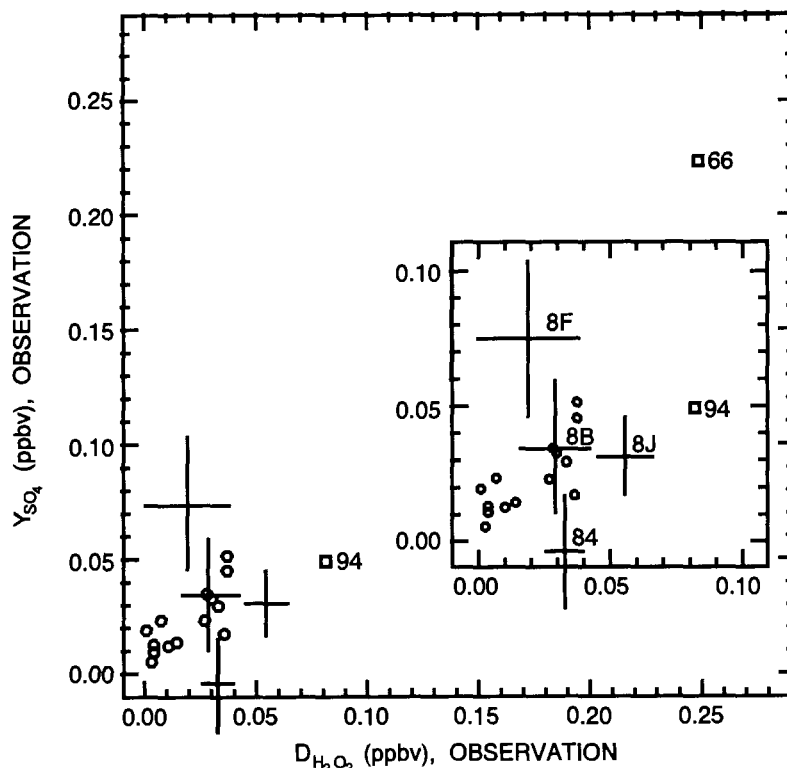


1 technique indicated that sulfate was produced by in-cloud reaction only at pH values below  
2 4.0, consistent with oxidation by  $\text{H}_2\text{O}_2$ , but not with oxidation by  $\text{O}_3$ .

3 Recently Snider and Vali (1994) reported studies of oxidation of  $\text{SO}_2$  in winter  
4 orographic clouds in which  $\text{SO}_2$  was released and the extent of increased concentrations of  
5 sulfate in cloudwater (relative to the unperturbed cloud) were compared to decreased  
6 concentrations of  $\text{H}_2\text{O}_2$  (sum of gaseous plus aqueous, inferred from aqueous concentrations).  
7 Despite considerable scatter, the data fall fairly close to the one-to-one line, indicative of the  
8 expected stoichiometry of reaction, Figure 3-11. The investigators also modeled the reaction  
9 kinetics. The rate of reaction is sensitive to the liquid water content (LWC) of the cloud  
10 during the time between the point of cloud condensation to the point of sampling. Since this  
11 profile was not known the investigators assumed a linear profile for LWC versus time. The  
12 resulting model predictions agreed closely with the extent of reaction inferred from changes  
13 in  $\text{H}_2\text{O}_2$  and sulfate concentrations, supporting the applicability of the model.

14 In contrast to the  $\text{H}_2\text{O}_2$  reaction, oxidation of  $\text{SO}_2$  by  $\text{O}_3$  exhibits a strong pH  
15 dependence. The reaction is quite rapid at high pH ( $\sim 6$ ) but is expected to greatly slow  
16 down as strong acid is produced in the course of the reaction. However, if concentrations of  
17  $\text{NH}_3$  or other basic materials are sufficiently high to maintain a pH above 5, the reaction can  
18 continue to proceed at a high rate.

19 Walcek et al. (1990) calculated that, during the passage of a midlatitude storm system,  
20 over 65% of the sulfate in the troposphere over the northeastern United States was formed in  
21 cloud droplets via aqueous-phase chemical reactions. The same authors indicated that,  
22 during a 3-day springtime period, chemical reactions in clouds occupying 1 to 2% of the  
23 tropospheric volume were responsible for sulfate production comparable to the gas-phase  
24 reactions throughout the entire tropospheric volume under consideration. McHenry and  
25 Dennis (1994) estimated that annually more than 60% of the ambient sulfate in Central and  
26 Eastern United States is produced in clouds with the non-precipitating cloud production  
27 dominating over precipitating cloud production. Spatial variability of emissions and ambient  
28  $\text{H}_2\text{O}_2$  concentrations induces spatial variability in the contribution of in-cloud sulfate  
29 production, making it highest in the south. These conclusions are in quantitative agreement  
30 with similar calculations of Dennis et al. (1994) and Karamachdani and Venkatram (1992).



**Figure 3-11. Comparison of observed  $\text{H}_2\text{O}_2$  depletions ( $D_{\text{H}_2\text{O}_2}$ , abscissa) and observed sulfate yields ( $Y_{\text{SO}_4}$ , ordinate). Errors associated with experiments 84, 8B, 8F, and 8J are indicated and data values from these experiments are labeled in the inset figure. Data values corresponding to experiments 94 and 66 are also labeled. The slope of the best fit line, forced through the origin, and calculated using only those data values indicated by circles is  $1.21 (\pm 0.13)$ .**

Source: Snider and Vali (1994).

Aqueous-phase oxidation in clouds is also the most important pathway for the conversion of  $\text{SO}_2$  to sulfate on the global scale (Hegg, 1985; Langner and Rodhe, 1991).

Clouds could under some conditions also be a significant source of aerosol nitrate during the night. Choularton et al. (1992) and Colvile et al. (1994) observed production of around  $0.5 \text{ mg m}^{-3}$  of nitrate during the processing of an air parcel by a cloud. They speculated that the sources of this nitrate were gaseous  $\text{N}_2\text{O}_5$  and  $\text{NO}_3$ .

Chemical heterogeneities in the droplet population affect significantly the overall sulfate production rate and the produced sulfate size distribution (Seidl, 1989; Twohy et al., 1989; Lin and Chameides, 1990; Pandis et al., 1990a,b; Ayers and Larson, 1990; Hegg and

Larson, 1990; Bower et al., 1991; Ogren and Charlson, 1992; Roelofs, 1992a,b; 1993; Carter and Borys, 1993; Bott and Carmichael, 1993; Collett et al., 1993b). Neglecting these chemical concentration differences could result in significant underestimations of the sulfate production rates in some cases (Hegg and Larson, 1990; Roelofs, 1993). Ice-related microphysical processes can also have a significant impact on cloud chemistry (Taylor, 1989; Wang and Chang, 1993; Collett et al., 1993a).

Fogs in polluted environments have the potential to increase aerosol sulfate concentrations but at the same time to cause reductions in the aerosol concentrations of nitrate, chloride, ammonium and sodium as well as in the total aerosol mass concentration (Pandis et al., 1990a). Pandis et al. (1992) calculated that more than half of the sulfate in a typical Los Angeles air pollution episode was produced inside a fog layer the previous night. This heterogeneously produced sulfate represented 5 to 8% of the measured PM<sub>10</sub> mass.

#### ***3.3.2.1.4 Cloud Effects On Aerosol Size/Composition Distribution***

Several measurements of the aerosol mass distributions in urban areas have shown that two distinct modes can exist in the 0.1 to 1  $\mu\text{m}$  diameter range (Hering and Friedlander, 1982; McMurry and Wilson, 1983; Wall et al., 1988; John et al., 1990). These are referred to as the condensation mode (approximate aerodynamic diameter 0.2  $\mu\text{m}$ ) and the droplet mode (aerodynamic diameter around 0.7  $\mu\text{m}$ ). Hering and Friedlander (1982) and John et al. (1990) postulated that the larger mode could result from aqueous-phase chemistry. Meng and Seinfeld (1994) proposed that growth of condensation mode particles by accretion of water vapor or by gas-phase or aerosol-phase sulfate production cannot explain the existence of the droplet mode. Activation of condensation mode particles, formation of cloud/fog drops followed by aqueous-phase chemistry, and aqueous droplet evaporation was shown by these authors to be a plausible mechanism for formation of the urban and regional aerosol droplet mode. The sulfate formed during fog/cloud processing of an air mass favors the aerosol particles that had access to most of the fog/cloud liquid water content, which are usually the particles with dry diameters around 1  $\mu\text{m}$  (Pandis et al., 1990b). These two submicron mass-distribution modes have been also observed in non-urban continental locations (McMurry and Wilson, 1983; Hobbs et al., 1985; Radke et al., 1989), but the frequency of their co-existence remains unknown. Thus, cloud processing of an air parcel can clearly

1 impact the scattering efficiency and in general the radiative properties of the corresponding  
2 aerosol (Hegg et al., 1992; Bower and Choularton, 1993).

3 The aerosol distribution is also modified during in-cloud processing by collision-  
4 coalescence of droplets and impaction scavenging of aerosols (Pruppacher and Klett, 1980).  
5 The aerosol scavenging by droplets is a relatively slow process, and collision coalescence  
6 among droplets of different sizes causes a redistribution of aerosol mass in such a manner  
7 that the main aerosol mass is associated with the main water mass (Flossmann et al., 1985).  
8 The processing of the remote aerosol distribution by clouds has been clearly demonstrated in  
9 a series of field studies (Frick and Hoppel, 1993). This multiple processing of remote  
10 aerosol by nonprecipitating clouds results in an extra mode in the aerosol number distribution  
11 (Hoppel et al., 1986; Frick and Hoppel, 1993).

12 Clouds and fogs can influence the atmospheric aerosol number and mass concentration  
13 and chemical composition, the shape of the aerosol size distribution, the aerosol acidity and  
14 radiative properties. These effects can be important in all environments (urban, rural and  
15 remote) and all seasons. Our qualitative understanding of the aerosol-cloud interactions has  
16 improved significantly, but, with few exceptions, the quantification of these effects remains  
17 uncertain (Altshuller, 1987; Kelly et al., 1989; Pandis et al., 1992).

### 19 **3.3.3 Aqueous-Phase Oxidation Of SO<sub>2</sub> In Clear-Air Aerosols**

20 Until recently it was thought that the low amount of liquid water associated with clear-  
21 air aerosols (volume fraction on the order of  $1 \times 10^{-10}$ , compared to clouds, for which the  
22 volume fraction is the order of  $1 \times 10^{-7}$ ) precluded significant aqueous-phase conversion of  
23 SO<sub>2</sub> in such droplets. However Sievering and colleagues have called attention to the  
24 possibility of rapid rate of oxidation of SO<sub>2</sub> by O<sub>3</sub> in aqueous sea-salt aerosols, which are  
25 buffered by the alkalinity of sea salt particles,. Indeed it appears that such a rate may  
26 initially be quite rapid,  $1 \mu\text{M s}^{-1}$  corresponding to  $8\% \text{ hr}^{-1}$ , in the example given by  
27 Sievering et al. (1991) for liquid water content  $50 \mu\text{g m}^{-3}$  and SO<sub>2</sub> concentration  $2 \text{ n mol m}^{-3}$   
28 3 (mixing ratio 0.05 ppb). Despite this rapid initial rate, it would appear that the extent of  
29 such oxidation may be quite limited. For the example given by Sievering et al. (1991), the  
30 sea-salt sodium concentration is given as  $100 \text{ n mol m}^{-3}$ . Based on the concentrations of  
31 (HCO<sub>3</sub><sup>-</sup> + CO<sub>3</sub><sup>2-</sup>) and Na<sup>+</sup> in seawater ( $2.25$  and  $454 \text{ m mol kg}^{-1}$ , respectively), the

1 alkalinity of the sea salt aerosol is expected to be  $0.5 \text{ n mol m}^{-3}$ . Consequently, after only  
2  $0.25 \text{ n mol m}^{-3}$  of  $\text{SO}_2$  is taken up in solution and oxidized (i.e., 12% of the initial  $\text{SO}_2$ ), the  
3 initial alkalinity would be exhausted, and the reaction rapidly quenched.

4 Sievering et al. 1994 have presented field measurements over Lake Michigan of coarse-  
5 mode sulfate (diameter  $5\text{--}20 \mu\text{m}$ ), which they ascribe at least in part to oxidation of  $\text{SO}_2$  in  
6 such particles derived from wind driven spray of lake water, in which the pH is maintained  
7 high by alkalinity present in the lake water. Calculations were carried out for liquid water  
8 volume fraction of  $13 \times 10^{-12}$  ( $13 \mu\text{g m}^{-3}$ ). The alkalinity was inferred from the measured  
9 cation minus anion difference (cations  $\text{NH}_4^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ; anions  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ) in the  
10 coarse mode, which averaged  $26 \text{ neq m}^{-3}$ , corresponding to an aqueous alkalinity of  $2 \times 10^{-5}$   
11 M. In the absence of mass transport limitation the rate of the aqueous-phase  $\text{O}_3\text{--SO}_2$  reaction  
12 was calculated to be  $7 \pm 3 \times 10^{-4} \text{ M s}^{-1}$ ; however, mass transport limitation reduced this  
13 rate by a factor of 20 to 40 at pH 7. The conversion rate referred to gas-phase  $\text{SO}_2$  was  
14 calculated as 0.5 to 1.7 %  $\text{hr}^{-1}$ . The investigators concluded that this mechanism is a  
15 significant contributor to the  $\text{SO}_2$  oxidation under these conditions. Again, however, concern  
16 may be raised with that conclusion, namely that the indicated oxidation rate,  $2 \times 10^{-5} \text{ M s}^{-1}$   
17 after taking mass transport limitation into account, would quickly produce an acidity equal to  
18 the initial alkalinity, thereby quenching the reaction.

### 20 **3.3.3 Physical and Chemical Considerations in Particulate Sampling and** 21 **Analysis**

#### 22 **3.3.3.1 Semi-Volatile Organic Compounds (SOCs)**

##### 23 *General*

24 SOC<sub>s</sub> are defined here to be organic compounds with intermediate pure compound, sub-  
25 cooled liquid vapor pressures ( $p_L^0$ ). Definition ranges vary somewhat, but SOC<sub>s</sub> can be  
26 thought to include compounds with  $p_L^0$  values in the range  $10^{-2}$  down to  $10^{-9}$  torr. For SOC<sub>s</sub>  
27 and for semi-volatile inorganic materials, there are health and sampling reasons for under-  
28 standing the factors controlling the relative amounts that are in the gaseous (G) and aerosol  
29 particulate (P) phases. G/P partitioning of SOC<sub>s</sub> has often been considered to involve mainly  
30 simple physical adsorption to particle surfaces (e.g., Junge, 1977; Yamasaki et al., 1982;  
31 Pankow, 1987). However, absorptive phase partitioning must also often play some role

(Pankow, 1994) as into aerosol particles containing plant wax as well as organic carbon from primary emissions (Turpin et al., 1991) and from secondary organic aerosol formation (Pandis et al., 1992).

### Theory

A useful parameterization of G/P partitioning is (Yamasaki et al., 1982; Pankow, 1991)

$$K_p = \frac{F / TSP}{A} \quad (3-9)$$

where:  $K_p$  ( $\text{m}^3 \mu\text{g}^{-1}$ ) = partitioning constant;  $TSP$  ( $\mu\text{g m}^{-3}$ ) = concentration of total suspended particulate matter; and  $F$  ( $\text{ng m}^{-3}$ ) and  $A$  ( $\text{ng m}^{-3}$ ) = the P-associated and G concentrations of the compound of interest, respectively. The symbols  $F$  and  $A$  originate in the common usage of a filter followed by an adsorbent to collect the P and G portions, respectively. With urban particulate matter (UPM), a given SOC at a given temperature  $T$  tends to exhibit similar  $K_p$  values from sampling event to sampling event. The fraction  $\phi$  of the total compound that is on/in the P phase is given by

$$\phi = \frac{F}{A + F} = \frac{K_p TSP}{K_p TSP + 1} \quad (3-10)$$

Though not yet used in practice, it may also prove useful to define  $K_{p,10} = (F_{10} / PM10) / A$  where  $PM10$  ( $\mu\text{g m}^{-3}$ ) = concentration of particles with aerodynamic diameters smaller than  $10 \mu\text{m}$ , and  $F_{10}$  ( $\text{ng m}^{-3}$ ) =  $PM10$ -associated concentration of the compound of interest.

Theory (Pankow, 1994) predicts that the values of  $K_p$  for a given compound class will be given by a relation of the form  $K_p = [C_1 + C_2] / p_L^0$ , where  $C_1/p_L^0$  and  $C_2/p_L^0$  represent the adsorptive and absorptive contributions to  $K_p$ , respectively. Log  $K_p$  values measured under given conditions (*e.g.*,  $T$ ) for a compound class such as the polycyclic aromatic hydrocarbons (PAHs) will thus tend to be linearly correlated with the corresponding log  $p_L^0$  values according to  $\log K_p = m_r \log p_L^0 + b_r$ . For PAHs sorbing to UPM in Osaka, Japan,  $m_r \approx -1.028$  and  $b_r \approx -8.11$  (Pankow and Bidleman, 1992). (Table 3-2 gives  $p_L^0$  values for several PAHs at  $20^\circ\text{C}$ .) This correlation allows  $K_p$  to be predicted for a compound that is within the compound class of interest, but was not examined in a given study.  $K_p$  for a

TABLE 3-2. VALUES OF LOG  $P_L^0$  FOR VARIOUS PAHS AT 20 °C

Compound	log $P_L^0$ (torr)
Fluorene	-2.72
Phenanthrene	-3.50
Anthracene	-3.53
Fluoranthene	-4.54
Pyrene	-4.73
Benzo[a]fluorene	-5.24
Benzo[b]fluorene	-5.22
Benz[a]anthracene	-6.02
Chrysene	-6.06
Triphenylene	-6.06
Benzo[b]fluoranthene	-7.12
Benzo[k]fluoranthene	-7.13
Benzo[a]pyrene	-7.33
Benzo[e]pyrene	-7.37

given compound depends on  $T$  (Kelvin) according to  $\log K_p = m_p/T + b_p$  where  $m_p$  depends on the enthalpy of desorption; values of the intercept  $b_p$  will be similar within a given compound class (Table 3-3). Increasing the relative humidity from 40 to 90% appears to cause  $K_p$  values to decrease by a factor of about two for PAHs sorbing to UPM (Pankow et al., 1993).

For constant  $K_p$ , then  $\phi$  will increase as  $TSP$  increases. For constant  $TSP$  and  $T$ , as volatility increases (*i.e.*, as  $P_L^0$  increases), then  $K_p$  and  $\phi$  will decrease. When  $\phi \approx 0$ , one can sample just the G phase when determining the atmospheric concentration of an SOC; when  $\phi \approx 1$ , one can sample just the P phase; when  $\phi$  is between 0 and 1, one must sample both phases.

**TABLE 3-3.  $m_p$  Values for PAHs Sorbing to UPM in Osaka, Japan. Obtained by Fitting to a Common  $y$ -Intercept  $b_r$  of -18.48.**

Compound	$m_p$
Phenanthrene & Anthracene	4,124
Methylphenanthrene & Methylanthracene	4,240
Fluoranthene	4,412
Pyrene	4,451
Benzo[a]fluorene & Benzo[b]fluorene	4,549
Benz[a]anthracene, Chrysene, & Triphenylene	4,836
Benzo[b]fluoranthene & Benzo[k]fluoranthene	5,180
Benzo[a]pyrene & Benzo[e]pyrene	5,301

Source: Pankow, 1991.

### ***Sampling Methods and Associated Sampling Artifacts***

Atmospheric SOC<sub>s</sub> can be determined using a filter followed by an adsorbent. These collect the P and G portions, respectively. Filter types include glass fiber filters (GFFs), quartz fiber filters (QFFs), and teflon membrane filters (TMFs). Adsorbent types include polyurethane foam (PUF), Tenax, and XAD resins. Safe sampling volumes for G-phase SOC<sub>s</sub> on Tenax and PUF can be predicted based on studies of retention volumes on these adsorbents (Pankow, 1988 and 1989). *Volatilization losses from particles (i.e., "blow-off")* can occur from a filter/adsorbent when  $T$  increases during sampling, when the general level of air contamination decreases during sampling, and/or when a large pressure drop develops across the filter (Zhang and McMurry, 1991). In the first case,  $K_p$  for a given compound and the already-filtered particles will decrease, leading to desorption from the sampled P-phase. In the second case, even with  $T$  constant, if  $A$  in the air being sampled decreases, then desorption losses from the collected particles can occur. Volatilization is of particular concern with long sampling times since large overnight  $T$  cycles and/or large changes in the level of contamination are then more likely. Material volatilized from the filter will be collected on the adsorbent following the filter. *Adsorption gains to particles* from the gas phase due to decreases in  $T$  and/or increases in  $A$  during sampling is a second possible



artifact type with filter/adsorbent samplers. *Adsorption to the filter* from the G phase is a third artifact type. In this last case, a portion of the value of  $A$  for an SOC of interest sorbs directly to the filter and so incorrectly contributes to the measured value of  $F$  for the compound. It is difficult to generalize regarding the magnitudes of the first two artifact types. One can attempt to correct for the third artifact type through the use of a backup-filter (Hart et al., 1994). For sampling of UPM in Portland, Oregon, Hart et al. (1994) estimated that failure to correct for gas adsorption to the filter caused  $F$  values for PAHs to be overestimated by a factor of  $\sim 1.4$ . Correction of the G-adsorption effect through the use of a backup filter is subject to two possible confounding effects: 1) the atmospheres to which the front and back filters are exposed may differ, making for different G-adsorption to the two filters; 2) organic compounds sorbed to a backup filter could have in part volatilized from the front filter. Table 3-4 summarizes how the three artifact types act to cause measured values of  $F$ ,  $A$ , and  $\phi$  to deviate from the true, volume-averaged values.

**TABLE 3-4. Effects of Three Types of Artifacts on Volume-Averaged Values of  $\phi$  Measured Using a Filter/Adsorbent Sampler**

Artifact	Artifact Effect	
	On $A$	On $F$ and $\phi$
Volatilization from collected particles	Too large	Too small
Adsorption to collected particles	Too small	Too large
Gas adsorption to filter itself	Too small	Too large

A sampler employing a diffusion denuder may avoid some of the artifact problems of filter/adsorbent samplers. Air drawn into a diffusion denuder can be stripped of G-phase SOCs by a sorbent that coats the walls of the denuder: G-phase SOCs diffuse from the core of the air flow toward the walls. Sorbent coatings that have been used include silicones, gas chromatographic stationary phases (Krieger and Hites, 1992 and 1994), and finely divided XAD resin (Gundel et al., 1994; Kamens et al., 1995). The majority of the P-phase SOCs do not deposit on the walls of the denuder because aerosol particles have much smaller dif-

fusion coefficients than do gaseous molecules. The particles exiting the denuder are collected on a filter. Because the air stream flowing onto the filter has been largely stripped of G-phase SOCs, some desorption of the filtered P-phase SOCs can occur, and so an adsorbent is often placed after the filter to collect any such desorbed SOCs.  $F$  for a given compound is taken as the sum of the amounts on the filter and the subsequent adsorbent. Analysis of the denuder sorbent provides  $A$ . When the denuder sorbent cannot be analyzed (as with silicone rubber),  $A$  can be determined by difference using a second, total ( $A + F$ ) determination for SOCs (Lane et al., 1988; Coutant et al., 1988 and 1992; and Eatough et al., 1989 and 1993). Although sampling artifacts are not often discussed for denuder-based samplers, artifacts cannot be assumed to be absent. *In the denuder section*, less than 100% efficiency for G-phase collection will tend to make measured  $A$  values too small and  $F$  and  $\phi$  values too large; greater than 0% efficiency for P-phase collection will tend to make measured  $A$  values too large and  $F$  and  $\phi$  values too small. Turpin et al. (1993) have presented a new denuder design which does not use a sorbent-coated wall. Rather, a laminar flow separator is used to separate a portion of the G phase from a mixed G+P flow; collection of the G-phase compounds on a sorbent like PUF allows determination of the G-phase concentrations. P-phase concentrations are determined by difference. Other sampling and analysis issues are discussed in Chapter 4 of this document.

### 3.3.4 Particulate Nitrates

#### 3.3.4.1 Sources

By analogy to the sulfur system sources of aerosol nitrates might be distinguished into primary, gas-phase, and aqueous-phase. However, as primary nitric acid emissions are considered to be small, the present discussion focuses on in-situ production mechanisms in the atmosphere.

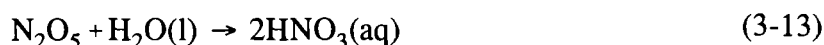
#### 3.3.4.2 Gas-phase

The principal mechanism for gas-phase production of nitrates is reaction of OH with  $\text{NO}_2$  to form  $\text{HNO}_3$ .



Here, as with  $\text{SO}_2$ , the mechanism and rate of the gas-phase reaction is well established from laboratory studies (see NAPAP SOST, 1990), and the principal source of uncertainty in describing the reaction rate is the concentrations of the reagent species, mainly OH. As noted above substantial progress has been made in the past few years in measurement of OH. It may thus be expected that improved knowledge of the concentration of this species will allow more confident evaluation of the rate of this reaction in specific situations and ultimately in regional-scale models.

A second key pathway for formation of nitric acid is the reaction sequence:



In addition, in daytime, photolysis of  $\text{NO}_3$  must be considered:



Other reactions of  $\text{NO}_3$  and/or  $\text{N}_2\text{O}_5$ , for example  $\text{N}_2\text{O}_5$  with aromatics (Pitts et al., 1985) must also be considered. Reaction of  $\text{N}_2\text{O}_5$  with liquid water appears to be rapid and irreversible. Studies of the uptake of  $\text{N}_2\text{O}_5$  on aqueous sulfuric droplets give mass accommodation coefficients of about 0.1 (Mozurkewich and Calvert, 1988; Van Doren et al., 1990; Fried et al., 1994). Thus the overall rate and yield of this reaction can be evaluated

1 from the pertinent gas-phase rate constants and the mass transfer rate constant for uptake of  
2  $\text{N}_2\text{O}_5$  by aqueous aerosol or cloud droplets.

3 Recently a study has been reported which claims to provide indication of uptake of  
4 nitrogen oxides to nitrate during passage of an airstream through a hill cap cloud (Colville et  
5 al. 1994). However, as noted above, claims of this sort must be viewed with caution. In  
6 this particular study it was necessary to invoke corrections for entrainment and dry deposition  
7 of magnitude comparable to the measured differences.

### 8 9 **3.3.5 Water Content and Aerosol Equilibria**

#### 10 **3.3.5.1 Water Content of Atmospheric Aerosols, and Its Dependence on Ambient** 11 **Humidity**

12 Water is an important ingredient of atmospheric aerosols (AA). The water content of  
13 AA and the behavior of AA with respect to changes in ambient humidity are of great  
14 importance in the global water cycle, the global energy budget, and also in atmospheric  
15 chemistry and optics. Understanding the relationship between AA and water has proven to  
16 be a difficult problem. Most of the water associated with AA is "unbound" (Pilinis et al.,  
17 1989) i.e., it can increase or decrease with ambient humidity in a non-linear manner. This  
18 non-linear relationship depends on particle size and composition, indeed on size-dependent  
19 composition. More recent studies have included monitoring of particle size distributions  
20 (either directly, or indirectly through light scattering and use of Mie theory) and size-  
21 dependent chemical composition under controlled RH (e.g., Covert and Heintzenberg, 1984;  
22 Rood et al., 1985). Such studies have presented increasing evidence in favor of external  
23 mixtures in particles. Covert and Heintzenberg (1984) found that size spectra of sulfur-  
24 bearing species were sensitive to RH while those of EC were not, and concluded that sulfur  
25 and EC are, to some extent, externally mixed. Harrison (1985) segregated the particles into  
26 CCN (cloud condensation nuclei) and non-CCN fractions and measured their chemical  
27 compositions. Both fractions contained sulfate, nitrate and soot, but sulfate was 15% of the  
28 CCN mass and only 5.8% of the non-CCN mass. Again, this was taken as evidence of  
29 external mixture to some extent. The differential mobility analyzer (DMA) has been a useful  
30 tool permitting study of particle properties for monodispersed size classes. Using the DMA,  
31 Covert et al. (1990) and Hering and McMurry (1991) showed that monodispersed particles

scatter varying amounts of light in a single particle optical counter, indicating different refractive indices, and hence, different chemical composition. Using a Tandem DMA (TDMA), McMurry and Stolzenberg (1989) showed that hygroscopic and hydrophobic particles of the same size co-exist frequently in Los Angeles, again an indication of external mixing.

### **3.3.5.2 Equilibria with water vapor**

The principal equilibrium of concern pertinent to ambient aerosols is that with water vapor. This equilibrium is important as it influences the size of the particles and in turn their aerodynamic properties (important for deposition to the surface, to airways, following inhalation, and to sampling instrumentation) and their light scattering properties. This section reviews recent work describing this equilibrium as it pertains to ambient aerosols.

Briefly the interaction of particles with water vapor may be described as follows. As relative humidity increases, crystalline soluble salts in aerosol particles 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 growth is such that the vapor pressure of the solution (concentration of which decreases as additional water is accreted) is maintained equal to that of the surrounding relative humidity; the particle thus 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 (supersaturated solution) to considerably lower relative humidities. Ultimately the particle abruptly loses its water vapor (efflorescence), returning typically to the initial, stable crystalline form. This behavior has been amply demonstrated in numerous laboratory studies (Tang and Munkelwitz, 1977; Tang, 1980). Recently Tang and Munkelwitz (1994) have presented data for water activity (equilibrium relative humidity) as a function of composition for several sulfate salts.

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

1 deliquescence point of the several components, and with subsequent growth as crystalline  
2 material in the particle dissolves according to the phase diagram for the particular  
3 multicomponent system. Under such circumstances a single particle may undergo several  
4 more or less abrupt phase transitions until the soluble material is fully dissolved. At  
5 decreasing relative humidity such particles tend to remain in solution to relative humidities  
6 well below the several deliquescence points; such behavior has been amply demonstrated. In  
7 the case of the sulfuric acid-ammonium sulfate-water system the phase diagram is fairly  
8 completely worked out, but in the case of the mixed anion system with nitrate, there are  
9 remaining uncertainties (Tang et al, 1978, 1981; Spann and Richardson, 1985). Spann and  
10 Richardson also give the compositional dependence of the relative humidity of efflorescence.  
11 For particles of composition intermediate between  $\text{NH}_4\text{HSO}_4$  and  $(\text{NH}_4)_2\text{SO}_4$  this transition  
12 occurs in the range from 40% to below 10%, indicating that for certain compositions the  
13 solution cannot be dried in the atmosphere. Particles of this composition would likely be  
14 present at low relative humidities in the atmosphere as supersaturated salts and exhibit  
15 apparent hygroscopic rather than deliquescent behavior.

16 Evidence of the interaction of ambient aerosol particles with water vapor has been  
17 obtained by several investigators. Koutrakis et al. (1989) found systematically increasing  
18 aerosol mean diameter with increasing relative humidity, which they attributed to water  
19 accretion on sulfates. Rood et al. (1989) examined the response of light scattering coefficient  
20 of ambient aerosols to increase in temperature (effectively, reduced relative humidity) and  
21 established that metastable supersaturated aerosols were essentially "ubiquitous". More  
22 detailed information regarding the size dependence of hygroscopic properties has been  
23 obtained examining the change in particle size of a monodisperse size cut selected with a  
24 mobility analyzer, subjecting that aerosol to an increase or decrease in relative humidity, and  
25 reanalyzing the size at the new humidity. Studies of this phenomenon in the Los Angeles  
26 area indicate this phenomenon, but also frequently indicate the presence of externally mixed  
27 aerosol, in which some of the aerosol exhibits the growth expected of soluble salts, where  
28 another, apparently hydrophobic, fraction does not exhibit such growth (McMurry and  
29 Stolzenburg, 1989). Such bimodal RH growth is exhibited for particles present at Hopi Point  
30 Arizona (Pitchford and McMurry (1994). In the latter study the relative humidity  
31 dependence of the size of the more hygroscopic fraction was found to be consistent with that

1 expected for sulfate salts. Such external mixtures have also been commonly observed in  
2 European aerosols (Hansson and Svenningsson, 1994).

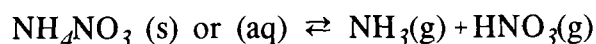
3 The time constant that characterizes the rate of exchange of water vapor between the  
4 gas phase and a solution droplet is of interest relative to the rate of response of particles to  
5 changes in relative humidity in the ambient environment, especially in the vicinity of  
6 surfaces, and relative to changes experienced by particles following inhalation or during  
7 sampling. It is generally assumed that the rate of this water exchange is rapid. The  
8 characteristic time for diffusional growth in response to a change in relative humidity was  
9 calculated by Pilinis et al. (1989) to be about  $1 \times 10^{-7}$  s. However Klystov et al. (1993)  
10 noted that this estimate was erroneously low by several orders of magnitude. The latter  
11 investigators examined the characteristic time for establishment of phase equilibrium in  
12 response to a change in relative humidity for  $(\text{NH}_4)_2\text{SO}_4$  aerosol particles (dry radius  $0.5$   
13  $\mu\text{m}$ ). The characteristic time increases from ca 1 ms at 8% RH to 1.6 s at 99% RH. Above  
14 99% RH the characteristic time can become much longer because of the large change in  
15 droplet radius at such relative humidities. These calculations indicate that the water  
16 equilibrium can be expected to be rapidly achieved in the ambient environment. A possible  
17 but important exception is near 100% RH, pertinent to dry deposition of particles to  
18 vegetation or to water, where the equilibrium size might not be reached in the time required  
19 for the particle to traverse the diffusive layer adjacent to the surface.

20 The lability of water associated with ambient aerosol has been evidenced in  
21 comparisons by Malm et al. (1994) of measured particulate light scattering coefficient  
22 obtained with an integrating nephelometer with values reconstructed from aerosol  
23 composition, taking into account the relative humidity dependence of light scattering  
24 coefficients of the aerosol components. The reconstructed values were found to  
25 systematically exceed the measured value. However when in the reconstruction the relative  
26 humidity was taken as that in the nephelometer chamber (invariably lower than ambient  
27 because of heating in the chamber) the reconstruction was markedly improved.

### 28 29 **3.3.5.3 Ammonium Nitrate Vaporization Equilibria**

30 In the sulfate system the vapor pressure of  $\text{H}_2\text{SO}_4$  is negligible, so that all sulfate may  
31 be considered present in the particles. Also, at least for acidic sulfates (that is, not fully

neutralized) the vapor pressure of NH<sub>3</sub> is likewise negligible. Even for fully neutral (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> any hydrolysis of NH<sub>4</sub><sup>+</sup> to form NH<sub>3</sub> that might escape to the vapor phase is suppressed by the resultant acidity. In contrast, nitrates in aerosols are distinguished from sulfates because of the volatility of NO<sub>3</sub><sup>-</sup> (as HNO<sub>3</sub>) and of NH<sub>4</sub>NO<sub>3</sub> (as NH<sub>3</sub> + HNO<sub>3</sub>). The equilibrium



is such that at ambient conditions the partial pressures of NH<sub>3</sub> and/or HNO<sub>3</sub> are appreciable above crystalline NH<sub>4</sub>NO<sub>3</sub> and likewise above solutions containing NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> ions (of not necessarily equal concentrations). It is thus necessary to consider these equilibria not just for the crystalline material but also for solutions, in the latter case as a function of concentration or, equivalently, water activity. Such a treatment has been given in detail by Stelson and Seinfeld (1982a,b), and that study is the basis for much subsequent interpretation of field measurements.

As an example of such a study, Harrison and Msibi (1994) show comparison of measured concentration product of HNO<sub>3</sub> and NH<sub>3</sub> versus the equilibrium constant for the reaction. Agreement is found roughly within a factor of 2 or so based on assumption of equilibrium with pure NH<sub>4</sub>NO<sub>3</sub> (crystal or solution). However when the observations were stratified by RH, no strong trend of measured concentration product with RH was evidenced.

As noted above, the time scale of reaching this equilibrium is of interest, for example as it may influence dry deposition or accommodation to changing gaseous environments, as in human airways. Wexler and Seinfeld (1990) modeled the time dependence of achieving this equilibrium and concluded that equilibrium is generally reached within seconds to minutes for typical aerosol loadings. However they caution that at low temperatures and low aerosol loadings the time constant for achieving this equilibrium can be a day or more.

An important implication of the high vapor pressure of ammonium nitrate (as NH<sub>3</sub> + HNO<sub>3</sub>) is that ammonia will distill from any ammonium nitrate if there is an acidic site present, for example acidic sulfate that is less than fully neutralized by ammonia. As a consequence ammonium nitrate aerosol is not expected to coexist with acidic aerosol. As



noted above this situation appears generally to obtain, for example in the work of Gebhart et al. (1994).

A further consequence of this equilibrium is the influence it may exert on dry deposition. Sievering et al. 1994 report high rates of deposition of particulate nitrate 2 to 9 cm s<sup>-1</sup>, comparable to that of HNO<sub>3</sub>, to forest canopies, inferred from steep gradients of NH<sub>4</sub>NO<sub>3</sub> concentration with height above the canopy. They attribute this to the large particle size of the nitrate, 2 to 2.5 μm mean diameter, citing calculation of Peters and Eiden (1992). An alternative explanation of the observations, which does not appear to be ruled out, is that the deposition is actually of HNO<sub>3</sub>; that deposition of HNO<sub>3</sub> perturbs the equilibrium of NH<sub>4</sub>NO<sub>3</sub> with NH<sub>3</sub> + HNO<sub>3</sub>, leading to decrease of NH<sub>4</sub>NO<sub>3</sub> in the vicinity of the surface and apparent deposition of this species.

### **3.3.6 Carbon-containing Particulate Matter**

#### **3.3.6.1 Introduction**

The carbonaceous fraction of ambient particulate matter consists of both elemental (EC) and organic carbon (OC). Elemental carbon, also called black carbon or graphitic carbon, has a chemical structure similar to impure graphite and is emitted directly into the atmosphere predominantly during combustion. Organic carbon is either emitted directly by sources (primary OC) or can be formed *in situ* by condensation of low volatility products of the photooxidation of hydrocarbons (secondary OC). The primary carbonaceous aerosol (sum of primary EC and OC) is traditionally called soot. Small additional quantities of aerosol carbon may exist either as carbonates (e.g., CaCO<sub>3</sub>) or CO<sub>2</sub> adsorbed onto particulate matter such as soot (Appel et al., 1989; Clarke and Karani, 1992).

#### **3.3.6.2 Elemental Carbon**

Elemental carbon is a strong absorber of visible radiation and is the major species responsible for light absorption by atmospheric particles (Novakov, 1984; Goldberg, 1985; Finlayson-Pitts and Pitts, 1986; Japar et al., 1986; Sloane et al., 1991; Hamilton and Mansfield, 1991). Elemental carbon found in atmospheric particles is a complex three dimensional array of carbon with small amounts of other elements such as oxygen, nitrogen, and hydrogen incorporated in its graphitic hexagonal structure (Chang et al., 1982).

1 Wood-burning fireplaces and diesels are major sources of EC (Mulhbaier and Williams,  
2 1982; Dasch and Cadle, 1989; Brown et al., 1989; Dod et al., 1989; Hansen and Rosen,  
3 1990; Burtcher, 1992). In areas where wood burning is significant, more particulate  
4 graphitic carbon is expected in winter than in summer. Tracer techniques have been  
5 developed for the calculation of the source contribution to the EC concentrations, including  
6 use of K as a woodsmoke tracer (Currie et al., 1994) and use of the carbon isotopic tracers  
7  $^{14}\text{C}$  and  $^{12}\text{C}$  (Lewis et al., 1988; Klouda et al., 1988; Currie et al., 1989). Around 47% of  
8 the EC in Detroit, 93% in Los Angeles and 30 to 60% in a rural area in Pennsylvania has  
9 been attributed to motor vehicle sources (Wolff and Korsog, 1985; Pratsinis et al., 1988;  
10 Keeler et al., 1990). The corresponding contribution of diesel emissions to EC  
11 concentrations in Western Europe is estimated to be 70 to 90% (Hamilton and Mansfield,  
12 1991). Elemental carbon was also a major constituent of the Kuwait oil fires, with  
13 concentrations as high as  $178 \text{ mg m}^{-3}$  inside the plume (Cofer et al., 1992; Daum et al.,  
14 1993; and references therein). Global emissions of EC were estimated by Penner et al.  
15 (1993) to be 12.6 to 24 Tg C yr $^{-1}$ , while the EC emission for the US was 0.4 to 1.1 Tg yr $^{-1}$   
16 and for the rest of North America 0.2 Tg yr $^{-1}$ .

17 Elemental carbon also scatters light (Appel et al., 1985) although its light scattering  
18 efficiency is smaller than the efficiencies of the other aerosol principal components (Sloane  
19 et al., 1991). Because EC both absorbs and scatters light, its contribution to total light  
20 extinction exceeds its contribution to fine particle mass. For example, in Los Angeles, EC  
21 was found to represent 8.5 to 10% of the fine particulate mass, but to account for 14 to 21%  
22 of the total light extinction (Pratsinis et al., 1984). A significant fraction of the dark colored  
23 fine EC particles is able to penetrate the indoor atmosphere of buildings and may constitute a  
24 soiling hazard of objects like works of art (Ligocki et al., 1993).

25 The concentration of EC varies significantly depending on location and season.  
26 Elemental carbon concentrations in rural and remote areas usually vary from 0.2 to 2.0 mg  
27  $\text{m}^{-3}$  (Wolff, 1981; Clarke et al., 1984; Goldberg, 1985; Cadle and Dash, 1988; Japar et al.,  
28 1986; Shah et al., 1986; Pinnick et al., 1993) and from 1.5 to 20 mg  $\text{m}^{-3}$  in urban areas  
29 (Wolff, 1981; Delumyea and Kalivretenos, 1987; Pratsinis et al., 1984, 1986; Grosjean,  
30 1984; Heitzenberg and Winkler, 1984; Goldberg, 1985; Shah et al., 1986; Rau, 1989). The  
31 concentration of EC over the remote oceans is approximately 5 to 20 ng  $\text{m}^{-3}$  (Clarke, 1989).

1 Average EC concentration values are around 1.3 and 3.8 mg m<sup>-3</sup> for U.S. rural and urban  
2 sites respectively (Shah et al., 1986). Average PM<sub>10</sub> EC values exceeding 10 mg m<sup>-3</sup> are  
3 common for some urban locations (Chow et al., 1994). The ratio of EC to total carbon has  
4 been observed to vary from 0.15 to 0.20 in rural areas, to 0.2 to 0.6 in urban areas (Wolff et  
5 al., 1982; Gray et al., 1984; Grosjean, 1984; Pratsinis et al., 1984; Chow et al., 1993). The  
6 annual mean of this ratio was approximately 0.4 for the Los Angeles basin in 1982 (Gray et  
7 al., 1986), while this ratio in the same area decreases to 0.2 during summer midday periods  
8 (Larson et al., 1989; Wolff et al., 1991). Aging of an air mass results in lowering of the EC  
9 fraction of the aerosol due to its mixing with non-combustion particles or by condensation of  
10 material from the gas phase (Burtscher et al., 1993).

11 The distribution of EC emitted by automobiles is unimodal with over 85% of the mass  
12 in particles smaller than 0.12 mm aerodynamic diameter (Venkataraman et al. 1994). The  
13 ambient distribution of EC is bimodal with peaks in the 0.05 to 0.12 mm (mode I) and 0.5 to  
14 1.0 mm (mode II) size ranges (Nunes and Pio, 1993; Venkataraman and Friedlander, 1994).  
15 The creation of mode II is mainly the result of accumulation of secondary aerosol products  
16 on primary aerosol particles.

17 The degree of mixing of EC particles with the rest of the aerosol components remains a  
18 controversial issue. Particles emitted from spark-ignition engines have been found to consist  
19 of a core of EC covered with a layer of PAHs and an outermost shell of volatile compounds  
20 (Steiner et al., 1992). Ambient carbonaceous aerosol in urban areas has been found to  
21 consist of aggregated spherules, with a range of carbon structures from amorphous (OC) to  
22 graphitic (EC) within aggregates (Katrinak et al., 1992). These aggregates are often  
23 (especially during summer months) coated with sulfates and nitrates (Katrinak et al., 1992,  
24 1993). However, often sulfate and EC are externally mixed (Covert and Heintzenberg,  
25 1984). Coating of EC with organic compounds may alter its hygroscopicity and its lifetime  
26 in the atmosphere (Andrews and Larson, 1993). Noone et al. (1992) reported that the  
27 interstitial aerosol inside urban fogs is enriched in EC, something that would tend to increase  
28 its lifetime in the atmosphere with respect to other species like sulfate or OC (Nunes and  
29 Pio, 1993). However, the degree of incorporation of EC in droplets is highly variable (0 to  
30 80%) and its behavior appears to vary from hygroscopic to hydrophobic (Hansen and

Novakov, 1988). Our lack of understanding of these processes makes a quantitative estimate of the atmospheric lifetime of EC problematic.

The participation of EC and soot in atmospheric chemical reactions with SO<sub>2</sub>, O<sub>3</sub> and NO<sub>2</sub> has been the subject of a series of studies (Baldwin, 1982; Dlugi and Günsten, 1983; Akhter et al., 1985; 1985; Jassim et al., 1989; Sergides et al., 1987; Gundel et al., 1989; Chughtai et al., 1991). The strong dependence of the often conflicting results of these studies on the nature of the samples is inhibiting the extrapolation of their conclusions to the atmosphere. Chughtai et al. (1991) reported that oxidation and hydrolysis of accessible reactive sites on the soot surface result in particle solubilization and accelerated particle removal from the atmosphere. DeSantis and Allegrini (1992) suggested that NO<sub>2</sub> reactions in the presence of SO<sub>2</sub> on carbon-containing particles could be a source of HNO<sub>2</sub> in the urban environment. The reaction of soot with ozone is faster than its reaction with NO<sub>2</sub> that is in turn faster than the reaction with SO<sub>2</sub> (Smith et al., 1989).

### 3.3.6.3 Organic Carbon

The organic component of ambient aerosol both in polluted and remote areas is a complex mixture of hundreds of organic compounds (Cass et al., 1982; Seinfeld, 1986; Rogge, 1993; Hahn, 1980; Simoneit and Mazurek, 1982; Zafiriou et al., 1985; Graedel, 1986). Compounds identified in the ambient aerosol include n-alkanes, n-alkanoic acids, n-alkanals, aliphatic dicarboxylic acids, diterpenoid acids and retene, aromatic polycarboxylic acids, polycyclic aromatic hydrocarbons, polycyclic aromatic ketones and quinones, steroids, N-containing compounds, regular steranes, pentacyclic triterpanes, iso- and anteiso-alkanes, etc. (Graedel, 1986; Mazurek et al., 1989; Hildemann et al., 1993; Rogge, 1993). OC does not strongly absorb light, but its light scattering efficiency in urban hazes is similar to that of nitrate and sulfate.

Aerosol OC measurements are often subject to sampling artifacts due to adsorption of organic vapors on the filters used or evaporation of the collected mass. These sampling problems are discussed in Section 3.3.3.1. Wolff et al. (1991) found that this sampling error represented roughly 20% of the measured OC under urban polluted conditions. McMurry and Zhang (1989) observed in ambient and smog chamber measurements that a consistently large fraction of the OC (40 to 70%) was collected on the quartz filters following their

1 impactors. The strong possibility of sampling artifacts in the laboratory and field  
2 measurements presented below, increases the uncertainty of our current knowledge about  
3 aerosol OC. Most of the investigators report the OC concentration as concentration of  
4 carbon. These values neglect the contribution to the aerosol mass of the other elements  
5 (namely oxygen, hydrogen and nitrogen) of the organic aerosol compounds. Wolff et al.  
6 (1991) suggested that the measured OC values should be multiplied by a factor of 1.5 for the  
7 calculation of the total organic mass associated with the OC.

8 The concentration of OC is around  $3.5 \text{ mg C m}^{-3}$  in rural locations (Stevens et al.,  
9 1984) and 5 to  $20 \text{ mg C m}^{-3}$  in polluted atmospheres (Grosjean, 1984a; Wolff et al., 1991).  
10 Wolff et al. (1991) and Chow et al. (1994) summarizing measurements during the summer  
11 and fall of 1987 in the Los Angeles basin, reported that OC represented on average 10 to  
12 18% of the  $\text{PM}_{10}$  mass and 11 to 24% of the  $\text{PM}_{2.5}$  mass during the summer and 15 to 25%  
13 of the  $\text{PM}_{10}$  and 16 to 25% of the  $\text{PM}_{2.5}$  during the fall. Wolff et al. (1991) suggested that  
14 these values should be reduced by roughly 20% to correct for the sampling bias and then  
15 multiplied by 1.5 to account for the non-carbon mass of the organic aerosol compounds (an  
16 overall increase by roughly a factor of 1.3). In rural areas of the western U.S. particulate  
17 OC concentrations are comparable to sulfate (White and Macias, 1989). In other areas OC  
18 contributes roughly 10 to 15% of the  $\text{PM}_{2.5}$  and  $\text{PM}_{10}$  mass (Stevens et al., 1984). Organic  
19 compounds accumulate mainly in the submicrometer aerosol size range (Finlayson-Pitts and  
20 Pitts, 1986; McMurry and Zhang, 1989) and their mass distribution is typically bimodal with  
21 the first peak around diameter of  $0.2 \text{ }\mu\text{m}$  and the second around  $1 \text{ }\mu\text{m}$  (Pickle et al., 1990;  
22 Mylonas et al., 1991).

23 The contribution of the primary and secondary components of aerosol OC have been  
24 difficult to quantify. The lack of a direct chemical analysis method for the identification of  
25 either of these OC components has led researchers to the employment of several indirect  
26 methods. These methods include the use of tracer compounds for either the primary or the  
27 secondary OC (Larson et al., 1989; Turpin and Huntzicker, 1991; Turpin et al., 1991), the  
28 use of models describing the emission and dispersion of primary OC (Gray, 1986; Gray et  
29 al., 1986; Larson et al., 1989; Hildemann, 1990) and the use of models describing the  
30 formation of secondary OC (Pilinis and Seinfeld, 1988; Pandis et al., 1992; Pandis et al.,  
31 1993). The above studies concluded that the secondary OC contribution is maximized in the

early afternoon of summer days, varying from 30 to 60% of the total OC depending on location. The yearly averaged contribution of secondary OC is smaller, accounting for 10 to 40% of the OC.

The interactions of the OC compounds with each other and the inorganic aerosol species are poorly understood. The compounds have the potential to form organic films around the inorganic and EC core of the aerosol (Gill et al., 1983). Goschnich et al. (1990) provided evidence for such formation by reporting that carbon compounds and organic hydrogen were enriched within the particles' outer layer, while inorganics like  $\text{NH}_4\text{NO}_3$  were enriched inside the particles. The presence of such films can inhibit the transport of water and other inorganic components between the gas and aerosol phases (Otani and Wang, 1984; Rubel and Gentry, 1984).

#### 3.3.6.4 Primary Organic Carbon

Primary carbonaceous particles (OC) are produced by combustion (pyrogenic), chemical (commercial products), geological (fossil fuels), and natural (biogenic) sources. The complexity of the mixture molecular composition of OC is such that tracer compounds are still necessary to decouple the contributions of the various sources. Rogge et al. (1991) suggested that fine aerosol cholesterol could be used as a tracer for meat smoke. An alternative proposed meat smoke tracer set consists of myristic acid (n-tetradecanoic acid), palmitic acid (n-hexadecanoic acid), stearic acid (n-octadecanoic acid), oleic acid (cis-9-octadecenoic acid), nonanal and 2-decanone (Rogge et al., 1991). Benzothiazole has been used as a tracer for tire wear contributions to ambient aerosol (Kim et al., 1990; Rogge et al., 1993b). Steranes and pentacyclic triterpanes (hopanes) can be used as tracer compounds for the vehicular sources (Rogge et al., 1993a). The odd carbon number n-alkanes ranging from  $\text{C}_{27}$  to  $\text{C}_{33}$  can serve as a molecular tracer assemblage for biogenic primary OC (green, dead, and degraded plant wax material directly emitted or resuspended from soil and road dust) (Mazurek and Simoneit, 1984; Simoneit, 1989; Rogge et al., 1993c). The iso- and anteiso- alkanes can be used to trace the cigarette smoke contribution to the outdoor atmosphere (Rogge et al., 1994),

Primary biogenic organic matter consists predominantly of lipids, humic and fulvic acids, and often represents a major fraction of the carbonaceous aerosol mass (Duce et al.,

1983; Gagosian et al., 1987; Mazurek et al., 1989, 1991; Simoneit, 1984, 1986, 1989).  
Mamane et al. (1990) reported that most coarse OC in the Great Lakes region is of biologic  
origin while most fine OC is anthropogenic.

### *Secondary Organic Carbon*

Secondary organic aerosol material is formed in the atmosphere by the condensation on  
already existing particles of low vapor pressure products of the oxidation of organic gases.  
As the hydrocarbons are oxidized in the gas-phase by species such as the hydroxyl radical  
(OH), ozone (O<sub>3</sub>) and the nitrate radical (NO<sub>3</sub>), their oxidation products accumulate in the  
gas-phase. If the concentration of such a product is smaller than its saturation concentration,  
the species remains mainly in the gas-phase. Small amounts of the species can be adsorbed  
on aerosol surfaces or dissolved in the aerosol phase at this stage (Yamasaki et al., 1982;  
Pankow, 1987; Ligocki and Pankow, 1989; Pankow and Bidleman, 1991; Pankow, 1994a, b;  
Pandis et al., 1992). If the gas-phase concentration of a species exceeds its saturation  
concentration, the species condenses on the available aerosol surface so that at equilibrium its  
gas-phase concentration equals its saturation concentration. If this gas-phase concentration is  
reduced to less than the saturation value as a result of dilution, deposition or chemical  
reaction, the aerosol species evaporates in an effort to maintain thermodynamic equilibrium  
(Pilinis and Seinfeld, 1988). Many volatile organic compounds (VOC) do not form aerosol  
under atmospheric conditions due to the high vapor pressure of their products (Grosjean and  
Seinfeld, 1989). These VOC include all alkanes with up to six carbon atoms (from methane  
to hexane isomers), all alkenes with up to six carbon atoms (from ethylene to hexene  
isomers), benzene and many low-molecular-weight carbonyls, chlorinated compounds and  
oxygenated solvents.

Organic aerosols formed by gas-phase photochemical reactions of hydrocarbons, ozone  
and nitrogen oxides have been identified in both urban and rural atmospheres (Grosjean,  
1977). Most of these species are di- or poly-functionally substituted alkane derivatives.  
These compounds include aliphatic organic nitrates (Grosjean and Friedlander, 1975),  
dicarboxylic acids (adipic and glutaric acids) (O'Brien et al., 1975), carboxylic acids derived  
from aromatic hydrocarbons (benzoic and phenylacetic acids), polysubstituted phenols and  
nitroaromatics from aromatic hydrocarbons (Kawamura et al., 1985; Satsumakayashi et al.,

1 1989, 1990). Some species that have been identified in ambient aerosol and are believed to  
2 be secondary in nature are depicted in Table 3-5. Despite the above studies, the available  
3 information about the molecular composition of atmospheric secondary OC and about the  
4 composition of the OC produced during the oxidation of specific hydrocarbons remains  
5 incomplete. The reaction mechanisms leading to the observed products are to a great extent  
6 speculative at present (Finlayson-Pitts and Pitts, 1986). Natural hydrocarbons like the  
7 monoterpenes ( $C_{10}H_{16}$ ) and isoprene ( $C_5H_8$ ) are emitted by various types of trees and plants.  
8 In the United States the biogenic hydrocarbon sources are estimated to produce 30 to 60 Mt  
9 of carbon per year (isoprene and monoterpenes combined) whereas anthropogenic  
10 hydrocarbon sources have been estimated to account for 27 Mt of carbon per year (Lamb et  
11 al., 1987; Zimmerman, 1979; Altshuller, 1983). Laboratory investigations have indicated  
12 that biogenic hydrocarbons are very reactive under typical atmospheric conditions (Arnts and  
13 Gay, 1979). The aerosol forming potential of biogenic hydrocarbons has been investigated in  
14 a series of smog chamber studies (Kamens et al., 1981, 1982; Hatakeyama et al., 1989;  
15 1991; Pandis et al., 1991; Zhang et al., 1992) and it has been suggested that isoprene  
16 photooxidation does not contribute to the production of secondary aerosol under ambient  
17 conditions. On the contrary, pinenes and other monoterpenes form secondary aerosol in their  
18 reactions with  $O_3$  and OH and have the potential to contribute significantly to aerosol in  
19 areas with high vegetation coverage. Monoterpenes were estimated to contribute around  
20 15% of the secondary organic aerosol (SOA) in urban areas with low vegetation like Los  
21 Angeles, while they are expected to dominate the SOA in areas with high vegetation  
22 coverage like Atlanta (Pandis et al., 1991, 1992). The chemical composition of the majority  
23 of the aerosol products of the monoterpene photooxidation remains unknown or is speculative  
24 (Paulson et al., 1990; Palen et al., 1992). The few products that have been identified  
25 include nopinone, pinanediol, pinonic acid and 5-(1-hydroxy-1-methylethyl)-2-methyl-2-  
26 cyclohexen-1-one. Several investigators have studied the SOA formation from selected  
27 anthropogenic hydrocarbons. The literature data up to 1976 have been reviewed by Grosjean  
28 (1977). Other studies focused on toluene and other aromatic hydrocarbons (Leone et al.,  
29 1985; Stern et al., 1987; Gery et al., 1985, 1987; Izumi and Fukuyama, 1990), styrenes  
30 (Izumi and Fukuyama, 1990), cyclic olefins (Hatakeyma et al., 1985, 1987; Izumi et al.,  
31 1988), cresols and nitrocresols (Grosjean, 1985) and alkenes with more than six carbon



**TABLE 3-5. SOME SECONDARY ORGANIC COMPOUNDS IDENTIFIED IN  
AMBIENT PARTICLES IN URBAN AIR**

Compound	n
$\text{HOOC}(\text{CH}_2)_n\text{COOH}$	1-8
$\text{HOOC}(\text{CH}_2)_n\text{CHO}$	3-5
$\text{HOOC}(\text{CH}_2)_n\text{CH}_2\text{OH}$	3-5
$\text{HOOC}(\text{CH}_2)_n\text{CH}_2\text{ONO}$ or $\text{CHO}(\text{CH}_2)_n\text{CH}_2\text{ONO}_2$	3-5
$\text{CHO}(\text{CH}_2)_n\text{CHO}$	3-5
$\text{CHO}(\text{CH}_2)_n\text{CHO}$	3-5
$\text{HOOC}(\text{CH}_2)_n\text{COONO}$ or $\text{HOOC}(\text{CH}_2)_n\text{COONO}_2$	3-5
$\text{CHO}(\text{CH}_2)_n\text{COONO}$	3-4
$\text{HOOC}(\text{CH}_2)_n\text{COONO}$	3-4
$\text{HOOC}(\text{CH}_2)_n\text{COONO}_2$	4-5
$\text{HOOC}(\text{CH}_2)_n\text{CH}_2\text{ONO}_2$	3-4
$(\text{C}_6\text{H}_5)-(\text{CH}_2)_n\text{COOH}$	1-3
$\text{HOOC}-(\text{C}_6\text{H}_5)-(\text{CH}_2)_n$	1-3

atoms (Grosjean, 1984b; McMurry and Grosjean, 1985; Wang et al., 1992). Measured and estimated aerosol yields from a variety of SOA precursors have been tabulated by Grosjean and Seinfeld (1989) and Pandis et al. (1992).

The calculated contribution of the main individual secondary organic aerosol precursors to the secondary organic aerosol concentration in Los Angeles on August 28, 1987 is presented in Table 3-6 (Grosjean and Seinfeld, 1989; Pandis et al., 1992). Toluene, the nonmethane hydrocarbon with the highest emission rate in the Los Angeles area ( $165 \text{ t d}^{-1}$ ) was predicted to contribute 28% of the secondary organic aerosols. Differences were attributed to sampling artifacts and calibration uncertainties during the interpretation of the ambient data.

Grosjean (1992) calculated the daily production rates of various chemical functionalities of the secondary organic aerosol formed *in situ* during a smog episode in Los Angeles using the precursor hydrocarbon emission inventory and the results of smog chamber studies. His

**TABLE 3-6. PREDICTED PER CENT CONTRIBUTION TO SECONDARY ORGANIC AEROSOL CONCENTRATIONS AT LOS ANGELES**

Species	Contribution	
	Grosjean and Seinfeld (1989)	Pandis et al. (1992)
Aromatics	58	65
Biogenic Hydrocarbons	10	16
Alkanes	21	15
Olefins	11	4

estimates are presented in Table 3-7. These predictions were compared with the available measurements of ambient OC functional group relative abundances (Grosjean, 1992).

**TABLE 3-7. AMOUNT OF SECONDARY AEROSOL PRODUCED IN A TYPICAL LOS ANGELES SMOG EPISODE ACCORDING TO FUNCTIONAL GROUPS (GROSJEAN, 1992)**

Precursor	Aerosol produced (kg day <sup>-1</sup> )			
	Carbonyls	Aliphatic Acids	Nitrophenols	Aliphatic Nitrate
Alkenes	-	608	-	-
Cyclic olefins	62	131	-	9
Terpenes	295	623	-	41
Alkanes	243	-	-	121
Cycloalkanes	72	-	-	72
Aromatics	-	-	3118	-
<b>TOTAL</b>	<b>672</b>	<b>1362</b>	<b>3118</b>	<b>243</b>

Pickle et al. (1990) and Mylonas et al. (1991) argued that the SOA mass size distribution in urban areas like Los Angeles is typically bimodal with maxima in the 0.1 and 1.0  $\mu\text{m}$  size ranges. Our understanding of the mechanisms of creation of these two modes

remains tentative (Pandis et al., 1993). The effect of relative humidity in the SOA partitioning between gas and aerosol phases is generally not understood. Thibodeaux et al. (1991) developed a theoretical model based on classical adsorption theory and predicted that as air relative humidity increases (remaining less than 60%) the equilibrium secondary organic carbon content on the aerosol particles decreases due to competition for adsorption sites with water molecules. This theoretical result seems to be supported by the little available experimental information, but the necessary experimental data for the incorporation of these relative humidity effects on SOA partitioning in aerosol model do not exist. Knowledge of the saturation concentrations of the organic condensable species remains incomplete. These concentrations are expected to vary significantly with temperature. The few available relevant measurements include the saturation vapor concentrations of monocarboxylic and dicarboxylic acids (Tao and McMurry, 1989) and the  $\beta$ -pinene aerosol products (Pandis et al., 1991). The saturation vapor concentrations of condensable products from the oxidation of some aromatic hydrocarbons (toluene, m-xylene, and 1,3,5-trimethylbenzene) were estimated to lie in the range 3 to 30 ppt (Seinfeld et al., 1987). McMurry and Grosjean (1985) estimated saturation vapor concentrations for condensable products from the oxidation of 1-heptene (0.14 to 1.28 ppb), o-cresol (0.06 to 1.6 ppb) and nitrocresol (1.7 to 2.2 ppb).

### ***Polycyclic Aromatic Hydrocarbons (PAH)***

Polycyclic aromatic hydrocarbons are formed during the incomplete combustion of organic matter, for example, coal, oil, wood and gasoline fuel (National Academy of Sciences, 1983; Bjorseth, 1983). Stationary sources (residential heating, industrial processes, open burning, power generation) are estimated to account for roughly 80% of the annual total PAH emissions in the US with the remainder produced by mobile sources (Peters et al., 1981; Ramdahl et al., 1983). Mobile sources are however the major contributors in urban areas (National Academy of Sciences, 1983; Freeman and Cattell, 1990). More than one hundred PAH compounds have been identified in urban air. The PAH observed in the atmosphere range from bicyclic species such as naphthalene, present mainly in the gas phase, to PAH containing seven or more fused rings, such as coronene, which are present exclusively in the aerosol phase (Finlayson-Pitts and Pitts, 1986). Intermediate PAH such as

pyrene and athracene are distributed in both the gas and aerosol phases (see also Section 3.3.3.1).

Measurements of the size distribution of PAH indicate that while they are found exclusively in the 0.01 to 0.5  $\mu\text{m}$  diameter mode of fresh combustion emissions (Venkataraman et al., 1994) they exhibit a bi-modal distribution in ambient urban aerosol, with an additional mode in the 0.5 to 1.0  $\mu\text{m}$  diameter range (Venkataraman and Friedlander, 1994). The growth of nuclei-mode particles by condensation of secondary aerosol species like nitrate, sulfate and secondary organic aerosol has been proposed as an explanation of this distribution.

Polycyclic aromatic hydrocarbons adsorbed on the surfaces of combustion generated particles are released into an atmosphere containing gaseous co-pollutants including  $\text{O}_3$ ,  $\text{NO}_2$ ,  $\text{SO}_2$ ,  $\text{HNO}_3$ , PAN, radicals and are exposed to sunlight. Under these conditions PAH undergo chemical transformations that might lead to significant degradation and formation of products more polar than the parent PAH (National Academy of Sciences, 1983). Several studies have focused on the reaction rates and products of reactions of PAH adsorbed on specific substrates and exposed in the dark or in the light to other pollutants. However, the extrapolation of these laboratory results to real atmospheric conditions remains difficult.

Benzo(a)pyrene (BaP) and other PAH on a variety of aerosol substrates react with gaseous  $\text{NO}_2$  and  $\text{HNO}_3$  to form mono- and dinitro-PAH (Finlayson-Pitts and Pitts, 1986). The presence of  $\text{HNO}_3$  along with  $\text{NO}_2$  is necessary for PAH nitration. The reaction rate depends strongly on the nature of the aerosol substrate (Ramdahl et al., 1984), but the qualitative composition of the products does not. The aerosol water is also a favorable medium for heterogeneous PAH nitration reactions (Nielsen et al., 1983). Nielsen (1984) proposed a reactivity classification of PAH based on chemical and spectroscopic parameters (Table 3-8). The PAH nitration rate under typical urban conditions remains poorly understood. Bjorseth et al. (1979) observed a lack of significant PAH reactions during their transport from central to northern Europe and suggested that these reactions are slow in most environments. However, this may not be the case in heavily polluted areas with high  $\text{NO}_2$  and  $\text{HNO}_3$  concentrations and acidic particles (Finlayson-Pitts and Pitts, 1986). Reactions of fluoranthene and pyrene with  $\text{NO}_2$  in the gas phase and condensation the 2-nitro-PAH

**TABLE 3-8. REACTIVITY SCALE FOR THE ELECTROPHILIC REACTIONS OF PAH (REACTIVITY DECREASES IN THE ORDER I TO VI)**

I	Benzo(a)tetracene, dibenzo(a,h)pyrene, pentacene, tetracene
II	Anthanthrene, anthracene, benzo(a)pyrene, cyclopenta(cd)pyrene, dibenzo(a,l)pyrene, dibenzo(a,i)pyrene, dibenzo(a,c)tetracene, perylene
III	Benz(a)anthracene, benzo(g)chrysene, benzo(ghi)perylene, dibenzo(a,e)pyrene, picene, pyrene
IV	Benzo(c)chrysene, benzo(c)phenanthrene, benzo(e)pyrene, chrysene, coronene, dibenzanthracene, dibenzo(e,l)pyrene
V	Acenaphthylene, benzo(a)fluoranthene, fluranthene, indeno(1,2,3-cd)fluoranthene, indeno(1,2,3-cd)pyrene, naphthalene, phenanthrene, triphenylene
VI	Biphenyl

derivatives on the aerosol surface have been proposed as an alternative reaction pathway for the production of the observed aerosol nitro-PAH (Pitts et al., 1985a).

Nitrogen oxide ( $\text{N}_2\text{O}_5$ ) has been proposed as an additional nitrating agent for certain PAH during nighttime (Kamens et al., 1990). Pitts et al. (1985b) exposed six PAH to  $\text{N}_2\text{O}_5$  and proposed the following reactivity order: pyrene > fluoranthene > BaP > benz(a)anthracene > perylene > chrysene. Nitro-PAH photodecompose into quinones and possibly phenolic derivatives. For example 6- $\text{NO}_2$ -BaP on silica gel photolyses to the 1,6-, 3,6-, and 6,12- isomers of BaP quinones and a host of other oxy-PAH (Finlayson-Pitts and Pitts, 1986). These reactions are expected to depend strongly on the chemical composition and structure of the aerosol substrate and are not well understood for ambient particles.

Aerosol PAH react with  $\text{O}_3$  to produce oxidized PAH. Pyrene, BaP and anthracenes react rapidly and the benzo(a)fluoranthenes slowly (Finlayson-Pitts and Pitts, 1986; Alebic-Juretic et al., 1990). Reaction rates of 15 to 30%  $\text{hr}^{-1}$  were observed for the most reactive PAH adsorbed on filters during exposure to 200 ppb of  $\text{O}_3$  (Pitts et al., 1986). However, other researchers (Atkinson and Aschmann, 1986; Coutant et al., 1988; De Raat et al., 1990) have suggested that the PAH- $\text{O}_3$  reaction is of negligible importance for typical atmospheric conditions. Relatively little is known about the full ranges of products and the mechanisms of their formation. Polycyclic aromatic hydrocarbons exposed to sunlight have been found to

photodegrade in a series of laboratory studies (Valerio and Lazzarotto, 1985; Behymer and Hites, 1988). The photodegradation rates depend strongly on the chemical composition and the pH of the aerosol substrate (Dlugi and Güsten, 1983; Valerio and Lazzarotto, 1985; Behymer and Hites, 1988). Polycyclic aromatic hydrocarbons appear to be more stable when adsorbed on ambient aerosol than when present in pure form or in solution or on artificial surfaces (Baek et al., 1991). The occurrence of PAH-SO<sub>x</sub> reactions remains uncertain (Baek et al., 1991).

### 3.3.7 Metals and Other Trace Elements

The major components of fine particles are sulfate, nitrate, organic and elemental carbon, ammonium ions and a variety of trace elements (Godish, 1985; Pitts and Pitts, 1986). Trace elements that are found predominantly in the fine particle size distribution are Na, Cs, Cl, Br, Cu, Zn, As, Ag, Cd, In, Sn, Sb, W, and Pb, and greater than 75% of their mass is associated with particles of diameter less than 2  $\mu$ m. Metals which are found in both fine and coarse modes are V, Cr, Mn, Fe, Co, and Se, while elements found primarily within large particle distributions are Ca, Al, Ti, Sc, and La (Klee, 1984). The concentrations and the relative proportions of these species in the various particle size ranges depend on a number of factors such as the nature of the emissions, the photochemical activity and the meteorology (Pitts and Pitts, 1986). The concentration ranges of various elements associated with particulate matter in the atmosphere are shown in Table 3-6. For most elements the range in concentrations is greater than three orders of magnitude. This reflects the different sources and the different pollution control strategies that exist in each area. This information was compiled by Schroeder et al. (1987), and includes a large number of studies from the United States, and abroad, which indicates the need to complete site specific evaluations for high end concentrations (references can be found in the original paper by Schroeder et al., 1987).

In general, remote areas recorded measurable concentrations of some elements associated with crustal origin, as well as some elements indicative of anthropogenic sources. This supports hypotheses which suggest that long range transport occurs in these remote areas (Schroeder et al., 1987). The urban data (Table 3-9) reflect elemental concentrations in different parts of the world. Elements such as lead, iron, and copper are measured in

**TABLE 3-9 CONCENTRATION RANGES OF VARIOUS ELEMENTS ASSOCIATED WITH PARTICULATE MATTER IN THE ATMOSPHERE (ng/m<sub>3</sub>)**

Elements	Remote	Rural	Urban (USA)
As	0.007 - 1.9	1.0 - 28	2 - 2,320
Cd	0.003 - 1.1	0.4 - 1,000	0.2 - 7,000
Ni	0.01 - 60.0	0.6 - 78	1 - 328
Pb	0.007 - 64	2 - 1,700	30 - 96,270
V	0.001 - 14	2.7 - 97	0.4 - 1,460
Zn	0.03 - 460	11 - 403	15 - 8,328
Co	0.001 - 0.9	0.08 - 10.1	0.2 - 83
Cr	0.005 - 11.2	1.1 - 44	2.2 - 124
Cu	0.029 - 12	3 - 280	3 - 5,140
Fe	0.62 - 4,160	55 - 14,530	130 - 13,800
Hg	0.005 - 1.3	0.05 - 160	0.58 - 458
Mn	0.01 - 16.7	3.7 - 99	4 - 488
Se	0.0056 - 0.19	0.01 - 3.0	0.2 - 30
Sb	0.0008 - 1.19	0.6 - 7.0	0.5 - 171

Source: Schroeder et al., 1987

greatest abundance in particulate matter from all locations, while elements such as cobalt, mercury and antimony are found in the smallest quantities (Schroeder et al., 1987).

Potential sources of trace metals found in fine airborne particles are primarily anthropogenic and include combustion of coal and oil, wood burning, waste incineration, and metal smelting operations. Biomass burning which includes residential wood combustion and forest fires, is another source for the release of trace elements in the atmosphere. In a profile of biomass burning, zinc was the characteristic trace element present in the fine particles in concentration ( $0.0866 \pm 0.0355$  %) of primary mass emitted. Other trace elements present were Cl ( $1.9083 \pm 0.6396$  %), K ( $3.9926 \pm 1.2397$  %) and S ( $0.5211 \pm 0.1761$  %) (Chow et al., 1992).

The chemical composition of particulate matter analyzed in New Jersey as part of the Airborne Toxic Element and Organic Substances project (ATEOS), identified the trace

elements Pb, Fe, Zn, V and As (Daisey, 1987; Morandi et al., 1991). The main source for atmospheric lead concentration is the combustion of leaded gasoline in motor vehicles. However with increased use of unleaded gasoline, levels of atmospheric lead have been reduced, and other sources of lead tend now to be more significant components of the residual lead. Morandi (1985) has reported evidence of contributions to airborne lead from resuspended soil, oil burning and small scale smelting, which taken together accounted for more than half of the airborne lead at a New Jersey site. Vanadium levels were derived from oil burning for space heating and power production, while Zn is attributed to a zinc smelter in the area (Daisey, 1987).

Road dust aerosols are analyzed for trace elements in a variety of studies (Barnard et al., 1987; Barnard et al, 1988; Warren et al., 1987). Recent source apportionment studies in California's South Coast Air Basin, provide additional information on trace element concentrations in roadside dusts as well as in motor vehicle exhaust for particle sizes  $< 2.5 \mu\text{m}$  (Watson et al., 1994). In addition to elemental carbon, Al, Si, K, Ca, Ti and Fe were present in paved road dust in abundances which exceeded 1%. Elevated concentrations of Pb and Br were detected, which illustrated the deposition from the tailpipe exhaust from vehicles that burned leaded fuels (Watson et al. 1994; Chow et al., 1992). Significant amounts of  $\text{SO}_4^{=}$ , Br,  $\text{Cl}^-$ , and Pb were detected in the motor vehicle exhaust profile, though Pb levels were much lower than those reported in earlier tests (Watson et al., 1994; Pierson and Brachaczek, 1983).

Ambient measurements of the mass and chemical composition of  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$ , and associated source profiles have been taken through the years. Data base summaries identify locations, sampling times and chemical species of data available since 1988, complementing previous existing databases (Watson and Chow, 1992; Liroy et al., 1980). Size specific measurements show that over 90% of the mass from geological material is in the coarse particle size fraction, while the combustion related source categories contained ~90% of their mass concentrations in the  $\text{PM}_{2.5}$  size fraction (Chow et al., 1992). In a municipal incinerator profile, elements in the fine particle fraction include Cu, Zn, As, Cd, Sb, Pb and Ba, while trace elements in the coarse particle fraction include Ca, Cr, Mn, and Ni (Olmez et al., 1988). In an oil-fired power plant, trace elements such as V, Ni, Co, Ba and Cu are present in both fine and coarse particles (Olmez et al., 1988).



Although a knowledge of the elemental and ionic composition of ambient particles is necessary in order to understand their sources and chemistry, the chemical forms in which important species exist are not known. For example, sulfates, nitrates and ammonium ions, which are the main constituents of fine particles, may exist in forms other than simple ammonium salts (Pitts and Pitts, 1986). Table 3-10 lists some compounds identified in aerosols by a roadway at Argonne National Laboratory, and Table 3-11 lists compounds observed in aerosols in a forested area, at State College, Pennsylvania (Tani et al., 1983). However, there are uncertainties associated with the compounds shown in Tables 3-10 and 3-11. Tani et al. pointed out that both physical and chemical changes may occur during or following impaction of aerosol particles on a collector, which would lead to the formation of compounds not initially present in the ambient aerosols (Tani et al., 1983).

**TABLE 3-10. COMPOUNDS OBSERVED IN AEROSOLS BY A ROADWAY AT ARGONNE NATIONAL LABORATORY**

SiO <sub>2</sub>	K <sub>2</sub> Sn(SO <sub>4</sub> ) <sub>2</sub>
CaCO <sub>3</sub>	(NH <sub>4</sub> ) <sub>2</sub> Co(SO <sub>4</sub> ) <sub>2</sub> · 6H <sub>2</sub> O
CaMg(CO <sub>3</sub> ) <sub>2</sub>	(NH <sub>4</sub> ) <sub>3</sub> H(SO <sub>4</sub> ) <sub>2</sub> (letovicite)
CaSO <sub>4</sub> ·2H <sub>2</sub> O	3(NH <sub>4</sub> NO <sub>3</sub> )·(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>
(NH <sub>4</sub> ) <sub>2</sub> Pb(SO <sub>4</sub> ) <sub>2</sub>	2(NH <sub>4</sub> NO <sub>3</sub> )·(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>
(NH <sub>4</sub> ) <sub>2</sub> Ca(SO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O	NH <sub>4</sub> MgCl <sub>3</sub> ·6H <sub>2</sub> O
(NH <sub>4</sub> )HSO <sub>4</sub>	NaCl
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	(NH <sub>4</sub> ) <sub>2</sub> Ni(SO <sub>4</sub> ) <sub>2</sub> · 6H <sub>2</sub> O

Source: Tani et al., 1983.

**TABLE 3-11. COMPOUNDS OBSERVED IN AEROSOLS IN A FORESTED AREA, STATE COLLEGE, PA.**

(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>
(NH <sub>4</sub> ) <sub>3</sub> H(SO <sub>4</sub> ) <sub>2</sub> (letovicite)
(NH <sub>4</sub> )HSO <sub>4</sub>
2(NH <sub>4</sub> NO <sub>3</sub> )·(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>
(NH <sub>4</sub> ) <sub>2</sub> Pb(SO <sub>4</sub> ) <sub>2</sub>

Source: Tani et al., 1983

1 Metals such as Al, Ca, Fe, Mg and Pb known to be present in atmospheric aerosols,  
2 also exist in uncertain chemical forms (Pitts and Pitts, 1986). This is partially due to the use  
3 of analytical techniques that normally provide information on total metal content (Schroeder  
4 et al., 1987). It is generally assumed that many of the elements, especially from combustion  
5 sources, are present in the form of oxides (Olmez et al. 1988), while trace elements in  
6 incinerator emissions may be in the form of chlorides (Schroeder, 1987). Data from Los  
7 Angeles indicate that arsenic may be present in two chemical forms in atmospheric aerosols,  
8 as arsenite and arsenate. Both forms were identified in both the fine and coarse particle  
9 fractions (Rabano et al., 1989).  $\text{Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{AlPO}_4$  have been identified in  
10 roadside particulate matter (Biggins and Harrison, 1980). Ca and Mg may exist in the form  
11 of oxides (i.e.,  $\text{CaO}$ ,  $\text{MgO}$ ), although in the presence of water, Stelson and Seinfeld (1981)  
12 suggest that, on equilibrium considerations,  $\text{CaO}$  and  $\text{MgO}$  should react to form their  
13 hydroxides,  $\text{Ca}(\text{OH})_2$  and  $\text{Mg}(\text{OH})_2$ , respectively. Similarly the oxides  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$   
14 should form  $\text{NaOH}$  and  $\text{KOH}$  when water is present. Lead has been observed in roadside  
15 particulate matter in a wide variety of forms, such as  $\text{PbSO}_4$ ,  $\text{Pb}_3\text{O}_4$ ,  $\text{PbSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4$ ,  
16  $\text{PbO} \cdot \text{PbSO}_4$ ,  $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$ ,  $2\text{PbBrCl} \cdot \text{NH}_4\text{Cl}$ ,  $\text{PbBrCl}$ ,  $(\text{PbO})_2\text{PbBrCl}$ ,  
17  $3\text{Pb}_3(\text{PO}_4)_2 \cdot \text{PbBrCl}$ , and elemental lead (Biggins and Harrison, 1980; Post and Buseck,  
18 1985).

19 Heterogeneous oxidation of sulphur dioxide in air can be catalyzed by species such as  
20 iron, manganese (Barrie and Georgii, 1976) and cadmium, while vanadium is suspected to  
21 catalyze the formation of sulfuric acid during oil combustion. Oxides of iron, manganese  
22 and lead are reported to absorb  $\text{SO}_2$  (Schroeder, 1987).

23 It has been suggested that the elements arsenic, cadmium, manganese, nickel, lead,  
24 antimony, selenium, vanadium and zinc volatilize at high temperatures during fossil fuel  
25 combustion and condense uniformly on surfaces of entrained flyash particles as the  
26 temperature falls beyond the combustion zone (Linton et al., 1976;). Accumulation of trace  
27 metals in the fine fraction of airborne dust sampled in iron foundries showed Pb and Zn  
28 localized on the surface of the fine particles (Michaud et al., 1993). From the viewpoint of  
29 toxicity, such emissions are more important than natural sources where trace elements are  
30 usually bound within the matrix of natural aerosols and thus less mobile and bioavailable  
31 (Schroeder, 1987).

1 Trace metal compounds found in road dust can accumulate from anthropogenic or  
2 natural sources. Subsequently these can become re-entrained in the atmosphere. In such  
3 samples lead and zinc were found to be strongly associated with carbonate and iron-  
4 manganese oxide phases, with small amounts being associated with an organic phase. Half  
5 of cadmium was associated with carbonate and iron-manganese oxide phases, while copper  
6 was mainly associated with the organic phase. These associations influence the relative  
7 mobility and bioavailability of trace metals in the environment (Harrison et al., 1981).

8 Resuspension of particles from contaminated surfaces may also contribute to an  
9 increase in the toxic trace elements in airborne particles (Kitsa et al., 1992, Kitsa and Lioy,  
10 1992; Pastuszka and Kwapulinski, 1988; Falerios et al., 1992). Kitsa et al. (1992) measured  
11 elemental concentrations in particles resuspended from a waste site in New Jersey. Close to  
12 the resuspension source, coarse particles were dominant, but farther downwind from the site,  
13 fine particles were prevailing. The fine particles were enriched in chromium and lead,  
14 indicating the potential for elevated human exposure through inhalation. Chromium may  
15 exist in different valence states, but the most stable and abundant are the trivalent and  
16 hexavalent states. Hexavalent chromium is classified as a known respiratory carcinogen in  
17 humans.

18 Oxidation of the species present in aerosols results from interaction with various  
19 atmospheric oxidants, such as molecular oxygen, ozone or hydrogen peroxide. The presence  
20 of oxides of As, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Sb, Se, V and Zn has been measured in  
21 emissions of cement plants, blast furnace and sintering operations, secondary iron foundries,  
22 non-ferrous smelting of arsenic-bearing ores, zinc and lead smelters and many other sources  
23 (Schroeder et al., 1987).

24 Sulphation, and possibly nitration, of metallic oxides can be surmised to be an  
25 important transformation as particles age. A statistical assessment of multielemental  
26 measurements in a study in the rural and urban atmospheres of Arizona showed strong  
27 correlations of lead, copper, cadmium and zinc with sulfates in the rural atmosphere and  
28 moderate correlation of lead and copper with sulfates and nitrates in urban atmosphere  
29 (Moyers et al., 1977). Nickel has also great affinity for sulfur which may lead to the  
30 emission of nickel sulfate containing particulates from combustion sources. In the absence of

sulfur, nickel oxides or complex metal oxides containing nickel may form (U.S. Environmental Protection Agency, 1986a).

Lead is emitted in the air from automobiles as lead halides and as double salts with ammonium halides (e.g.  $\text{PbBrCl} \cdot 2\text{NH}_4\text{Cl}$ ). From mines and smelters, the dominant species are  $\text{PbSO}_4$ ,  $\text{PbO} \cdot \text{PbSO}_4$ , and  $\text{PbS}$ . In the atmosphere lead is present as sulfate with minor amounts of halides. Lead sulfide is the main constituent of samples associated with ore handling and fugitive dust from open mounds of ore concentrate. The major constituents from sintering and blast furnace operations appeared to be  $\text{PbSO}_4$  and  $\text{PbO} \cdot \text{PbSO}_4$  respectively (U.S. Environmental Protection Agency, 1986b).

### 3.3.8 Removal Processes

Removal of accumulation mode aerosol particles from the atmosphere occurs largely by the precipitation process (e.g., Slinn, 1983). These particles are the dominant particles on which cloud droplets form (cloud condensation nuclei, CCN); once a cloud droplet (of diameter of a few up to about 20 micrometers) is formed, it is much more susceptible to scavenging and removal in precipitation than is the original submicrometer particle. The fraction of aerosol particles incorporated in cloud droplets on cloud formation is the subject of active current research. Earlier work yielded a fairly wide spread in this fractional incorporation, based in part on limitations of then existing techniques and in part on definitions of incorporation efficiencies (based on number, mass, light scattering efficiency, or amount of specific compounds; ten Brink et al., 1987). More recent work indicates a high fractional incorporation at low concentrations of aerosol particles decreasing as the aerosol particle loading increases (Leaitch et al., 1992; Gillani et al., 1992). Model calculations of the efficiency of incorporation of accumulation-mode aerosol particles into cloud droplets and precipitation are highly sensitive to assumptions and approach (Jensen and Charlson, 1984; Flossmann et al., 1985; Hänel, 1987; Ahr et al., 1989; Alheit et al., 1990).

The dominance of precipitation removal processes for accumulation mode particles results in high variability in temporal patterns of aerosol loadings, that may be attributed to the episodicity of precipitation events and synoptic scale meteorology that delivers air of differing origins to a given location (e.g., Waldman et al., 1990). This variability leads to difficulties in attempts to estimate mean residence times based on budget considerations

(Junge, 1963; Schwartz, 1979). A unique approach to estimation of the mean residence time of accumulation mode aerosol particles was presented by measurement of the decay of atmospheric concentrations of  $\text{Ce}_{137}$  at several mid-latitude surface stations in Europe and Asia in the weeks following the Chernobyl accident (Cambray et al., 1987); the  $\text{Ce}_{137}$  was present largely in this size range. This study led to an estimate for the mean residence time of 7 days, consistent with other estimates. It may be noted, however, that this residence time is applicable to particles in the free troposphere, where the  $\text{Ce}_{137}$  was mainly present during the several week period. The mean residence time of accumulation mode particles in the boundary layer is expected to be somewhat less (Benkovitz et al., 1994).

## 3.4 TRANSPORT AND TRANSFORMATIONS TO SECONDARY PARTICULATE MATTER

### 3.4.1 Aqueous-Phase Chemical Equilibria and Chemical Kinetics of Transformations to Secondary Particulate Matter

#### 3.4.1.1 Aqueous-Phase Equilibria

The liquid water content of the atmosphere,  $w_L$ , is usually expressed either in g of water per  $\text{m}^3$  of air or as a dimensionless volume fraction  $L$  (e.g.,  $\text{m}^3$  of liquid water per  $\text{m}^3$  of air). Typical liquid water content values are 0.1 to 1  $\text{g m}^{-3}$  ( $L = 10^{-7}$  -  $10^{-6}$ ) for clouds, 0.05 to 0.5  $\text{g m}^{-3}$  ( $L = 5 \times 10^{-7}$  -  $5 \times 10^{-6}$ ) for fogs, and only  $10^{-5}$  to  $10^{-4} \text{g m}^{-3}$  ( $L = 10^{-11}$  -  $10^{-10}$ ) for aerosols.

For dilute solutions the equilibrium distribution of a reagent gas A between the gas and aqueous phases is given by Henry's law

$$[A] = H_A p_A \quad (3-15)$$

where  $p_A$  is the partial pressure of A in the gas-phase,  $[A]$  is the equilibrium aqueous-phase concentration of A and  $H_A$  is the Henry's law coefficient for species A. The customary units of  $H_A$  are  $\text{mole l}^{-1} \text{atm}^{-1}$ .  $H_A$  can be viewed as the equilibrium constant of the reaction

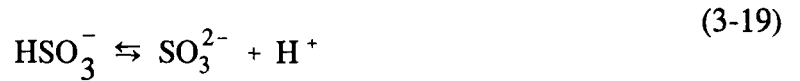


Table 3-12 gives the Henry's law coefficients of some atmospheric gases in liquid water at 298 K. The values given reflect only the physical solubility of the gas regardless of the subsequent fate of the dissolved species A. Some of the species included in Table 3-12 dissociate after dissolution or react with water. Henry's law constants do not account for these processes, and the modifications necessary will be discussed in the next paragraph. Henry's law coefficients generally decrease for increasing temperatures, resulting in lower solubilities at higher temperatures (Seinfeld, 1986).

**TABLE 3-12. HENRY'S LAW COEFFICIENTS OF SOME ATMOSPHERIC GASES DISSOLVING IN LIQUID WATER**

Species	H (M/atm) (298 K)
O <sub>2</sub>	1.3x10 <sup>-3</sup>
NO	1.9x10 <sup>-3</sup>
C <sub>2</sub> H <sub>4</sub>	4.8x10 <sup>-3</sup>
NO <sub>2</sub>	1.0x10 <sup>-2</sup>
O <sub>3</sub>	1.13x10 <sup>-2</sup>
N <sub>2</sub> O	2.5x10 <sup>-2</sup>
CO <sub>2</sub>	3.4x10 <sup>-2</sup>
H <sub>2</sub> S	0.12
SO <sub>2</sub>	1.23
CH <sub>3</sub> ONO <sub>2</sub>	2.6
CH <sub>3</sub> C(O)O <sub>2</sub> NO <sub>2</sub>	2.9
CH <sub>3</sub> O <sub>2</sub>	6.0
OH	25.
HNO <sub>2</sub>	49.
NH <sub>3</sub>	75.
CH <sub>3</sub> OH	220.
CH <sub>3</sub> OOH	227.
CH <sub>3</sub> C(O)OOH	473.
HCl	727.
HO <sub>2</sub>	2.0x10 <sup>3</sup>
HCOOH	3.5x10 <sup>3</sup>
HCHO	6.3x10 <sup>3</sup>
CH <sub>3</sub> COOH	8.7x10 <sup>3</sup>
H <sub>2</sub> O <sub>2</sub>	7.45x10 <sup>4</sup>
HNO <sub>3</sub>	2.1x10 <sup>5</sup>
NO <sub>3</sub>	2.1x10 <sup>5</sup>

Several gases, after dissolving in the aqueous-phase, ionize and establish an aqueous-phase chemical equilibrium system. For example for SO<sub>2</sub>,



with

$$H_{\text{SO}_2} = \frac{[\text{SO}_2 \cdot \text{H}_2\text{O}]}{P_{\text{SO}_2}}, K_{s1} = \frac{[\text{HSO}_3^-][\text{H}^+]}{[\text{SO}_2 \cdot \text{H}_2\text{O}]}, K_{s2} = \frac{[\text{SO}_3^{2-}][\text{H}^+]}{[\text{HSO}_3^-]} \quad (3-20)$$

$K_{s1}$  and  $K_{s2}$  are the first and second dissociation constants for SO<sub>2</sub>. It is convenient to consider the total dissolved sulfur in oxidation state IV as a single entity and refer to it as S(IV),

$$[\text{S(IV)}] = [\text{SO}_2 \cdot \text{H}_2\text{O}] + [\text{HSO}_3^-] + [\text{SO}_3^{2-}] \quad (3-21)$$

The three sulfur species are in rapid equilibrium and therefore [S(IV)] changes only when SO<sub>2</sub> is transferred between the gas and aqueous phases. The total dissolved sulfur, S(IV), can be expressed as a function of only the pH and the partial pressure of SO<sub>2</sub> over the solution by:

$$[\text{S(IV)}] = H_{\text{SO}_2} P_{\text{SO}_2} \left[ 1 + \frac{K_{s1}}{[\text{H}^+]} + \frac{K_{s1}K_{s2}}{[\text{H}^+]^2} \right] \quad (3-22)$$

The above equation can be expressed in a form similar to Henry's law as

$$[S(IV)] = H_{S(IV)}^* p_{SO_2} \quad (3-23)$$

where  $H_{S(IV)}^*$  is the effective (or modified) Henry's law coefficient given for S(IV) by

$$H_{S(IV)}^* = H_{SO_2} \left[ 1 + \frac{K_{s1}}{[H^+]} + \frac{K_{s1}K_{s2}}{[H^+]^2} \right] \quad (3-24)$$

The modified Henry's law coefficient relates the total dissolved S(IV) (and not only with the  $SO_2$  vapor pressure over the solution. The effective Henry's law coefficient always exceeds the Henry's law coefficient, indicating that the dissociation of a species enhances its solubility in the aqueous phase.

Several of the species that are in rapid equilibrium can be also considered as single entities:

$$[S(IV)] = [H_2SO_4(aq)] + [HSO_4^-] + [SO_4^{2-}]$$

$$[N(V)] = [HNO_3(aq)] + [NO_3^-]$$

$$[HO_2^T] = [HNO_2(aq)] + [O_2^-]$$

$$[HCHO^T] = [HCHO] + [H_2C(OH)_2]$$

Equations relating the total concentrations of these aqueous-phase species with the corresponding equilibrium concentrations of the gas-phase species can be derived similarly to those for S(IV).



### 3.4.1.2 Aqueous-Phase Transformation of SO<sub>2</sub> to Sulfate

The aqueous-phase conversion of dissolved SO<sub>2</sub> to sulfate is thought to be the most important chemical transformation in cloudwater. Dissolution of SO<sub>2</sub> in water results in the formation of three chemical species: hydrated SO<sub>2</sub> (SO<sub>2</sub> · H<sub>2</sub>O), the bisulfite ion (HSO<sub>3</sub><sup>-</sup>) and the sulfite ion (SO<sub>3</sub><sup>2-</sup>). At the pH range of atmospheric interest (pH =2-7) most of the S(IV) is in the form of HSO<sub>3</sub><sup>-</sup>, whereas at low pH (pH <2), all of the S(IV) occurs as SO<sub>2</sub> · H<sub>2</sub>O. At higher pH values (pH >7), (SO<sub>3</sub><sup>2-</sup>) is the preferred S(IV) state (Seinfeld, 1986). The individual dissociations are fast, occurring on timescales of milliseconds or less (Martin, 1984; Schwartz and Freiberg, 1981; Seinfeld, 1986). Therefore, during a reaction consuming one of the three species, SO<sub>2</sub> · H<sub>2</sub>O, HSO<sub>3</sub><sup>-</sup>, or SO<sub>3</sub><sup>2-</sup>, the corresponding aqueous-phase equilibria are re-established instantaneously. The dissociation of dissolved SO<sub>2</sub> enhances its aqueous solubility and the total amount of dissolved S(IV) always exceeds that predicted by Henry's law for SO<sub>2</sub> alone and is quite pH dependent. The Henry's law coefficient for SO<sub>2</sub> alone, H<sub>SO<sub>2</sub></sub>, is 1.23 M atm<sup>-1</sup> at 298 K, while for the same temperature, the effective Henry's law coefficient for S(IV), H<sub>S(IV)</sub><sup>\*</sup>, is 16.4 M atm<sup>-1</sup> for pH=3, 152 M atm<sup>-1</sup> for pH=4 and 1,524 M atm<sup>-1</sup> for pH=5. Equilibrium S(IV) concentrations for SO<sub>2</sub> gas-phase concentrations of 0.2-200 ppb, and over a pH range 1-6 vary approximately from 0.001 to 1000 mM.

Several pathways for S(IV) transformation to S(VI) have been identified involving reactions of S(IV) with O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, O<sub>2</sub> (catalyzed by Mn<sup>+</sup> and Fe<sup>3+</sup>), OH, SO<sub>5</sub><sup>-</sup>, HSO<sub>5</sub><sup>-</sup>, SO<sub>4</sub><sup>-</sup>, PAN, CH<sub>3</sub>OOH, CH<sub>3</sub>C(O)OOH, HO<sub>2</sub>, NO<sub>3</sub>, NO<sub>2</sub>, N(III), HCHO and Cl<sub>2</sub><sup>-</sup> (Pandis and Seinfeld, 1989a).

Although ozone reacts very slowly with SO<sub>2</sub> in the gas phase, the aqueous-phase reaction is rapid. The possible importance of O<sub>3</sub> as an aqueous-phase oxidant for S(IV) was first suggested by Penkett (1972) and the kinetics of



have been studied by several investigators (Erickson et al., 1977; Penkett et al., 1979; Maahs, 1983). Hoffmann and Calvert (1985), after a detailed investigation of existing

experimental kinetic and mechanistic data, suggested the following expression for the rate of the reaction of S(IV) with dissolved ozone:

$$R_1 = -\frac{d[S(IV)]}{dt} = (k_0[SO_2 \cdot H_2O] + k_1[HSO_3^-] + k_2[SO_3^{2-}])[O_3] \quad (3-26)$$

recommending the values  $k_0 = 2.4 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ ,  $k_1 = 3.7 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$  and,  $k_2 = 1.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ . They also proposed that this reaction proceeds by nucleophilic attack on ozone by  $SO_2 \cdot H_2O$ ,  $HSO_3^-$ , and  $SO_3^{2-}$ . An increase in the aqueous-phase pH results in an increase of all three,  $[SO_2 \cdot H_2O]$ ,  $[HSO_3^-]$  and  $[SO_3^{2-}]$ , equilibrium concentrations and therefore in an increase of the overall reaction rate. For an ozone gas-phase mixing ratio of 30 ppb, the reaction rate varies from less than  $0.001 \text{ mM h}^{-1} (\text{ppb } SO_2)^{-1}$  at pH=2 (or less than  $0.01\% SO_2 (\text{g}) \text{ h}^{-1} (\text{g water} / \text{m}^3 \text{ air})^{-1}$ ) to  $3,000 \text{ mM h}^{-1} (\text{ppb } SO_2)^{-1}$  at pH=6 ( $7,000\% SO_2 (\text{g}) \text{ h}^{-1} (\text{g water} / \text{m}^3 \text{ air})^{-1}$ ). The gas-phase  $SO_2$  oxidation rate is of the order of  $1\% \text{ h}^{-1}$  and therefore the S(IV) heterogeneous oxidation by ozone is significant for pH values greater than 4. The strong positive dependence of the reaction rate on the pH renders this reaction self limiting. The production of sulfate by this reaction lowers the pH and effectively decreases the rate of further reaction. The availability of atmospheric ozone guarantees that this reaction will play an important role both as a sink of gas-phase  $SO_2$  and as a cause of cloudwater acidification as long as the pH of the atmospheric aqueous phase exceeds 4.

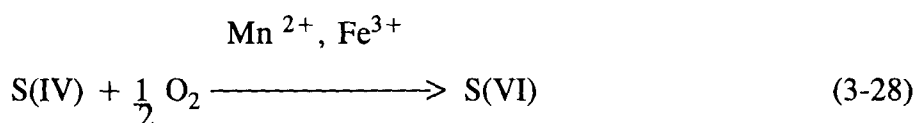
Hydrogen peroxide,  $H_2O_2$ , is one of the most effective oxidants of S(IV) in clouds and fogs (Pandis and Seinfeld, 1989a).  $H_2O_2$  is very soluble in water and under typical ambient conditions its aqueous-phase concentration is approximately six orders of magnitude higher than that of ozone. This reaction has been studied in detail by several investigators (Hoffmann and Edwards, 1975; Penkett et al., 1979; Martin and Damschen, 1981; Cocks et al., 1982; Kunen et al., 1983; McArdle and Hoffmann, 1983) and the reproducibility of the measurements suggests a lack of susceptibility of this reaction to influence of trace constituents. The proposed rate expression is (Hoffmann and Calvert, 1985)

$$R_2 = -\frac{d[S(IV)]}{dt} = \frac{k[H^+][H_2O_2][HSO_3^-]}{1 + K[H^+]} \quad (3-27)$$

with  $k=7.45 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  and  $K=13 \text{ M}^{-1}$  at 298 K. Noting that  $H_2O_2$  is a very weak electrolyte, and from 6.3, 6.4, and 6.5 that  $[H^+][HSO_3^-] = H_{SO_2} K_{s1} p_{SO_2}$  and that for  $pH > 2$ ,  $1 + K[H^+] \approx 1$ , one concludes that the rate of this reaction is practically pH independent in the pH range of atmospheric interest. For a  $H_2O_2(g)$  mixing ratio of 1 ppb the rate is roughly  $300 \text{ mM h}^{-1} (\text{ppb SO}_2)^{-1}$  ( $700\% \text{ SO}_2(g) \text{ h}^{-1} (\text{g water / m}^3 \text{ air})^{-1}$ ). The near pH independence can also be viewed as the result of the cancellation of the pH dependence of the S(IV) solubility and the reaction rate constant. The reaction is very fast and indeed both field measurements (Daum et al., 1984) and theoretical studies (Pandis and Seinfeld, 1989b) have suggested that  $H_2O_2(g)$  and  $SO_2(g)$  rarely coexist in clouds and fogs. The species with the lowest concentration before the cloud or fog formation is the limiting reactant, and is rapidly depleted inside the cloud or fog layer.

Organic peroxides have been also proposed as potential aqueous-phase oxidants of dissolved sulfur (Graedel and Goldberg, 1983; Lind and Lazrus, 1983; Hoffmann and Calvert, 1985).

Simulations for typical continental clouds suggest that these reactions are of minor importance for the S(IV) oxidation and represent small sinks for the gas-phase hydroperoxide ( $0.2\% \text{ CH}_3\text{OOH h}^{-1}$ ) and peracetic acid ( $0.7\% \text{ CH}_3\text{C(O)OOH h}^{-1}$ ). The S(IV) oxidation by  $O_2$  is known to be catalyzed by  $Fe^{3+}$  and  $Mn^{2+}$



This reaction has been the subject of considerable interest (Hoffmann and Boyce, 1983; Martin, 1984; Hoffmann and Jacob, 1984; Hoffmann and Calvert, 1985; Clarke and Radojevic, 1987) and significantly different measured reaction rates, rate laws and pH dependencies have been reported (Hoffmann and Jacob, 1984). Martin and Hill (1987a,b) have demonstrated that this reaction is inhibited as ionic strength increases. They explained

most of the literature discrepancies by differences in these factors during the various laboratory studies.

In the presence of oxygen, iron in the ferric state, Fe(III), catalyzes the oxidation of S(IV) in aqueous solutions. Fe(II) appears not to catalyze directly the reaction and is first oxidized to Fe(III) before S(IV) oxidation can begin (Huss et al., 1982a,b).

For pH values from 0 to 3.6 the iron-catalyzed S(IV) oxidation rate is first order in iron, first order in S(IV) and is inversely proportional to  $[H^+]$  (Martin and Hill, 1987a),

$$r = -\frac{d[S(IV)]}{dt} = k_1 \frac{[Fe^{3+}][S(IV)]}{[H^+]} \quad (3-29)$$

This reaction is inhibited by ionic strength and sulfate and these effects are described by:

$$k_1 = k_1^* 10^{\frac{-2I}{1+I}} \quad (3-30)$$

and

$$k_1 = k_1^* \frac{1}{1 + 150[S(VI)]^{2/3}} \quad (3-31)$$

where  $I$  is the ionic strength of the solution and  $[S(VI)]$  is in M. A rate constant  $k_1^* = 6 \text{ s}^{-1}$  has been recommended by Martin and Hill (1987a). Sulfite appears to be almost as equally inhibiting as sulfate.

The rate expression for the same reaction changes completely above pH 3.6. This suggests that the mechanism of the reaction differs in the two pH regimes, and is probably a free radical chain at high pH and a non radical mechanism at low pH (Martin et al., 1991). The low solubility of Fe(III) above pH 3.6 presents special experimental problems. At high pH the reaction rate depends on the amount of iron in solution, rather than on the total amount of iron present. At this range the reaction is second order in dissolved iron (zero order above the solution iron saturation point) and first order in S(IV). The reaction is still

not very well understood and Martin et al. (1991) proposed the following phenomenological expressions (in  $\text{M s}^{-1}$ )

$$\text{pH4.0: } -\frac{d[\text{S(IV)}]}{dt} = 1 \times 10^9 [\text{S(IV)}][\text{Fe}^{3+}]^2$$

$$\text{pH5.0-6.0: } \frac{d[\text{S(IV)}]}{dt} = 1 \times 10^{-3} [\text{S(IV)}]$$

$$\text{pH7.0: } -\frac{d[\text{S(IV)}]}{dt} = 1 \times 10^{-4} [\text{S(IV)}]$$

for the following conditions:

$$[\text{S(IV)}] \approx 10\mu\text{M}, [\text{Fe}^{3+}] > 0.1\mu\text{M}, I < 0.01\text{M}, [\text{S(VI)}] < 100\text{M}, \text{ and } T = 298\text{K}.$$

Note that iron does not appear in the pH 5-7 rates because it is assumed that a trace of iron will be present under normal atmospheric conditions. This reaction is important in this high pH regime (Pandis and Seinfeld, 1989a, b; Pandis et al., 1992).

Martin et al. (1991) also found that non-complexing organic molecules (e.g. acetate, trichloroacetate, ethylalcohol, isopropyl alcohol, formate, allyl alcohol, etc.) are highly inhibiting at pH values of 5 and above, and are not inhibiting at pH values of 3 and below. They calculated that, for remote clouds, formate would be the main inhibiting organic, but by less than 10%. In contrast, near urban areas formate could reduce the rate of the catalyzed oxidation by a factor of 10-20 in the high pH regime.

The manganese catalyzed S(IV) oxidation was initially thought to be inversely proportional to the  $\text{H}^+$  concentration. Martin and Hill (1987b) suggested that ionic strength, not hydrogen ion, accounts for the pH dependence of the rate. These authors were also able to explain some unusual behavior described in the literature on this reaction and to partially reconcile some of the literature rates. The manganese catalyzed reaction obeys zero-order kinetics in S(IV) in the concentration regime above 100 mM S(IV),

$$-\frac{d[S(IV)]}{dt} = k_o[Mn^{2+}]^2 \quad (3-32)$$

$$k_o = k_o^* 10^{\frac{-4.07 \downarrow \Gamma}{1+\downarrow \Gamma}}$$

with  $k_o^* = 680 \text{ M}^{-1} \text{ s}^{-1}$  (Martin and Hill, 1987b). For S(IV) concentrations below 1 mM the reaction is first order in S(IV),

$$-\frac{d[S(IV)]}{dt} = k_o[Mn^{2+}][S(IV)] \quad (3-33)$$

$$k = k_o^* 10^{\frac{-4.07 \downarrow \Gamma}{1+\downarrow \Gamma}}$$

with  $k_o^* = 1,000 \text{ M}^{-1} \text{ s}^{-1}$  (Martin and Hill, 1987b). It is still not clear which rate law is appropriate for use in atmospheric calculations, although Martin and Hill (1987b) suggested the provisional use of the first order, low S(IV) rate.

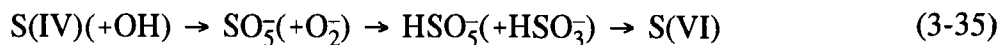
When both  $Fe^{3+}$  and  $Mn^{2+}$  are present in atmospheric droplets, the overall rate of the S(IV) reaction is enhanced over the sum of the two individual rates. Martin (1984) reported that the rates measured were 3 to 10 times higher than expected from the sum of the independent rates. Martin and Good (1991) obtained at pH 3.0 and for  $[S(IV)] < 10 \text{ mM}$  the following rate law

$$-\frac{d[S(IV)]}{dt} = 750[Mn(II)][S(IV)] + 2600[Fe(III)][S(IV)] + 1.0 \times 10^{10}[Mn(II)][Fe(III)][S(IV)] \quad (3-34)$$

and a similar expression for pH 5.0 in agreement with the work of Ibusuki and Takeuchi (1987).

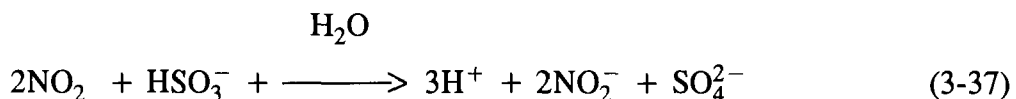
Free radicals, such as OH and  $HO_2$ , either heterogeneously scavenged by the aqueous phase or produced in the aqueous phase, participate in a series of aqueous phase reactions (Graedel and Weschler, 1981; Chameides and Davis, 1982; Graedel and Goldberg, 1983; Schwartz, 1984; Jacob, 1986; Pandis and Seinfeld, 1989a).

Pandis and Seinfeld (1989a) proposed that under typical remote continental conditions there are two main radical pathways resulting in the conversion of S(IV) to S(VI):



with the first of these two pathways typically being faster than the second.

Nitrogen dioxide has a low water solubility and therefore its low resulting aqueous-phase concentrations suggests that its oxidation of S(IV)



should be of minor importance in most cases. This reaction has been studied by Lee and Schwartz (1983) at pH 5.0, 5.8 and 6.4 and was described as a reaction that is first order in  $\text{NO}_2$  and first order in S(IV), with a pH-dependent rate constant. The evaluation of this rate expression was considered tentative by Lee and Schwartz, in view of evidence for the formation of a long-lived intermediate species. The apparent rate constant was found to increase with pH. This reaction is considered of secondary importance at the concentrations and pH values representative of clouds. However, Pandis and Seinfeld (1989b) reported that for fogs occurring in urban polluted areas with high  $\text{NO}_2$  concentrations this reaction could be a major pathway for the S(IV) oxidation, if the atmosphere has enough neutralizing capacity, e.g. high  $\text{NH}_3$  (g) concentrations.

Sulfite and bisulfite can form complexes with various dissolved aldehydes. One important example is the reaction of sulfite or bisulfite with formaldehyde to produce hydroxymethanesulfonate ion (HMS) (Boyce and Hoffmann, 1984; Munger et al., 1984, 1986; Olson and Hoffman, 1989; Faccini et al., 1992).

The HMS formed acts as a S(IV) reservoir protecting it from further oxidation, and its formation has been advanced to explain high S(IV) concentrations that have been observed in clouds and fogs. The rates of S(IV) complexation and oxidation are highly dependent on cloud pH and on the concentrations of HCHO and oxidants. Characteristic times for S(IV) depletion through complexation and oxidation can be compared for typical ranges of HCHO,  $\text{H}_2\text{O}_2$ , and pH. At pH values below about 4, the rate of reactions 6.26 and 6.27 are several orders of magnitude slower than the reaction of S(IV) with dissolved  $\text{H}_2\text{O}_2$ . Thus, in this

range oxidation predominates over complexation. The characteristic times of the two reactions become approximately comparable at pH around 5 so that complexation with HCHO becomes competitive with oxidation by H<sub>2</sub>O<sub>2</sub>. When pH exceeds 6, the reactions of S(IV) with HCHO became more important than reaction with H<sub>2</sub>O<sub>2</sub>. HMS formation can inhibit S(IV) oxidation if the S(IV) complexation rate is comparable to, or greater than, the S(IV) oxidation rate and the rate of SO<sub>2</sub> mass transport into the drop controls the rate of S(IV) oxidation. The effectiveness of HMS as a S(IV) reservoir depends critically on its resistivity to OH attack.

#### 3.4.1.3 Aqueous-phase Transformation of NO<sub>2</sub> to HNO<sub>3</sub> and NH<sub>4</sub>NO<sub>3</sub>

Aside from reaction of N<sub>2</sub>O<sub>5</sub> with liquid water, there does not appear to be any other aqueous-phase reaction of nitrogen oxides that contributes substantially to atmospheric nitrate.

In contrast to the sulfate system, the nitrate system exhibits a gaseous equilibrium that admits to a substantial gas-phase fraction (as nitric acid vapor) under ambient conditions. Thus, the chemical kinetics of the aqueous-phase oxidation of NO by O<sub>2</sub> has been reexamined by two groups (Lewis and Deen, 1994; Pires et al., 1994), with confirmation of a third-order rate law,

$$R = k[\text{NO}(\text{aq})]^2[\text{O}_2(\text{aq})], \quad (3-38)$$

analogous to the gas-phase reaction, with  $k = (7 \pm 1) \times 10^6 \text{ M}^{-2} \text{ s}^{-1}$  at 296 K. Evaluation of the rate of this reaction in cloudwater confirms that the reaction rate is negligible under atmospheric conditions, as indicated earlier by Schwartz and White (1983).

#### 3.4.2 Transport and Transformations in Plumes

In the 1970s, many field studies were plume studies or urban-scale studies, and most models were Lagrangian and limited to linearized treatment of chemistry and other non-linear processes. Some of these field studies, along with regional visibility information and back-trajectories from local pollution episodes, pointed to the existence of long range transport and to the regional nature of air pollution and haze (Hall et al., 1973; Gillani and Husar, 1976; Wolff et al., 1977). In response, some of the major field studies in the 1980s had a regional



scope with focus on acidic depositions, oxidants, or aerosols and visibility. That decade also saw major strides in measurement technology and in the development of increasingly sophisticated Eulerian air quality models with explicit treatment of non-linear processes. In these models, however, the treatment of plumes, particularly point-source plumes, was grossly distorted by varying degrees depending on the spatial resolution of the grid. New interest also began to emerge in global climate change, global data, and global modeling. In the decade of the 1990s, the principal interests in modeling and measurements appear to be in two areas: global-scale issues, with particular focus on clouds and aerosols; and, regional and sub-regional issues, with special interests in comprehensive linked study of oxidants, aerosols and acidic depositions, and in multi-scale interactions (e.g., nested gridding and the treatment of subgrid-scale processes related to plumes, clouds, and air-surface interactions).

Topics related to field measurements are also covered in other parts of this document: methodologies for sampling and analysis of PM and acidic deposition in Chapter 4; ambient air measurements of PM concentrations and properties in Chapter 7; and field studies of visibility and PM in Chapter 10. The focus in this section is on North American field studies of the past 15 years or so, particularly as they relate to the following objectives: better understanding of atmospheric processes (formation, transformation, transport, and removal) which *modify* the concentration, size and composition of PM; evaluation of source- or receptor- oriented models of PM air quality; and generation of model inputs.

#### **3.4.2.1 Field Studies of Transport Processes**

Except for the gravitational settling of coarse particles (included in dry deposition), the transport of PM is similar to that of gases. Following their emissions, gases and fine aerosols rise due to buoyancy effects, are advected downwind by the prevailing mean flow field, and are dispersed horizontally and vertically by ambient turbulence, wind-shear effects, and cloud processes. These dispersive mechanisms result from the interaction of large air masses, or from the disturbance of the larger-scale flow in a given air mass by insolation-driven surface fluxes of heat and moisture, and by surface drag effects. The influence of these surface effects is largely confined to the atmospheric boundary layer (ABL), the height of which varies diurnally and seasonally, peaking typically at between 1 and 3 km on

1 summer afternoons over the continental U.S.A. Pollutant emissions may be within the ABL  
2 or above it (depending on emission height and buoyancy), and their dispersion is markedly  
3 different in the two cases, being much more rapid and vigorous in the daytime convective  
4 boundary layer (CBL) than in the stable layers aloft or in the stable nocturnal boundary  
5 layer. Quantitative study of these transport and dispersion processes requires, ideally,  
6 simultaneous measurements of a large number of variables related to insolation and clouds,  
7 surface characteristics and surface fluxes of heat and moisture, and dynamic 3-D fields of  
8 flow, temperature, humidity and concentrations of trace pollutants in the ambient atmosphere.  
9 Transport and dispersion processes also have a critical influence on plume chemistry and dry  
10 deposition, which are often diffusion-limited. Meteorological measurements must therefore  
11 be an integral part of any plume study, even when the focus is on chemistry or deposition.  
12 The shift to Eulerian grid modeling in the 1980s did not include measures to preserve the  
13 essence of the sub-grid-scale features of plumes, which were instantaneously dispersed over  
14 the entire emission grid cell (a volume of  $\approx 10^{12} \text{ m}^3$  in RADM with 80 km horizontal  
15 resolution), thereby also grossly distorting plume chemistry, aerosol formation, and pollutant  
16 budgets. There is growing awareness now of the need for more realistic treatment of plumes  
17 in grid models.

18 A large body of literature exists on studies (including field studies) of ABL structure  
19 and dynamics, and on the characteristics of the wind, temperature and moisture fields in the  
20 ABL and, to a lesser extent, in the free troposphere aloft. Those studies are outside the  
21 present scope. Some of the recent major advances in the knowledge about the ABL are  
22 reviewed by Briggs and Binkowski (1985). Our scope here is limited to field studies of the  
23 transport and dispersion of PM and their precursors (e.g.,  $\text{SO}_x$  and  $\text{NO}_x$ ). Prior to 1975,  
24 most such field studies were limited to the behavior of point-source plumes in the  
25  $\gamma$ -mesoscale range ( $\lesssim 20 \text{ km}$ ), i.e., on plume rise and short-range dispersion. Such behavior  
26 is well understood qualitatively; quantitatively, it is well enough represented in models at the  
27 time scales characteristic of most commonly-used plume dispersion models ( $\approx 1 \text{ h}$ ), but not  
28 at the much shorter time scales of relevance to plume chemistry and plume visibility. In this  
29 near-source range, instantaneous plume behavior is very different from the larger scale  
30 average behavior. In an intercomparison of four plume visibility models, it was concluded  
31 that much of the variation in visibility observed in the Navajo power plant plume in northern

1 Arizona was probably due to fluctuations in source emissions and plume dispersion at scales  
2 below those resolvable by the models (White et al., 1985). Since the atmospheric residence  
3 of fine PM in the lower troposphere is on the order of days, our interest here is more on the  
4 transport and dispersion of plumes over the  $\beta$ - and  $\alpha$ - mesoscale ranges ( $\approx 20$  to 200 and  
5 200 to 2,000 km). Quantitative determination of transport over the mesoscale requires  
6 special field studies with controlled tracer releases. Such studies are relatively recent and  
7 very few, and they represent only a few isolated meteorological scenarios.

#### 8 9 *3.4.2.1.1 Field Measurements Related to Transport Modeling*

10 Routine meteorological field measurements include surface weather observations of a  
11 broad variety of meteorological variables made every three hours at several thousand sites  
12 across the country by the National Weather Service, as well as upper-air soundings  
13 (radiosondes) of wind, temperature and relative humidity twice a day (noon and midnight) at  
14 a much more limited number of sites which, on average, are about 400 km apart. These  
15 data constitute the principal raw meteorological information used in regional transport  
16 models, which are either Lagrangian trajectory models or dynamic 3D Eulerian grid models.  
17 Most trajectory models are two-dimensional, with atmospheric flow patterns being analyzed  
18 on isobaric or terrain-following surfaces, or in bulk transport layers confined to the mixed  
19 boundary layer. These simplifying assumptions concerning vertical motions lead to large  
20 transport errors on the regional scale (Kuo et al., 1985). The vertical velocity can be  
21 calculated at grid points in a regional model domain from the continuity equation, but the  
22 temporal and spatial resolutions of the radiosonde data are so coarse in most areas that the  
23 result would be a gross approximation only. 3D flows may be best simulated by moist  
24 adiabatic trajectories, but since analysis methods cannot always resolve the stratified nature  
25 of the required moisture fields, the most reasonable simulations of 3D transport are probably  
26 dry adiabatic (isentropic) trajectories. Danielsen (1961) presented a case study showing a  
27 separation of  $\approx 1,300$  km after only 12 h of transport as simulated by isobaric and isentropic  
28 trajectories. It was probably an extreme case. The gridded wind field in regional Eulerian  
29 air quality models is typically generated by the application of dynamic 3D mesoscale  
30 meteorological models (e.g., PSU-MM5 and CSU-RAMS) which incorporate the routine  
31 NWS observations through a dynamic Four Dimensional Data Assimilation (FDDA)

1 technique. The NWS surface weather database also includes a measure of prevailing  
2 visibility as determined by human observers. A number of field studies have established the  
3 reliability of such subjective visibility observations (e.g., Horvath and Noll, 1969; Hoffman  
4 and Kuehnemann, 1979). They have proved to be a very useful indicator of regional haze  
5 and its long-range transport (Gillani and Husar, 1976), and have been used to study the long-  
6 term trends of the spatial-temporal variability of regional haze and air quality in the eastern  
7 U.S. over many decades (Husar et al., 1981; Sloane, 1982).

8 Special field studies of transport and dispersion are based on observations of the  
9 transport of pressurized (constant density) balloons (called tetroons if their shape is  
10 tetrahedral), and of the evolution of plumes resulting from pollutant emissions or controlled  
11 releases of artificial tracers. Balloons have been used in mesoscale studies in three ways: as  
12 isolated Lagrangian markers of pollutant emissions (e.g., Clarke et al., 1983); in sequential  
13 releases to provide one-particle diffusion estimates (e.g., Thomas and Vogt, 1990); and in  
14 cluster releases to study relative diffusion (e.g., Er-El and Peskin, 1981). Tetroons generally  
15 carry a transponder which permits continuous tracking with a radar, thus providing the  
16 complete detailed 3D trajectory. The range of the tetroon experiment is normally limited by  
17 the tracking range of the radar ( $<100$  km). This range can be extended to the full range of  
18 tetroon transport by including a tag which the finder can return with information about at  
19 least the terminal location. In some studies (e.g., Clarke et al., 1983), tetroons have been  
20 tracked continuously over much longer ranges by sequential tracking from the network of  
21 FAA radars used in support of aviation. Studies based on tracers and air pollutants also  
22 provide information about plume dispersion. Most early tracer studies were limited to a  
23 range of about 100 km due to the nature of the tracers then available and limitations of  
24 technology. Development of new tracers (e.g., the PFTs or perfluorocarbon tracers) and  
25 new sampling and analysis techniques have not only extended the range in more recent  
26 experiments by more than an order of magnitude, but the new data are also more reliable.

27 Pack et al. (1978) presented a detailed review of many early studies in which  
28 observations of the transport of pollutant plumes, tracers, or balloons were compared with  
29 results of diagnostic trajectory calculations. The models commonly used then were based on  
30 the kinematic approach (using objectively-analyzed wind fields based on measured winds) and  
31 a single transport layer. The observed winds were used as input in different ways: for

1 example, surface winds or adjusted surface winds representing average winds in the whole  
2 transport layer; or, upper air winds averaged over the transport layer. The adjustment of  
3 surface winds included enhancement of the speed by as much as a factor of two, and a veer  
4 of the wind direction by as much as 40°, to account for the real-world wind speed shear and  
5 directional veer with height. The advantage of using surface winds was due to their much  
6 higher spatial and temporal resolution, compared to the much coarser resolution of the upper-  
7 air radiosonde winds. The early results of comparisons of calculated and observed  
8 trajectories evidenced a broad range of discrepancy (10 to 54% of the trajectory length after  
9 only 100 km, and 55 to 60% after 650 km), and also the presence of large systematic errors,  
10 not always in the same direction, depending on the presence of complex flows due to fronts,  
11 complex terrain, etc. The best simulations were often obtained by the use of adjusted surface  
12 winds, and such adjustments varied between studies. The errors were found to be lowest for  
13 transport in the daytime CBL, and substantially larger for transport in stably-stratified layers.

14 Moran (1992) has tabulated (his Table 2-4) basic information about a number of formal  
15  $\beta$ - and  $\alpha$ - mesoscale tracer experiments since 1973, in which the release was at surface level  
16 and the measured transport range was at least 25 km (and up to 3,000 km). Table 3-16  
17 summarizes, in chronological order, some of the major field studies of the past 20 years with  
18 measurements and modeling of transport extending into the  $\alpha$ -mesoscale. It includes the  
19 major tracer studies as well as air quality and tetroon studies. The transport models in these  
20 studies were driven either by routine meteorological observations or by additional  
21 measurements made as part of the field studies. The following important observations are  
22 based on the studies listed in Table 3-13:

- 24 • The routine data of the radiosonde network ( $\approx 400$  km, 12 h) are too coarse both  
25 spatially (Kahl and Samson, 1986, 1988) and temporally (Rolph and Draxler, 1990;  
26 Kuo et al., 1985) for accurate simulation of long range transport.
- 27 • The error in calculated trajectories is greatest under conditions of high speeds which  
28 generally accompany complex mesoscale systems (Rolph and Draxler, 1990).
- 29
- 30

TABLE 3-13. RECENT FIELD STUDIES OF  $\alpha$ -MESOSCALE TRANSPORT AND TRAJECTORY MODEL

Study	Period	Tracer(s)	Release Sites(s)	Tracking/Sampling	Maximum Range (Airshed)	Model Comparison(s)	Ref(s)	Comments
INEL Study Idaho Nat'l Eng. Lab	Feb-May 74	Kr-85	INEL (Idaho) fuel reprocessing plant (76 m stack)	Samplers at 11 Midwestern NWS sites; 10-h day and night samples	~ 1,500 km	NOAA-ARL trajectory model with 300 m vertical resolution	Draxler (1982)	Small signal above b/g; 300 m layered approach to permit spread by wind dir'l shear necessary.
MISTT Midwest Interstate Sulfur Transport and Transformation Study	Summer 75 Summer 76	Plume sulfur	Labadie Power Plant near St. Louis, MO	In-situ aircraft measurements	~ 300 km	Simple particle trajectory model	Gillani et al. (1978) Gillani (1986)	Quasi-Lagrangian pibal measurements of winds along plume transport
VISTTA Visibility Impairment due to Sulfur Transport and Transformation in the Atmosphere	Jun, Jul, Dec-79	Anthropogenic aerosol, ozone	Los Angeles Basin	Detailed air quality and aerosol measurements at a Grand Canyon site	~ 750 km	CAPITA Monte Carlo particle transport model	Macias et al. (1981)	Evidence also of long-range impact of Copper smelter plumes
TPS Tennessee Plume Study	Aug-78	Tetroons (1 cu. m) with transponder	TVA Cumberland Steam Plant, TN	Radar to ~ 75 km; terminal point based on return tag.	~ 1,000 km (KY,IN,OH,ONT)	<ul style="list-style-type: none"> <li>• NOAA-ATAD</li> <li>• NCAR isentropic</li> <li>• CAPITA Monte Calo</li> </ul>	Clarke et al. (1983)	Part of a large plume transport/ chemistry study, including aircraft measts.
	15-Aug-78	"	"	"	~ 300 km (KY)	3D reg'l dyn. model	Warner (1981)	
NEROS Northeast Regional Oxidant Study	Summer 79 Summer 80	Tetroons (6 cu. m) Tetroons (1 and 6 cu. m)	MD, OH, PA, TN Columbus, OH	Continued FAA radars Radar and return tag.	~ 500 km to NE ~ 1,500 km to NE	NOAA, NCAR, CAPITA, as above	Clarke et al. (1983)	Part of a large urban and reg'l oxidant study
Mt. Isa Smelters Plume Study	Jul-79	Excess plume S and Aitken Nuclei Count (ANC)	Mt. Isa, Australia (Sulphide smelters, ~ 0.6 km apart)	Aircraft measts. of Total S, ANC, COSPEC-SO <sub>2</sub>	~ 1,000 km (Semi-arid region in N. Australia)	Simple layered wind trajectory model;	Carras and Williams (1981)	Exceptionally clean plume b/g.

**TABLE 3-13 (cont'd). RECENT FIELD STUDIES OF  $\alpha$ -MESOSCALE TRANSPORT  
AND TRAJECTORY MODELS**

Study	Period	Tracer(s)	Release Sites(s)	Tracking/Sampling	Maximum Range (Airshed)	Model Comparison(s)	Ref(s)	Comments
Great Plains Mesoscale Tracer Expt.	Jul-80	Two PFTs (PMCH and PDCH) and two heavy meghanes (ME-20, ME-21)	Norman, OK (1 m AGL)	Surface samplers: 17 600 km to N NE on arc at 100 km 38 on arc at 600 km and aircraft sampling		Different 3D regional models	Ferber et al. (1981) Moran (1992)	Important role of wind shear effects of nocturnal jet.
CAPTEX Cross-Appalachian Tracer Expt.	Sep/Oct 83	PFT (PMCH)	Dayton, OH Sudbury, ONT	Surface array of ~ 1,100 km >80 samplers at arcs (NE U.S.) from 300-1,100 km and aircraft sampling		Different 3D regional models; also MESOPUFF II	Ferber et al. (1986) Moran (1992) Godowitch (1989)	Terrain-effects found important. Enhanced upper air met measts.
ANATEX Across North America Tracer Expt.	Jan-Mar 87	3 PFTs (PMCP, PMCH, PDCH)	Glasgow, MT St. Cloud, MN	Surface network (77); ~ 3,000 km Towers (5); and (Eastern U.S.) aircraft sampling.		3 single-layer LAGR, 6 multi-layer LAGR, 2 multi-layer Eulerian	Draxler et al. (1991) Rolph and Draxler (1990) Clark and Cohn (1990)	Enhanced upper air met measts.
MISERS GOLD	1-Jun-89	Indium oxide (vapor deposits on particles)	White Sands Missile Range, NM	In-situ aircraft: filter ~ 1,400 km samples analysed for NM to MO tracer and particles.		Gifford's random-force diffusion theory	Kahl et al. (1991) Mason and Gifford (1992)	Dust plume from a military test explosion.

- Initial errors in trajectory simulations (both in direction and vertical spread) play a critical role in overall model uncertainty (Draxler et al., 1991).
- Single-layer Lagrangian trajectory models do not spread the "plume" adequately, while Eulerian models spread it too much. Multi-layer Lagrangian models perform the best in terms of dispersion of point-source emissions (Clark and Cohn, 1990).
- Vertical information about tracer trajectories, based on continuously-tracked tetroons and aircraft measurements, contain much useful information not captured by surface sampling alone (Clarke et al., 1983). There is, for example, evidence of cloud venting of ABL pollutants into the free troposphere, where their residence time is longer and the flow field may be quite different.
- Terrain-induced effects played an important role in CAPTEX, and effects related to the nocturnal jet were important in the Great Plains Experiment (Moran, 1992). Nocturnal wind directional shear plays a major role in effectively dispersing plumes which have been dispersed vertically during the preceding daytime CBL.
- Directional wind shear plays an important role in plume dispersion even in the CBL during  $\beta$ -mesoscale transport (Gillani, 1986).

The issue of substantial overdispersion by Eulerian models is important because the state-of-the-art as well as the future direction in mesoscale modeling (meteorological/air quality/aerosol) appear to favor the Eulerian approach. A significant source of the problem must be related to the gross initial overdispersion of plumes in regional Eulerian models, particularly of elevated point-source plumes (carriers of most of the U.S. anthropogenic emissions of sulfur). The instantaneous false dilution of fresh emissions of  $\text{NO}_x$  into the  $\text{NO}_x$ -limited surrounding environment (e.g., in the eastern U.S.) greatly distorts plume chemistry and aerosol formation. Proper sub-grid-scale treatment of plumes remains an important outstanding issue in regional modeling. Other sub-grid-scale effects in need of more attention pertain to complex mesoscale flows (e.g., storms, fronts, cloud venting, complex terrain effects, etc.). They too are an important source of model errors. A few special field studies have been carried out to investigate such flows: for example, VENTEX (Ching and Alkezweeny, 1986) and PRESTORM (Dickerson et al., 1987) for cloud venting, and ASCOT (Allwine, 1993) and the NGS Visibility Study (Richards et al., 1991) for flows over complex terrain. Thermal effects and drainage flows also evidently play an important role in influencing particulate air quality, as in the occurrence of the Denver "brown cloud" phenomenon (Sloane and Groblicki, 1981).



1        There is considerable field evidence also of synoptic scale transport ( $\leq 2,000$  km) of  
2        airborne particles (see, for example, Gordon, 1991). The impact of such transport is  
3        important on the global scale. That subject is beyond the present scope.

#### 5        **3.4.2.1.2 Field Measurements Related to Dispersion Modeling**

6        Gaussian semi-empirical models have been the basis of most applied diffusion modeling  
7        since their development around 1960. These models were based on Taylor's diffusion theory  
8        of stationary homogeneous turbulence (Taylor, 1921), and were built on a few field  
9        experiments that were quite limited in scope and technology. The results have been  
10       extrapolated far beyond the intended range of downwind distance and ambient conditions.  
11       Some of the extrapolations were guided by statistical theory, but most were freehand  
12       extrapolations (Briggs and Binkowski, 1985). Many research-grade field studies of  
13       atmospheric dispersion have since been performed, but most have been limited to the  
14        $\gamma$ -mesoscale range. These have been reviewed by Draxler (1984), Irwin (1983), Briggs and  
15       Binkowski (1985) and others.  $\beta$ - and  $\alpha$ -mesoscale studies, based on observations of the  
16       dispersion of pollutant and tracer plumes have been reviewed by Moran (1992). Pollutant  
17       plumes remain vertically narrow in stable flows (e.g., elevated power plant plumes released  
18       at night), but rapidly fill up the CBL after fumigation in the daytime (see, for example,  
19       Gillani et al., 1984). Information about spreads of plumes in the elevated stable layers is  
20       particularly limited. The most common basis for estimation of such spreads (expressed as  
21        $\sigma_y$  and  $\sigma_z$ , the RMS variances of lateral and vertical plume spreads) over distances under  
22       100 km or so is the well-known Pasquill-Gifford (P-G) curves for different stability classes  
23       (Gifford, 1961), which make use of the routine meteorological measurements to determine  
24       applicable stability class. The P-G curves were developed mostly from data collected within  
25       the mixing layer. Another set of parameterizations of elevated plume spreads was developed  
26       by TVA (Carpenter et al., 1971) based on twenty years of experience in plume observations  
27       and aerial monitoring. These require the temperature profile to establish atmospheric  
28       stability. More recently, Smith (1981) analysed aircraft measurements in elevated power  
29       plant plumes in different parts of the U.S., mostly in the stable layers, and determined that  
30       the P-G curves overestimated plume spread in stable layers quite substantially both vertically  
31       and horizontally, and that the TVA approach tended to underestimate the horizontal spread,

1 but possibly overestimate the vertical spread. Evidently, there continues to be uncertainty  
2 about plume spreads even at distances under 100 km. Of particular interest is horizontal  
3 plume dispersion, both because it is generally far greater over the mesoscale, and because it  
4 is highly variable. Close to the source, plume spread is largely by progressively larger  
5 turbulent eddies, but after the plume dimension substantially exceeds the scale of these eddies  
6 (typically less than 1 km), dispersion is increasingly by directional wind shear with height.  
7 Such shear is small for the vertically thin nocturnal plume, moderate for the plume in the  
8 CBL, but maximum for the daytime plume which, after maximum vertical spread in the  
9 CBL, enters the nocturnal regime which is often characterized by strong directional shear  
10 effects (Gillani et al., 1984). The average crosswind spread rates of plumes from a large tall  
11 stack power plant emitted within the CBL on summer days in the Midwest were observed to  
12 be in the range 0.25 to 1.0 km per km of downwind transport until the plume attained a  
13 width of about 30 km. Thereafter, further plume spread within the CBL was typically much  
14 slower (Gillani and Pleim, 1994).

15 A common approach in Lagrangian studies of dispersion over long distances has been  
16 to use semi-empirical "mesoscale" dispersion coefficients by analogy with parameterizations  
17 of microscale turbulent spread. An important consequence of Taylor's statistical theory was  
18 that, in stationary homogeneous turbulence,  $s_y$  grew linearly with time at first (for  $t \approx T_L$ ,  
19 the Lagrangian time scale,  $\approx 1$  to 2 min in the CBL), and then asymptotically as  $t^{1/2}$  within a  
20 few kilometers. Observations of a few  $\alpha$ -mesoscale field studies have been interpreted to  
21 suggest that the regime of linear time dependence may apply also at long distances (see, for  
22 example, Pack et al., 1978), with the characteristic time scale ( $T_L$ ) here being related to the  
23 diurnal and/or inertial scale ( $\approx 24$  h). Others have proposed parameterizations of mesoscale  
24  $\sigma_y$  which use powers of  $t$  ranging from 0.85 to 1.5 (see, for example, Carras and Williams,  
25 1988). Thus, there is no consensus about simplistic modeling of mesoscale diffusion over  
26 scales exceeding 24 h. Given the wide range of conditions that plumes can experience  
27 during long range transport in different air masses, over a variety of terrain types, and over  
28 multiple diurnal cycles during different seasons, such a controversy is not surprising. For  
29 transport in the first 24 h, the time and height of emission are critical influencing variables.  
30 Thus, for example, crosswind spreads after 24 h of transport of two plumes released from  
31 the same tall-stack power plant at 0800 and 2000 on a given day are likely to be very

different. During the next diurnal cycle, however, these spreads, as a fraction of downwind distance travelled, are likely to converge. Alternate semi-empirical approaches of representing mesoscale plume dispersion include simulation of relative dispersion of hypothetical co-emitted conservative particles. In conjunction with instantaneous wind data (e.g., pibal soundings), such models have proved to be satisfactory over  $\beta$ -mesoscale distances (e.g., Gillani, 1986), but more work is needed to establish their application over long distances based on hourly-average gridded wind data such as are produced by the meteorological preprocessors of regional Eulerian models. Overall, based on field evidence, particulate air quality is significantly influenced by regional transport and dispersion, but quantitative simulation of these processes is still subject to considerable error.

### **3.4.3 Transformations in Plumes**

#### **3.4.3.1 Gas-to-Particle Conversion in Plumes**

A number of field studies of gas-to-particle conversion have been conducted in the plumes of large point-sources of  $\text{SO}_x$  and  $\text{NO}_x$  (e.g., coal- and oil-fired power plants and metal smelters). Fewer studies have focused on urban-industrial plumes. These studies have focused principally on quantifying the rates of aerosol formation and, to a lesser extent, on investigating the mechanisms. Mechanistic studies are more difficult, particularly when multiple mechanisms are co-active, as is commonly the case. In the NAPAP emissions inventory for base year 1985 (Placet et al., 1991), about 70% of the U.S. anthropogenic emissions of  $\text{SO}_2$ , and about 25% of the corresponding emissions of  $\text{NO}_x$ , were attributed to large point-sources with stack heights exceeding 120 m (probably less than 150 individual sources). The contribution of such sources is even higher in the eastern U.S., particularly in the Ohio and Tennessee River Valleys. Clearly, these large emissions are very important in the context of regional aerosols. Fortunately, many of these sources are located in rural areas, and their plume chemistry can be studied in isolation from the complications of interactions with other plumes. Much of the remaining anthropogenic emissions of  $\text{SO}_x$  and  $\text{NO}_x$  are contributed by urban-industrial area sources.

### 3.4.3.1.1 *Plume Studies*

Power plant and urban plume studies of SO<sub>2</sub>-to-sulfate transformations published before 1980 have been reviewed by Newman (1981) and in the earlier 1982 PM/SO<sub>x</sub> Air Criteria Document (U.S. Environmental Protection Agency, 1982). Only a brief overview of those studies is provided here; the main focus here is on plume studies published after 1980. Since the plume mass is airborne, the most meaningful plume studies are based on measurements made from instrumented aircraft. Early studies (pre-1975) often reported SO<sub>2</sub> oxidation rates as high as 50% h<sup>-1</sup>. They are now generally considered to be flawed due to limitations in the measurement technology then available. This technology has made major strides since. For example, the development of the filter pack (Forrest and Newman, 1973) has proved to be a useful method of simultaneous collection of high-volume samples of SO<sub>2</sub> and particulate sulfur. Such samples, however, only provide average concentrations over entire plume cross-sections or, at best, over long crosswind plume traverses. The development of continuous monitors for both SO<sub>2</sub> and particulate sulfur (Huntzicker et al., 1978; Cobourn et al., 1978) made it possible to study sulfate formation with crosswind plume detail. Such detail during a single plume traverse contains a nearly instantaneous snapshot of the full spectrum of chemistry between the high-NO<sub>x</sub> regime in plume core to the low-NO<sub>x</sub> regime at plume edge (Gillani and Wilson, 1980). With cross-sectionally averaged measurements, such a spectrum can only be discerned in measurements ranging from near-source to far downwind. The technology of continuous measurements of nitrogen species with high sensitivity has also evolved greatly since 1980.

The period between 1974 and 1981 was very active in terms of plume studies focused particularly on estimating the rate of oxidation of SO<sub>2</sub>. Studies by Brookhaven National Laboratory (Newman et al., 1975a,b; Forrest and Newman, 1977a,b) and TVA (Meagher et al., 1978) in coal- and oil-fired power plant plumes as well as a nickel smelter plume generally yielded low oxidation of SO<sub>2</sub> (seldom exceeding 5% over 50 km and several hours of plume transport, with an uncertainty of about a factor of two). These investigators found the oxidation rate to be highest close to the source, where it appeared to be correlated with plume particulate loading, and interpreted the oxidation to be due to a heterogeneous second-order mechanism which became quenched as the plume diluted (Schwartz and Newman, 1978). These results were in sharp contrast to those of Husar et al. (1976) for a coal-fired

1 power plant plume, also over about 50 km of plume transport, which showed the oxidation  
2 rate to be slow during an early induction period, increasing thereafter to as much as 5% h<sup>-1</sup>.  
3 No mechanistic interpretation was proposed by these authors. This controversy was resolved  
4 by the subsequent findings of Gillani et al. (1978) resulting from two case studies which  
5 were remarkable for their coverage of downwind range exceeding 300 km and 10 to 12 h of  
6 transport of a coal-fired power plant plume during daylight as well as dark. The authors  
7 found the oxidation rate of SO<sub>2</sub> to be strongly correlated with sunlight, and also with the  
8 extent of plume dilution, and background ozone concentration (considered to be a surrogate  
9 for background reactivity). Maximum measured particulate sulfur as a fraction of total  
10 plume sulfur ranged as high as 18%. The daytime conversion rate in the plume was slow at  
11 first, but increased as the plume diluted, reaching maximum values on the two days of  
12 1.8 and 3.0% h<sup>-1</sup> in the afternoon. Such rates are consistent with theoretical rates based on  
13 the SO<sub>2</sub>-OH reaction (Calvert et al., 1978; Höv and Isaksen, 1981). The entire plume  
14 transport on both occasions was in fairly dry environment (R.H. < 70%). Presumably, the  
15 mixing of plume NO<sub>x</sub> and background VOC led to photochemistry which generated the  
16 necessary oxidants for gas-phase oxidation of SO<sub>2</sub>. The measurements of VOC in the  
17 background were both sparse and of limited reliability. The study also found the formation  
18 of substantial excess of ozone in aged plumes. The interpretation based on plume-  
19 background interaction satisfactorily explained the results of the BNL and TVA studies in  
20 which the measurements of low oxidation of SO<sub>2</sub> were all in coherent stable elevated plumes  
21 during early morning and evening hours (low sunlight and little plume dilution), as well as of  
22 Husar et al., whose measurements were in the more polluted and convective summer daytime  
23 CBL.

24 As of the end of the 1970s, a number of factors had been implicated as being relevant  
25 to plume sulfur chemistry. Gillani and Wilson (1980) conducted a systematic investigation of  
26 the dependence of ozone and aerosol formation in power plant plumes on a variety of  
27 possible influencing factors, based on the plume data of five case studies. They found that  
28 temperature variations in the range 28 to 33 °C, and R.H. variations in the range 50 to 80%  
29 did not have an appreciable influence; the importance of sunlight, plume dilution and  
30 background composition was reconfirmed. Eatough et al. (1981, 1982) have observed a

1 positive temperature dependence of a linear SO<sub>2</sub> oxidation rate in power plant and smelter  
2 plumes in western U.S. in the temperature range 0 to 30 °C.

3 Gillani and Wilson (1980) also presented direct evidence and interpretation of the role  
4 of plume-background interactions in plume photochemistry within the context of a common  
5 pattern of diffusion-limited plume chemical evolution through three stages in a moderately  
6 polluted environment. In the "early" stage, the plume is narrow and dominated by a high-  
7 NO<sub>x</sub> regime in which ozone and other oxidants are sharply depleted by reaction with plume  
8 NO and SO<sub>2</sub>; the VOC-NO<sub>x</sub> chemistry, SO<sub>2</sub> oxidation, and aerosol formation are inhibited in  
9 the plume in this stage. As the plume spreads and dilutes with a background characterized  
10 by relatively high VOC/NO<sub>x</sub> ratio, the VOC/NO<sub>x</sub> ratio increases also in plume edges. This  
11 "intermediate" stage of plume chemistry is characterized by rapid formation of ozone and  
12 aerosols in plume edges, leading to an observed excess there of ozone over the background  
13 (ozone "wings") while the plume core still has an ozone deficit. Sharp "wings" of Aitken  
14 nuclei concentration have also been observed in plume edges at times, indicating directly the  
15 nucleation of new aerosol (Wilson, 1978; Gillani et al., 1981). With continuing dilution, the  
16 plume ultimately develops a condition of low-NO<sub>x</sub>, high VOC/NO<sub>x</sub> ratio and, in the summer,  
17 an ozone "bulge" throughout. In this "mature" stage, the rate of oxidation of SO<sub>2</sub> to sulfates  
18 (and presumably also of NO<sub>x</sub> to secondary products) reaches its peak.

19 Gillani et al. (1981) provided a quantitative interpretation of the above observations by  
20 developing an empirical parameterization of the gas-phase conversion rate of SO<sub>2</sub> to sulfate  
21 in terms of measured variables representing sunlight, mixing and background reactivity. The  
22 parameterization was verified based on the "dry" data of three different power plant plumes  
23 over ten days of measurements in two different summer periods. Crosswind-resolved  
24 reactive plume models capable of facilitating plume-background interactions and including  
25 detailed simulation of chemical kinetics have been developed and applied by Höv and Isaksen  
26 (1981), Stewart and Liu (1981), and Gillani (1986). These models can depict the observed  
27 behavior of ozone in the three plume stages. Their applications have shown that the  
28 evolution of OH in the plume (a measure of oxidation potential) mimics the above description  
29 of ozone evolution (Höv and Isaksen, 1981), and that plume oxidant and aerosol formation  
30 are very sensitive to background VOC and their ingestion into the plume (Gillani, 1986).  
31 However, these models continue to remain unevaluated adequately owing to a continuing lack

1 of data characterizing the composition of plume background (especially VOC) and the  
2 crosswind detail of important intermediate and secondary species (e.g., OH, HO<sub>2</sub>, HNO<sub>3</sub>,  
3 etc.).

4 A number of plume studies have verified the sunlight dependence of the SO<sub>2</sub> oxidation  
5 process, observing higher seasonal conversion rates during summer, and higher diurnal rates  
6 during midday (Husar et al., 1978; Lusi et al., 1978; Roberts and Williams, 1979; Meagher  
7 et al., 1981; Hegg and Hobbs, 1980; Gillani et al., 1981; Forrest et al., 1981; Williams  
8 et al., 1981; Wilson, 1981; Wilson and McMurry, 1981; Liebsch and de Pena, 1982).

9 In these studies, the peak daytime conversion rate was typically between 1 and 5% h<sup>-1</sup> in the  
10 summer (higher under humid conditions), and much lower in winter. Wilson (1981)  
11 reviewed the data of twelve power plant and smelter plumes in the U.S., Canada and  
12 Australia, covering measurements during day and night, and summer and winter. The main  
13 conclusion was that diurnally, midday conversion rates were relatively high and quite  
14 variable (1 to 10% h<sup>-1</sup>), while the nighttime conversion rates were generally low (under  
15 0.5% h<sup>-1</sup>). Also, the rates were found to be lower in winter than in summer.

16 Geographically, the measured plume conversion rates in the arid and relatively clean  
17 southwestern U.S. environment were found to be particularly low (0.5% h<sup>-1</sup>) at all times,  
18 including summer midday. Williams et al. (1981) also found the rates to be low in a smelter  
19 plume in the arid, clean environment of north central Australia ( $\approx 0.15\%$  h<sup>-1</sup> averaged over  
20 24 h of transport).

21 Gillani et al. (1981) were able to formulate the parameterization of the gas-phase  
22 conversion rate by isolating case studies performed entirely in dry conditions when liquid-  
23 phase contributions were negligible. They also observed that for all cases when the plume  
24 had any history of wet exposure (clouds, fogs or high humidity), the oxidation of SO<sub>2</sub>  
25 invariably proceeded at a rate faster than that predicted by the gas-phase parameterization.  
26 Whereas the typical range of the peak summer daytime conversion rate was 1 to 5% h<sup>-1</sup> in  
27 Project MISTT (Missouri, Illinois), it was closer to 1 to 10% h<sup>-1</sup> in the more humid  
28 conditions of the Tennessee Plume Study (Tennessee, Kentucky). In the wetter daytime  
29 situations, evidently, liquid-phase chemistry was superposed over the underlying gas-phase  
30 chemistry. Gillani and Wilson (1983) focused their study on the plume data of such "wet"  
31 situations. They attributed to liquid-phase chemistry the part of the total measured

conversion rate which was in excess of the rate estimated by the gas-phase parameterization. The liquid phase was found to be due to clouds, fogs and light rain, or due to wetted aerosols under conditions of high ambient humidity (R.H. > 75%). The liquid-phase contribution to the conversion rate was found to be in excess of 40% of the total in two-thirds of the cases analysed, being as high as 8% h<sup>-1</sup> averaged over the whole plume over 6 h of transport in the most extreme case (clouds and light rain). Similar increases in conversion rates in power plant plumes interacting with high humidity have also been observed by others (e.g., Dittenhofer and de Pena, 1978; Eatough et al., 1984).

Determination of the liquid-phase conversion rate involves quantification not only of the kinetics, but also of the discrete and variable extent of plume-cloud interaction. Gillani et al. (1983) formulated a parameterization of the conversion rate for plume-cloud interaction in which the physical extent of such interaction was represented probabilistically, and the higher liquid-phase conversion rate was applied only for the in-cloud portion of the plume. The application of the parameterization to a case study corresponding to summer daytime plume transport within the CBL, in patchy contact with fair-weather cumulus above, permitted estimation of the average in-cloud conversion rate averaged over 7 h (1000 to 1700) to be 12% h<sup>-1</sup>. Considering that the corresponding average liquid water content in the clouds was certainly less than 1 g m<sup>-3</sup> (1 ppm), much higher actual oxidation rates within individual droplets are indicated. Gas-phase photochemistry at a much slower rate was concurrently quite active in the more extensive drier parts of the plume below, producing ozone and other oxidants which contributed to gas-phase as well as liquid-phase sulfur chemistry. It was not possible to relate the in-cloud kinetic rate to the critical variables controlling it, such as cloud liquid water content, H<sub>2</sub>O<sub>2</sub> concentration, or droplet pH, because such measurements were not made. The role of concurrent gas-phase photochemistry is indeed essential to provide the oxidizing agents of liquid-phase chemistry. Clark et al. (1984) found the contribution of liquid-phase chemistry in a power plant plume to be negligible during long-range transport over water in a shallow stratocumulus-filled boundary layer, with limited plume dilution, low insolation, and little photochemistry.

A quite different approach based on aerosol growth laws applied to aerosol size distribution data was taken by McMurry et al. (1981) and McMurry and Wilson (1982) to study relative contributions of the principal mechanisms of gas-to-particle conversion.



1 Theory predicts different growth laws for different chemical mechanisms of aerosol  
2 formation. The authors examined the functional dependence of calculated particle diameter  
3 growth rate on particle diameter. By matching field data with theoretical growth laws, it was  
4 possible to differentiate between mechanisms. Application of this approach indicated gas-  
5 phase chemistry and condensation of the product to be the predominant mechanism of aerosol  
6 formation in several power plant plumes in eastern and western U.S., with increasing  
7 contribution of heterogeneous mechanisms with increasing humidity (McMurry et al., 1981);  
8 in a case study of the urban plume of St. Louis, 75% and 25% of the aerosol formation were  
9 attributed to homogeneous and heterogeneous mechanisms, respectively, while most of the  
10 aerosol formation in the ambient air in the Great Smokey Mountains where relative  
11 humidities were high (up to 95%) was attributed to the droplet-phase mechanism (McMurry  
12 and Wilson, 1982).

13 In an overview of empirical parameterizations of sulfur transformations in power plant  
14 plumes, Gillani (1985) estimated that on a 24-h average basis, sulfate formation rates in a  
15 large power plant plume in the U.S. Midwest in July 1976 were likely to be  $0.8 \pm 0.3\% \text{ h}^{-1}$   
16 by gas-phase reactions (midday peak  $\approx 2.6\% \text{ h}^{-1}$ ) and at least half as much by liquid-phase  
17 reactions. Winter rates were estimated to be an order of magnitude lower than the summer  
18 rates for the gas-phase mechanism, but comparable for the liquid-phase mechanism. Since  
19 1981, no new field studies of chemistry in large point-source plumes have been conducted in  
20 the eastern U.S. A comprehensive plume study with state-of-the-art aircraft measurements of  
21 primary and secondary sulfur and nitrogen species, as well as VOC and ozone, is planned to  
22 occur in the summer of 1995 as part of the Southern Oxidant Study (SOS) Nashville Field  
23 Measurement Program.

24 Information about field measurements of nitrate formation in point-source combustion  
25 plumes is much more meager. Summertime plume measurements suggest that nitrate  
26 formation is principally in the form of nitric acid vapor (Hegg and Hobbs, 1979; Richards  
27 et al. 1981), and that oxidation of  $\text{NO}_x$  to  $\text{HNO}_3$  may proceed about three times faster than  
28 the rate of oxidation of  $\text{SO}_2$  (Richards et al., 1981; Forrest et al., 1981). Richards et al.  
29 (1981) observed that along the transport of the Navajo Generating Station in Arizona, there  
30 was adequate ammonia to neutralize the sulfate formed in the plume, but not enough to form  
31 ammonium nitrate. Forrest et al. (1981) found  $\text{NH}_4^+/\text{SO}_4^{2-}$  to increase with downwind

1 distance and was mostly less than 2 (not enough to fully neutralize the sulfate), but  
2 sometimes more than 2, indicating a possibility of the formation of some ammonium nitrate.  
3 Eatough et al. (1981) observed that in the western desert region, the neutralization of sulfuric  
4 acid in plumes was due not only to ammonia, but also to other basic material (e.g., metal  
5 oxides and  $\text{CaCO}_3$ ).

6 Field information about secondary formations in urban plumes is scantier than for  
7 power plant plumes for sulfur compounds, but possibly slightly more for nitrogen  
8 compounds. White et al. (1976, 1983) reported slow formation of ozone and aerosols at first  
9 in the St. Louis urban plume, but faster rates farther downwind. Average sulfate formation  
10 rates between successive downwind measurement locations on summer days were estimated  
11 at 2 to 4%  $\text{h}^{-1}$ . Isaksen et al. (1978) applied a reactive plume model to a subset of the  
12 St. Louis data, and estimated peak rates for the formation of sulfuric and nitric acid of 5 and  
13 20%  $\text{h}^{-1}$ , respectively. Based on the same data set, Whitby (1980) estimated that about  
14 1,000 tons of secondary fine aerosol may be produced in the plume in one summer  
15 irradiation day. Alkezweeny and Powell (1977) estimated peak sulfate formation rates in the  
16 St. Louis plume at 10 to 14%  $\text{h}^{-1}$ . Miller and Alkezweeny (1980) reported sulfate formation  
17 rates in the Milwaukee urban plume on two summer days in very different air masses to  
18 range from 1%  $\text{h}^{-1}$  (clean background) to 11%  $\text{h}^{-1}$  (polluted background). The most  
19 extensive studies of  $\text{NO}_x$  chemistry in urban plumes have been reported by Spicer and  
20 co-workers. They have reported results for the Los Angeles, Phoenix, Boston and  
21 Philadelphia urban plumes. In the Los Angeles studies, the transformation rate of  $\text{NO}_2$ -to-  
22 products was estimated at 5 to 15%  $\text{h}^{-1}$  (Spicer, 1977) and 5 to 10%  $\text{h}^{-1}$  (Spicer et al., 1979).  
23 The sum of transformation plus removal rates was estimated for the Phoenix and Boston  
24 plumes at <5%  $\text{h}^{-1}$  and 14 to 24%  $\text{h}^{-1}$ , respectively. The low rate for Phoenix was  
25 attributed partly to thermal decomposition of PAN after its formation in the plume. In a  
26 study of the Detroit plume, Kelly (1987) estimated the  $\text{NO}_x$  transformation rate at 10%  $\text{h}^{-1}$ ,  
27 with 67 to 84% of the products being in the form of  $\text{HNO}_3$ . Measured concentrations of  
28 nitric acid, however, were much lower because of its higher removal rate. All of the above  
29 urban plume studies, and most of the power plant plume studies, have been daytime studies.  
30 Field measurements of nighttime chemistry of nitrogen oxides in plumes are almost non-  
31 existent.

#### 3.4.3.1.2 Background Field Studies

Attention is now focused on studies of aerosol formation in background air. The plume studies have shown that the *rates* of oxidation of SO<sub>2</sub> and NO<sub>x</sub> in the background represent approximately the upper limit of the conversion rates in the plume. In non-humid, moderately polluted conditions, they range typically between 1 and 5% h<sup>-1</sup> for midday SO<sub>2</sub> oxidation in summer in the eastern U.S. (depending on the variability of VOC/NO<sub>x</sub> and the composition of VOC), and up to 1% h<sup>-1</sup> in the cleaner parts of the Western U.S. Winter rates are about an order of magnitude lower. By contrast, observed NO<sub>x</sub> to nitrate conversion rates are about three times faster in summer than in winter (Parrish et al., 1986). Aerosol nitrate formation depends strongly on availability of NH<sub>3</sub> and on temperature. Background aerosol is generally more aged and its acidity more neutralized than plume aerosol.

The situation is more complex in humid conditions. Field measurements of the compositions of cloudwater, rainwater and the precursor clear-air aerosol have shown that strong acidity is substantially greater in cloud and rain water than in the clear-air aerosol (Daum et al., 1984; Lazrus et al., 1983; Weathers et al., 1988). This is indicative of the contribution of aqueous-phase chemistry to cloudwater acidity in excess of that due to scavenged aerosol. Based on climatological data of clouds and SO<sub>2</sub> distribution, and assuming aqueous-phase oxidation of SO<sub>2</sub> by ozone, Hegg (1985) estimated contribution of the aqueous mechanism to global tropospheric sulfate production to be at least 10 to 15 times greater than that due to the gas-phase mechanisms. Applications of more comprehensive global models have given estimated aqueous-phase contributions of 40 to 95% of the total sulfate production (Langner and Rodhe, 1991 and references therein). Regional models for North America suggest 50 to 80% of the sulfate deposited in precipitation to be formed in clouds (Fung et al., 1991; McHenry and Dennis, 1991).

A number of ambient studies have attempted to study aqueous chemistry based on *in situ* measurements in clouds. Determination of the rates and mechanisms of aqueous-phase chemistry is particularly ambiguous for several reasons. First, it is difficult to distinguish between the contributions of *in situ* chemistry and aerosol scavenging to the observed concentration of the solute in the droplet phase. Also, aqueous chemistry rate depends not only on the change in concentration, but also on the change in time. It is difficult enough to

determine the difference in concentration of even one reactant or product species, but determining the corresponding *time* difference is even more difficult (Schwartz, 1987; Gervat et al., 1988; Kelly et al., 1989). In stratiform clouds, in particular, it is not always possible to determine what constitutes pre-cloud air corresponding to specific cloud water samples (Gillani et al., 1994). Finally, it is difficult, based on field data, to attribute the inferred chemistry to specific mechanisms (oxidation by  $\text{H}_2\text{O}_2$  or  $\text{O}_3$ , etc.). The conclusions regarding rates and mechanisms of aqueous chemistry based on measurements in clouds are therefore quite uncertain, and have been a source of considerable controversy (e.g., Hegg and Hobbs, 1982, 1983a,b versus Schwartz and Newman, 1983). One important finding in support of in-cloud oxidation of  $\text{SO}_2$  by  $\text{H}_2\text{O}_2$ , however, is the almost universal mutual exclusion of these two species in non-precipitating stratiform clouds (Daum et al., 1984; Daum, 1988). In such clouds, there is generally enough time available for the species to react fully until the one with the lower concentration in the precursor air is depleted. The implication is that the aqueous-phase oxidation of  $\text{SO}_2$  by  $\text{H}_2\text{O}_2$  takes precedence over other competing reactions.

Most field studies have been limited to estimating the amount or fraction of sulfate formed by the aqueous pathway, rather than the rate of formation. Liu et al. (1993) have summarized the results of a number of cloud studies between 1979 and 1991. In these studies, a number of different approaches have been used to resolve the contributions of aerosol scavenging and *in situ* chemistry to the observed cloudwater sulfate. The study of Liu et al. (1993), which was part of the first intensive (summer 1988) of the Eulerian Model Evaluation Field Study (EMEFS), used three different approaches for estimating the scavenged fraction of observed sulfate, and attributed 27 to 55% of cloudwater sulfate to *in situ* production. The inferred results for the aqueous-phase production of sulfate in the collective studies vary widely. In winter studies, such production is low (e.g., Strapp et al., 1988), while in summer studies, it is generally higher (e.g., Mohnen and Kedlacek, 1989). Many studies implicate  $\text{H}_2\text{O}_2$  as the principal oxidant (e.g., Van Valin et al., 1990), while others implicate ozone (e.g., Hegg and Hobbs, 1986).

There is a variety of evidence for and against the formation of  $\text{HNO}_3$  in the cloud environment (e.g., Lazrus et al., 1983; Daum et al., 1984; Hegg and Hobbs, 1986; Leaitch et al., 1986a). The heterogeneous mechanism involving  $\text{N}_2\text{O}_5$  has received attention mostly

1 as the "nighttime" mechanism (Lazrus et al., 1983; Richards, 1983) owing to the short life of  
2 the  $\text{NO}_3$  radical (precursor of  $\text{N}_2\text{O}_5$ ) in sunlight. To account for the comparable measured  
3 amounts of sulfate and nitrate deposited in winter storms in Ontario, Barrie (1985) suggested  
4 the possibility of the  $\text{N}_2\text{O}_5$  mechanism for wintertime formation of nitrate in clouds. Leaitch  
5 et al. (1988) found substantial enhancement of  $\text{NO}_3^-$  in and near clouds on 8 of 12 days of  
6 winter measurements in central Ontario under freezing conditions and low insolation.  
7 On these occasions, variations in  $\text{NO}_3^-/\text{SO}_4^{2-}$  were associated with  $\text{H}^+/\text{SO}_4^{2-}$  in the cloud water,  
8 implicating  $\text{HNO}_3$ . Also, the observed levels of  $\text{NO}_3^-$  could not be simulated in a model  
9 without invoking the  $\text{N}_2\text{O}_5$  mechanism. Based on a detailed examination of the nighttime  
10 behavior of the  $\text{NO}_3$  radical, Noxon (1983) concluded that there was a significant loss of  
11  $\text{NO}_3$  compared to  $\text{N}_2\text{O}_5$  by an unknown scavenger (wet particles?). In measurements at a  
12 rural site in central Ontario in August 1988 as part of EMEFS, Li et al. (1993) observed a  
13 gradual increase in the concentration of aerosol nitrate ( $\text{NO}_3^-$ ) from 1800 to midnight, and  
14 then a gradual decrease. In a diagnostic model study, they concluded that the observations  
15 could be explained by heterogeneous reactions of  $\text{NO}_3$  and  $\text{N}_2\text{O}_5$  on wet particles. They  
16 attributed more than 80% of the  $\text{NO}_3^-$  formation to  $\text{NO}_3$  and about 10% to  $\text{N}_2\text{O}_5$ , and less  
17 than 5% to  $\text{HNO}_3$ .

18 In visibility studies, the water content of aerosols is of crucial importance. The  
19 estimation of visibility impairment involves use of models in conjunction with ambient data  
20 of both aerosols and relative humidity. Frequently, both sets of data are not available  
21 concurrently for all stations in a monitoring network such as IMPROVE (Interagency  
22 Monitoring of PROtected Visual Environments). In such cases, gaps in information must be  
23 filled by the use of empirical relationships between average visibility impairment caused by  
24 soluble aerosols and average relative humidity derived from the available concurrent data.  
25 Such an application based on data at the 36 national IMPROVE sites is described by Sisler  
26 and Malm (1994).

27 Another important area which critically involves water uptake by soluble aerosols  
28 relates to aerosol-cloud interactions. Such interactions are a critical link in cloud formation  
29 and the global water cycle, in cloud optics and the global energy budget, in pollutant  
30 redistribution by clouds, in pollutant wet removal from the atmosphere, and in atmospheric  
31 chemistry. Of particular importance is the process of aerosol scavenging by clouds.

1 Interstitial aerosols in clouds may become incorporated into cloud droplets by "activation"  
2 (droplet nucleation), Brownian diffusion, inertial impaction, coalescence, and phoretic  
3 effects. Of these microphysical cloud processes, aerosol activation is by far the most  
4 important. A soluble particle (the CCN) is activated when water vapor supersaturation  
5 around it ( $S$ ) exceeds a critical value ( $S_c$ ) which depends principally on particle dry size ( $D_0$ )  
6 and composition (commonly expressed in terms of the water-soluble solute fraction,  $\epsilon$ ). The  
7 works of Köhler (1936), Junge and McLaren (1971) and Hänel (1976) provide the underlying  
8 theory for condensation of water on aerosols based on assumptions of internally mixed  
9 aerosols. Based on properties of representative continental and marine CCN, Junge and  
10 McLaren predicted that  $S_c$  would be sensitive to CCN size, but to CCN composition only for  
11  $\leq 0.1$ . Fitzgerald (1973) confirmed the insensitivity to  $\epsilon$  in the range 0.15 to 0.35 based on  
12 simultaneous measurements of CCN size,  $\epsilon$  and CCN activation spectra (functional  
13 dependence of activated fraction of aerosol on  $S$ ) for  $S$  between 0.35 and 0.75%.

14 More recently, based on extensive year-long measurements of CCN spectra for  
15 continental aerosols (representative of eastern U.S. background), separated into narrow size  
16 bands within the accumulation mode, Alofs et al. (1989) derived a simple semi-empirical  
17 expression relating  $S_c$  to  $D_0$  and  $\epsilon$  applicable down to  $S = 0.014\%$ . They also showed,  
18 based on their own data and a literature review, that for continental aerosols in industrialized  
19 regions,  $\epsilon \approx 0.5$  is a reasonable approximation, indicating that the activation of such  
20 aerosols is unlikely to be sensitive to particle composition. Based on their expression for  $S_c$   
21 and using  $\epsilon = 0.5$ , a supersaturation of about 0.1% (characteristic for stratiform clouds)  
22 would be adequate to activate most of the accumulation mode particles exposed to a cloud.  
23 Cumuliform clouds with higher  $S$  would activate many Aitken mode particles also. In  
24 cumulus clouds, peak supersaturation is typically attained near cloud base, which is where  
25 maximum activation is likely to occur. The cloud module of the Regional Acid Deposition  
26 Model (RADM) is based primarily on a cumulus parameterization, and makes the assumption  
27 of 100% cloud scavenging efficiency for sulfates formed from the oxidation of  $\text{SO}_2$  (Chang  
28 et al., 1990).

29 The principal interest in quantitative field studies of aerosol-cloud interactions is the  
30 scavenging of acidic aerosol mass by clouds. The focus of measurements in these studies  
31 (from aircraft or at fixed mountain sites) was on gross spatial averages (over 10s of km) of

species mass concentrations (mostly of sulfate and nitrate) based on batch samples collected in cloud water, and in cloud and clear air (Scott and Laulainen, 1979; Sievering et al., 1984; Daum et al., 1984, 1987; Hegg et al., 1984; Hegg and Hobbs, 1986; Leaitch et al., 1986b; Pueschel et al., 1986). In some studies, continuous measurements of aerosol size spectra were used to derive spatially-averaged aerosol volume concentrations (Leaitch et al., 1983; Hegg et al., 1984; Heintzenberg et al., 1989) based on which, aerosol volume scavenging efficiency was inferred. In one study, continuous measurements of light scattering coefficient were used as a surrogate for aerosol mass concentration (ten Brink et al., 1987). In these studies, inferences of the efficiency of aerosol scavenging were generally based on comparisons of species mass or volume concentrations (or their surrogates) in cloud water and/or cloud interstitial air with those in putative pre-cloud air. Such inferences can be confounded by incorrect identification of pre-cloud air, non-Lagrangian sampling, extended sampling periods and resultant averaging of spatial inhomogeneities (including clear air pockets within clouds), and inadequately resolved contributions of aqueous-phase chemistry. Not surprisingly, the results of the above studies varied quite widely. Most commonly, however, mass scavenging efficiency was found to be high ( $>0.8$ ).

The above studies based on spatially-averaged particle *mass* concentrations could not address the issue of main concern with respect to radiative transfer, namely, the partitioning of cloud particles between droplets and interstitial aerosol in terms of their local *number* concentrations. Field studies focused on aerosol scavenging based on particle number concentrations are relatively scarce. In the study of Leaitch et al. (1986) for stratiform and cumuliform clouds, the authors took special care to ensure Lagrangian adiabatic interpretation by comparing the instantaneous cloud droplet number concentration at a single location within the adiabatic updraft core near cloud base with the below-cloud aerosol number concentration. They found that activation efficiencies so defined were generally high when pre-cloud AMP concentrations were less than about  $750\text{ cm}^{-3}$ , but dropped off non-linearly at higher particle loading. Raga and Jonas (1993) made a similar observation when comparing droplet concentrations near cloud top with the sub-cloud aerosol concentrations on the assumption that the latter represented the pre-cloud condition.

Gillani et al. (1994) demonstrated that such an assumption was not generally valid in stratiform clouds which are layered and may include sharp inversions decoupling the layers

1 from each other and from the sub-cloud layer. For such clouds, the adiabatic assumption  
2 made in 1-D cloud models is not generally valid. To circumvent this difficulty with respect  
3 to identification of pre-cloud air, Gillani et al. defined fractional activation (F) in terms of  
4 local variables only, as the ratio of cloud droplet concentration (activated particles) to total  
5 particle concentration (droplet concentration + concentration of unactivated accumulation-  
6 mode particles, 0.17 to 2.07  $\mu\text{m}$  diameter). In their study (aircraft measurements in and near  
7 stratiform clouds near Syracuse, NY in the Fall of 1984), continuous *in situ* measurements  
8 were available for particle number concentrations in 15 size classes each for the droplets and  
9 for dried (by heating the probe inlet air) interstitial aerosols. Thus, they were able to  
10 determine F at a high spatial resolution throughout the clouds studied (continental stratiform).  
11 It was determined that accumulation-mode particles larger than 0.37  $\mu\text{m}$  were efficiently  
12 activated in the cloud under all measurement conditions, but that particles in the range 0.17  
13 to 0.37  $\mu\text{m}$  were often activated only partially. Partial activation generally correlated with  
14 high local total particle concentration ( $> 600 \text{ cm}^{-3}$ ) and with low temperature lapse rate  
15 (surrogate for cooling rate with ascent,  $dT/dt = w \cdot dT/dz$ , where  $w$  = the mean long-wave  
16 updraft speed), the two conditions most responsible for limiting supersaturation. It is  
17 important to note that  $w$  is a most difficult quantity to measure, and is not generally available  
18 in field measurements. Under the most polluted conditions in a stable stratus, fractional  
19 activation of the accumulation-mode particles was as low as 0.1 in the core of the cloud.  
20 Statistically, based on ten days of measurements in the Syracuse study, it exceeded 0.9 in  
21 36% of the data in cloud interior, but was below 0.6 in 28% of such data. It was generally  
22 quite low in cloud edges. Evidently, the assumption made in RADM of total activation is  
23 questionable for stratiform clouds.

24 Simple parameterizations of fractional activation in clouds have been developed based  
25 on 1-D adiabatic Lagrangian models (e.g., Twomey, 1959; Ghan et al., 1993), and generally  
26 highlight the significance of particle loading and updraft speed (model calculated). The 1-D  
27 adiabatic approach is useful near cloud base and in updraft cores, but it breaks down near  
28 cloud edges and in the upper portions of clouds where entrainment and mixing effects are  
29 substantial. It is also questionable in the presence of additional complexities such as cloud  
30 layering (Gillani et al., 1994) and lifting and sinking motions (Baker and Latham, 1979;  
31 Pruppacher and Klett, 1978). These complex effects result in three-dimensional spatial



1 inhomogeneities and multi-modal droplet size spectra which are uncharacteristic of the simple  
2 adiabatic model.

3 Noone et al. (1992) studied activation in ground fogs. They were able to infer size-  
4 segregated volume and number scavenging efficiencies of aerosols (using a counterflow  
5 virtual impactor) in the fog under conditions of very high particle loading and extremely low  
6 supersaturations. For such highly-polluted fog conditions, they found high activation  
7 efficiencies ( $> 0.8$ ) only for particles larger than  $0.8 \mu\text{m}$ .

8 In most cloud and fog studies which include considerations of particle composition, use  
9 is made of the concept of water-soluble mass fraction ( $\epsilon$ ). This implicitly assumes internally  
10 mixed particles. As was shown by Zhang et al. (1993), there may really be two  $\epsilon$ 's, one  
11 ( $\epsilon_m$ ) for the "more" hygroscopic particles, and one ( $\epsilon_l$ ) for the "less" hygroscopic aerosols.  
12 In the diagnostic modeling study of Pitchford and McMurry (1994), the two- $\epsilon$  concept was  
13 implemented. For clouds and fogs, this implies that  $S_c$  may be different for different  
14 particles in the same size range.

15 The interaction between aerosols and clouds modifies not only the clouds, but also the  
16 aerosols. The condensation-evaporation cycling of aerosols through non-precipitating clouds  
17 generally results in growth of the nuclei due to microphysical and chemical processes during  
18 their in-cloud residence (Hoppel, 1988; Hoppel et al., 1990).

## 21 3.5 DRY DEPOSITION

### 22 3.5.1 Theoretical Aspects of Dry Deposition

23 Dry deposition is commonly parameterized by the deposition velocity,  $V_d$  ( $\text{m s}^{-1}$ ) which  
24 is defined as the coefficient relating the pollutant deposition flux  $F$  ( $\text{g m}^{-2}\text{s}^{-1}$ ) and the  
25 pollutant concentration  $c$  ( $\text{g/m}^3$ ) at a certain reference height above the surface, i.e.,  
26

$$F = V_d c \quad (3-39)$$

27  
28 The deposition velocity can be expressed as the inverse of a sum of "resistances" in three  
29 layers adjacent to the surface (Sehmel, 1980; Hicks, 1982):  
30

1. The aerodynamic layer, i.e., the layer in which atmospheric turbulent fluxes are constant (typically extending to about 20 m above the ground). In this layer, pollutant transfer, whether gas or particle, is controlled by atmospheric turbulence.
2. The surface (or quasi-laminar) layer, a thin layer ( $\sim 1$  mm) just above the surface in which transport occurs by molecular diffusion. In this layer, gases transfer to the surface by molecular diffusion and particles undergo Brownian diffusion and inertial impaction.
3. The earth/canopy/vegetation surface, the actual pollutant sink

For gases, the deposition velocity is a function of these three types of resistance as follows:

$$V_d = (r_a + r_s + r_c)^{-1} \quad (3-40)$$

where  $r_a$  is the atmospheric resistance through the aerodynamic layer,  $r_s$  is the surface layer resistance, and  $r_c$  is the canopy/vegetation resistance. All resistances are in units of  $s\ m^{-1}$ .

The aerodynamic resistance  $r_a$  can be expressed (Wesley and Hicks, 1977) by:

$$r_a = \frac{1}{k u_*} [\ln(z_s/z_o) - \phi_h] \quad (3-41)$$

where  $z_s$  is the reference height (m) ( $\sim 10$  m),  $z_o$  is the roughness length (m),  $k$  is the von Kármán constant (0.4),  $u_*$  is the friction velocity ( $m\ s^{-1}$ ), and  $\phi_h$  is the stability correction factor. Roughness lengths vary from about  $10^{-5}$  m for very smooth surfaces (ice, mud flats) to 0.1 m for fully grown root crops, to 1 m for a forested area, to 5-10 m for an urban core (Seinfeld, 1986).

The surface layer resistance can be parameterized as a function of the Schmidt number  $Sc = \nu/D$ , where  $\nu$  is the kinematic viscosity of air ( $m^2/s$ ) and  $D$  is the molecular diffusivity ( $m^2/s$ ) of the species, as

$$r_s = d_1 \frac{Sc^{d_2}}{ku^*} \quad (3-42)$$

where  $d_1$ ,  $d_2$  are empirical parameters ( $d_1 \approx 1.6 - 16.7$ , and  $d_2 = 0.4 - 0.8$ , with a suggested choice of  $d_1 = 5$ ,  $d_2 = 0.66$ ).

The canopy resistance  $r_c$  for a gaseous species can be parameterized (Yamartino et al., 1989) as:

$$r_c = [LAAI/r_f + LAI/r_{cut} + 1/r_g]^{-1} \quad (3-43)$$

where  $LAI$  is the leaf area index (i.e., the ratio of leaf surface area divided by ground surface area),  $r_f$  is the internal foliage resistance,  $r_{cut}$  is the cuticle resistance, and  $r_g$  is the ground or water surface resistance. Values for  $r_f$  are discussed by O'Dell et al. (1977). The resistance  $r_{cut}$  is parameterized by Pleim et al. (1984).

For gaseous pollutants, solubility and reactivity are the major factors affecting surface resistance and net deposition velocity. For particles, the factor most strongly influencing the deposition velocity is the particle mass or, assuming similar densities, the particle size. Particles are transported toward the surface by turbulent diffusion, which for larger particles is enhanced by gravitational settling. Across the quasi-laminar surface layer very small particles ( $< 0.05 \mu m$  diameter) are transported primarily by Brownian diffusion, analogous to the molecular diffusion of gases. The larger particles possess inertia, which may enhance the flux through the quasi-laminar sublayer.

The downward pollutant flux is the sum of the turbulent diffusive flux and a flux due to gravitational settling, i.e.,

$$F(z) = F_d + V_g C = V_d C \quad (3-44)$$

where  $V_g$  is the gravitational settling velocity of the particle. Whereas in the formulation of the algorithm for gases the analogy with electrical resistance is straightforward, it is less so for particles. This is because at any height within the aerodynamic layer and surface layer the flux of trace gases is diffusive only and hence a function of the concentration gradient. Consequently, when equating the fluxes through each layer under the steady-state assumption, the deposition velocity may be cast in a form proportional to the inverse of a

sum of resistances. Nevertheless, the electrical resistance analogy can still be employed for particles. The gravitational settling velocity is merely represented by the reciprocal of an additional resistance acting in parallel with the diffusive resistance.

As noted earlier, for particles, the resistance in the vegetation layer ( $r_c$ ) is usually assumed to be zero, since particles that penetrate the surface layer are assumed to stick to the surface. The expression for deposition velocity in terms of the resistances, modified to include gravitational settling, is

$$V_d = (r_a + r_s + r_a r_s V_g)^{-1} + V_g \quad (3-45)$$

Therefore, the deposition velocity of particles may be viewed in terms of electrical resistance as the reciprocal of three resistances in series ( $r_a$ ,  $r_s$ , and  $r_a r_s V_g$ ) and one in parallel ( $1/V_g$ ). The third resistance in series is denoted here as a virtual resistance in view of the fact that it is a mathematical artifact of the equation manipulation and not a physical resistance. Equation (3-109) is usually implemented with  $r_a$  (particles) equal to  $r_a$  (gases), in which  $r_a$  is computed by Equation 3-105, and the surface layer resistance is

$$r_s = (Sc^{-2/3} + 10^{-3/St})^{-1} u_*^{-1} \quad (3-42)$$

where  $Sc$  is the Schmidt number based on  $D$ , the Brownian diffusivity of the particle in air, and  $St$  is the Stokes number,  $St = V_g u^2 / gn$ . The surface layer resistance incorporates the effects of both Brownian diffusion, through the Schmidt number, and inertial impaction effects, through the Stokes number.

The gravitational settling velocity  $V_g$  is a function of the particle size, shape and density. For spherical particles (Seinfeld, 1986),

$$V_g = \frac{d_p^2 g (\rho_p - \rho_a) C}{18\mu} \quad (3-46)$$

where  $d_p$  is the particle diameter (m),  $p_p$  is the particle density ( $\text{g}/\text{m}^3$ ),  $p_a$  is density of the air ( $\text{g}/\text{m}^3$ ),  $\mu$  is the viscosity of air ( $\text{g m}^{-1}\text{s}^{-1}$ ), and  $C$  is the slip correction factor

$$C = 1 + (2\lambda / d_p)[1.257 + 0.4\exp(-0.55d_p / \lambda)] \quad (3-47)$$

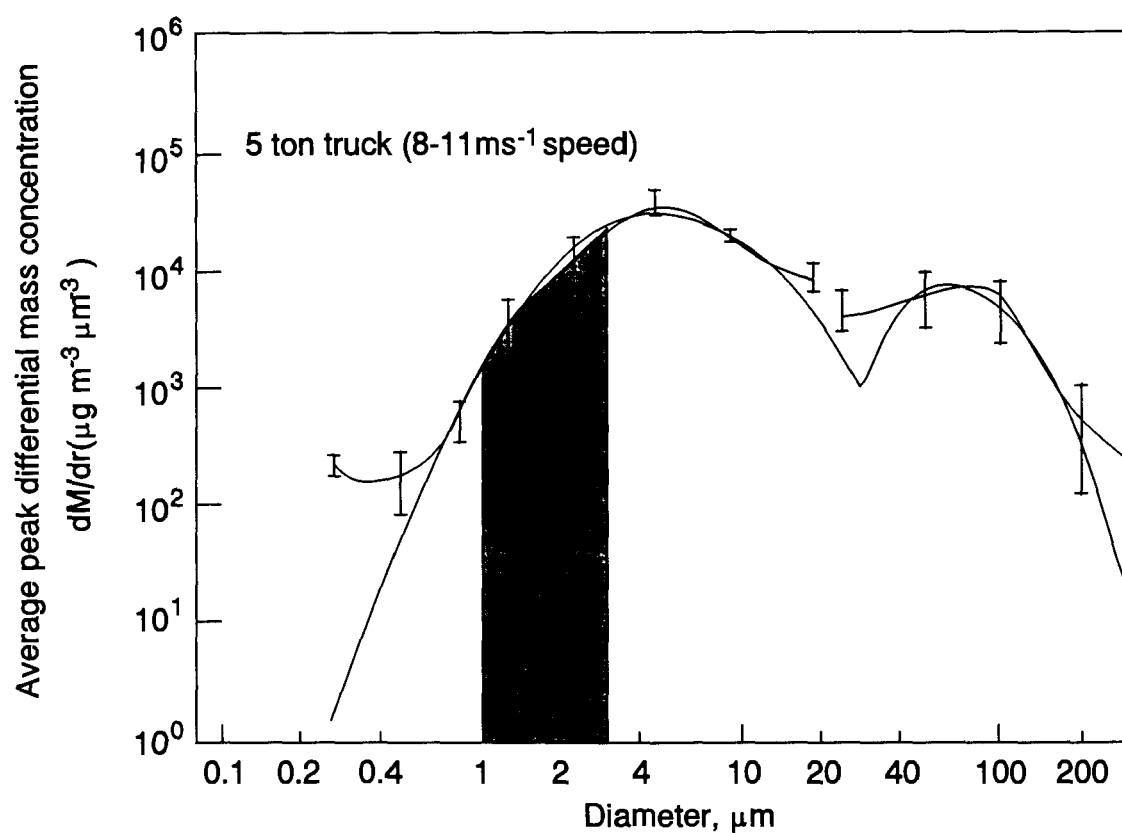
where  $\lambda$  is the mean free path of air molecules ( $\lambda = 6.53 \times 10^{-6}$  cm at 298K)

Figure 3-12 shows particle deposition velocities based on wind tunnel measurements. Deposition velocities are presented as a function of particle diameter, particle density, and surface roughness height. Particle deposition velocities exhibit a characteristic minimum as a function of particle size. For the smallest particles, deposition velocity increases as particle size decreases because diffusion by Brownian motion increases as particles get smaller. For the largest particles, gravitational settling becomes important as particles get larger so the deposition velocity increases as particles increase in size. A characteristic minimum in deposition velocity results in the range of 0.1 to 1.0  $\mu\text{m}$  diameter where neither Brownian diffusion nor gravitational settling is strong enough to control removal.

It is possible to obtain a rapid estimate of the atmospheric lifetime of particles with respect to removal by dry deposition. If the aerosol can be assumed to have a uniform concentration between the ground and a height  $h$ , then the residence time relative to removal by dry deposition is  $h/V_d$ . For example, for a 1000 m atmospheric layer, and a particle deposition velocity of 0.1 cm/s, the estimated residence time is 11.5 days.

### 3.5.2 Field Studies of Dry Deposition

In spite of many field measurements and considerable progress since 1980 in our understanding of dry deposition processes and their quantification, uncertainties remain substantial. The problem is extremely complex involving a large multiplicity of factors, and their complex interactions, which influence dry deposition of atmospheric particles and their precursors (see, for example, a tabulation of some of these in Davidson and Wu, 1990). These factors relate to characteristics of the atmosphere, nature of the deposition surface, and properties of the depositing species. It is impossible in field studies to measure all the pertinent variables over large enough spatial and temporal domains. In



**Figure 3-12.** Extrapolations from correlations of windtunnel measured deposition velocities for  $z = 1$  m, densities of 1, 4, and  $11.5 \text{ g cm}^{-3}$ .  $V_T$  represents terminal settling velocity.

Source: Sehmel, 1980, as presented by Nicholson, 1988.

1 essence, knowledge of dry deposition is limited by the inability to make the necessary  
2 measurements in other than special circumstances. This was a key statement of the NAPAP  
3 Workshop on Dry Deposition in Harpers Ferry, West Virginia (Hicks et al., 1986). The  
4 Workshop report also noted that there is presently a lack of fundamental knowledge  
5 concerning the chemical and biological processes influencing dry deposition, and there are  
6 serious hazards associated with scaling input information down from grid level to local, and  
7 scaling up the results of local measurements to broader domains. Information contained in  
8 the Workshop report and in subsequent research publications on the subject were reviewed  
9 by Davidson and Wu (1990, henceforth to be referred to as "DW90"). That review  
10 summarizes the results of a large number of field studies published since earlier reviews by  
11 McMahon and Denison (1979), Sehmel (1980), Hosker and Lindberg (1982) and Galloway  
12 et al. (1982). It also includes summaries of dry deposition processes, wind tunnel studies  
13 and empirical models, techniques for measuring deposition in the field, and comparisons of  
14 field data and model results. The summary presented in this section is based largely on  
15 DW90.

16 A large number of techniques have been used in measurements of dry deposition.  
17 They are generally grouped into two classes: surface analysis methods, which are based on  
18 examination of contaminant accumulations on natural or surrogate surfaces, and  
19 atmospheric flux methods, which involve ambient measurements of the species of interest  
20 and other related variables. These methods provide the deposition flux out of which the  
21 deposition velocity is inferred. *Surface analysis methods* include foliar extraction (by  
22 washing individual leaves), throughfall and stemflow (wet measurements above and within  
23 the canopy), watershed mass balance, tracer techniques, snow sampling, collection on  
24 surrogate surfaces, etc. These methods may provide useful data on the flux of coarse  
25 particles, but fail to simulate the physical processes which control the deposition of sub-  
26 micron particles to natural surfaces, and to give meaningful data on trace gas deposition.  
27 Deposition on surrogate surfaces may not mimic that on natural surfaces. *Atmospheric flux*  
28 *methods* include micrometeorological methods (eddy correlation and vertical gradients),  
29 aerometric mass balance in a box over the depositing surface, tracer techniques, etc.  
30 Micrometeorological methods also include what has come to be known as the inferential  
31 approach in which measured concentrations are combined with specified or calculated

deposition velocities based on meteorological data and surface information. This approach is used in long-term monitoring programs in which only simple measurements are possible at remote sites (e.g. weekly average species concentrations and routine meteorological measurements). For details of the various methods, see DW90 and the Workshop report.

### 3.5.2.1 Measured Deposition Velocities

Measurements of dry deposition in the field and in chambers have primarily involved six categories of contaminants: sulfur species, nitrogen species, chloride species, ozone, trace elements and atmospheric particles. The results of many of these studies published between 1978 and 1987 are reviewed in DW90, which includes extensive tabulations of the studies and their results. Of the reported studies on Sulfur Species, 20 pertain to  $\text{SO}_2$ . They give deposition velocities ranging from nearly 0 to 3.4 cm/s. The variations are due to differences in seasonal and diurnal conditions, aerodynamic transfer, surface characteristics (especially stomatal resistance), measurement methods, etc. Daytime values are generally higher, as expected (lower aerodynamic and stomatal resistances). Micrometeorological methods were used in 16 studies whose average values of  $v_d$  gave a grand average of  $0.95 \pm 0.62$  cm/s. Four studies provided an average value of  $0.13 \pm 0.09$  cm/s for deposition velocity on snow. For particulate sulfur, 34 studies are included, with 10 also including particle size measurements. A graph also includes results of earlier studies, and gives values of  $v_d$  in the range 0.01 to 10 cm/s. Results for  $v_d$  in cm/s based on different methods are as follows:  $0.55 \pm 0.65$  for micromet methods,  $0.26 \pm 0.25$  for surrogate surface exposures,  $0.23 \pm 0.24$  for foliar extraction, and  $1.00 \pm 0.41$  for throughfall. Since the micromet method is believed to be more specific for submicron particles while the surrogate surface method is biased in favor of larger particles, the difference in the results of those methods is opposite to that expected. The surrogate surface and foliar extraction results are close, but each has a large variance. Throughfall values are the largest probably partly because they include deposition of  $\text{SO}_2$ . Evidently, measurement methods themselves are an important variable because they do not measure the same thing.

Twenty two species are reported for Nitrogen Species, including  $\text{NO}_2$ ,  $\text{NO}_x$ ,  $\text{HNO}_3$ ,  $\text{NO}_3^-$ ,  $\text{NH}_3$ , and  $\text{NH}_4^+$ . The inferred values of  $v_d$  (cm/s) are: 0.012 to 0.5 for  $\text{NO}_2$  (2



1 studies), -2.6 to 0.3 for  $\text{NO}_x$  (4 studies), 0 to 2.9 for  $\text{HNO}_3$  (4 studies), 0.13 to 1.3 for  $\text{NO}_3^-$  (7 studies),  $1.9 \pm 1.55$  for  $\text{NH}_3$  (1 study), and 0.06 to 1.0 for  $\text{NH}_4^+$  (4 studies). The zero  
2 value for nitric acid was for snow in a chamber study; otherwise, the values for nitric acid  
3 are the highest, indicating low surface resistance. The values for particulate nitrate are  
4 somewhat larger than for sulfate; this may reflect larger particle size associated with nitrate.  
5 Four studies are reported for chloride-containing particles, giving values of 1.0 to 5.1 cm/s;  
6 a value for HCl of 0.73 cm/s on dew was obtained in one study. The highest values for  
7 chloride were in winter, related to road salt. Based on 11 studies using micromet methods,  
8  $v_d$  of ozone on vegetation ranged between nearly 0 and 1.5 cm/s (average of 15 values =  
9  $0.39 \pm 0.21$ ). Nighttime values were lower, but the day-night difference was less for ozone  
10 than for  $\text{NO}_2$ .  
11

12 Results of 19 studies included measurements for 21 trace elements, with particle size  
13 data in 15 studies. For these data, crustal element enrichment factors (EF) were  
14 determined. Values of  $\text{EF} \approx 1$  indicate crustal sources, while  $\text{EF} > 1$  (enriched) indicate  
15 non-crustal sources such as anthropogenic, natural combustion (volcanism, forest fires),  
16 biogenic, sea-spray, etc.. Large enrichment factors were found for Ag, As, Cd, Cu, In, Pb,  
17 Sb, Se and Zn. Ni and V were marginally enriched. Other elements were mainly soil-  
18 derived.  $v_d$  for these elements were generally higher ( $>1$  cm/s), while they were generally  
19 less than 1 cm/s for the enriched elements (smaller, submicron particles). A figure  
20 including these as well as data of earlier studies is presented, showing a positive correlation  
21 between  $v_d$  and MMD (mass median diameter). For Pb, the values ranged between 0.1 and  
22 1.0 cm/s. Friedlander et al. (1986) have used CO as a tracer for automobile emissions to  
23 estimate the deposition velocity for Pb, by comparing the ratio Pb/CO in ambient air to that  
24 in a tunnel. They found the former to be lower, indicating deposition compared to its value  
25 in fresh emission (tunnel). Based on these data, they estimated  $v_d$  for Pb to be 0.26 cm/s,  
26 which is consistent with the range given above. DW90 also report the results of 5 other  
27 field studies with micromet measurements of dry deposition for submicron particles, and  
28 particle size measurements also.  $v_d$  was generally less than 1 cm/s, in general agreement  
29 with results for sulfate and the enriched trace elements.

30 DW90 have also presented results of *comparisons between measured values of  $v_d$*   
31 *with predicted values based on six model calculations*. These results are from published

1 studies with size distribution data for aerosol sulfate and trace elements. The measured  
2 values of  $v_d$  are for the full size range; the model value is the concentration-weighted  
3 average of the calculated values for all size classes. For sulfate, the predicted values were  
4 generally smaller than the measured values. Good agreement was, however, not expected  
5 because of differences in ambient conditions and surface conditions between values used in  
6 the model compared to the corresponding measured values. Similar comparisons for 24  
7 trace elements were also tenuous: out of 11 of the 24 elements for which more than one or  
8 two data points only were available, the measured values were in the predicted range; for  
9 Al, Ca and Fe, the predictions were low, while for Zn, the predictions were too high. For  
10 the other 13 elements with sparse measured data, the agreement was generally much poorer.

## 11 12 13 **3.6 WET DEPOSITION**

### 14 **3.6.1 Introduction**

15 Although detailed physico-chemical models are needed to describe the details of  
16 in-cloud and below-cloud scavenging of particles, there has been a benefit in using  
17 comparatively simple formulations of precipitation scavenging that provide a convenient  
18 picture of the process as a whole. These simple methods are not designed to explain  
19 detailed variations in wet deposition with time or space, but they are useful in describing  
20 average deposition rates over large areas. Two alternative techniques have become popular.  
21 The first relates concentrations of material in precipitation to the quantity available in the  
22 air, thus describing the overall efficiency of precipitation as a removal path. By relating  
23 concentrations in precipitation to those in the air, dimensionless scavenging ratios can be  
24 determined. The second common method is based on the first-order removal of airborne  
25 gases or particles as rain falls through the atmosphere. Concentrations in the air will  
26 decrease exponentially and a scavenging rate can then be determined.

27 Below-cloud scavenging rates for particles of about  $3 \times 10^{-5} \text{ s}^{-1}$  appear to be typical;  
28 in-cloud scavenging leads to rates typically ten times larger (Hicks and Meyers, 1989).  
29 Hygroscopic particles are scavenged more readily than hydrophobic ones.

30 Based on the wet flux  $W$  the wet deposition velocity may be defined as  
31

$$V_w = \frac{W}{c(x,y,0,t)} \approx \bar{\Lambda}h \quad (3-48)$$

where the last equality assumes that the pollutant is uniformly distributed between  $z = 0$  and  $z = h$ . The wet deposition velocity  $V_w$  can be computed by

$$V_w = w_r p_o \quad (3-49)$$

where  $w_r$  is the washout ratio (i.e., the dimensionless ratio of the concentration of material in surface-level precipitation to the concentration of the material in surface-level air) and  $p_o$  is the precipitation intensity ( $\text{mm hr}^{-1}$ ). For example, if  $w_r = 10^6$  and  $p_o = 1 \text{ mm h}^{-1}$ , then  $V_w = 28 \text{ cm s}^{-1}$ , which gives, for  $h = 1,000 \text{ m}$ ,  $\bar{\Lambda} = 2.8 \times 10^{-4} \text{ s}^{-1}$ . Seinfeld (1986) provides a detailed discussion of precipitation scavenging of particles, including the calculation of collision efficiencies and scavenging rates.

Scavenging ratios relate concentrations in precipitation to those in air. Although such ratios depend on many factors, they provide a simple way to include wet deposition processes in air quality models. The washout (or "scavenging") ratio is

$$w_r = \frac{[c]_{\text{rain}} \rho_a}{[c]_{\text{aerosol}}} \quad (3-50)$$

with  $[c]_{\text{rain}}$  in  $\text{mg g}^{-1}$ ,  $[c]_{\text{aerosol}}$  in  $\text{mg m}^{-3}$ , and  $\rho_a (=1,200 \text{ g m}^{-3})$ , the density of air. The definition of this ratio presumes that the aerosol measured at ground level is vertically uniform and that there are no factors limiting the collection of aerosol by the droplets, such as solubility. Scavenging ratios of about 400 appear to be appropriate in the case of particles well mixed in the lower atmosphere but originating near the surface, while values of about 800 appear characteristic of material derived from the free troposphere (Hicks and Meyers, 1989).

### 3.6.2 Field Studies of Wet Deposition

The removal of pollutants from the atmosphere by precipitation is the terminal step of a three-step sequence. In the first step, the pollutant or its precursor(s) must be delivered by transport processes to the precipitating cloud or to the air below it; in the second step, the species must become incorporated into the precipitating droplets either within the cloud (in-cloud scavenging) or below it (washout). We have already addressed field measurements of transport and in-cloud scavenging in liquid water clouds. The focus here will be on field studies of the third step. Wet deposition measurements are made principally to meet three objectives: (1) to determine the regional spatial-temporal distribution and chemistry of wet deposition; (2) to study pathways and mechanisms of pollutant wet removal from the atmosphere; and, (3) to generate data for diagnostic evaluations of precipitation scavenging modules. The first of these objectives is best studied based on data of routine monitoring programs. These are reviewed in detail in SOST Report No. 6 of NAPAP (1991), and are not covered here. Our focus here is on recent research field studies aimed at objectives (1) and (2) above.

The scavenging coefficient and the scavenging ratio, in common use in the Lagrangian models of the 1970s, represent highly lumped representations of the complex of processes involved in wet removal. They are empirical entities which, by themselves, contain little mechanistic information. While reporting their measurements of scavenging ratio during a year-long study in Paris, Jaffrezo and Colin (1988) included a table (Table 3-14) which summarized not only their own data but also those of other earlier studies. The various results are not directly comparable owing, at least partly, to differences in measurement methods. Of particular interest in their study is the interpretation of elemental composition data. They were able to separate the measured elements into three groups which differed in terms of their solubility and also, by the mechanisms of their scavenging. The measured concentrations in precipitation and in air were nearly proportional for the insoluble species Al, Si, and Fe; this was interpreted to imply that their scavenging was mostly a local mechanism (below-cloud impaction). At the other extreme, the local concentrations of the very soluble species Na and Cl in the two phases were least correlated, indicating a more complex and progressive process of enrichment of one medium relative to the other (in-

TABLE 3-14. SCAVENGING RATIOS (DIMENSIONSLESS)

Reference	n	G.M.	Med. (1)	S.D.	A.M.	A.M. (2)	G.M. (3)	G.M. (4)	A.M. (5)	A.M. (6)	G.M. (7)	A.M. (8)	A.M. (9)	A.M. (10)
Cl	78	2,941	2,917	4.73	7,710	600	350	1,400				2,300	4,100	
S	82	743	753	1.98	940	700			1,000					370*
Na	81	444	530	3.17	744	560	360	2,100				2,900	5,500	490
K	82	951	970	2.30	1,325	620	300	2,000		548				
Mg	81	596	682	2.39	816	850	400			457				
Ca	82	1,048	1,097	2.49	1,579	1,890	320	1,100		352		2,100		
Zn	69	767	707	2.65	1,226		790		820	179	612	1,050	1,030	
Al	82	291	283	2.72	459		580	1,300			756	620	430	
Si	82	373	405	2.35	533									
Fe	82	184	194	2.51	267		390	600		253	468	890	270	
Ti	9	305		1.30	378									
Mn	7	146		1.36	171		250	2,100	3,600	370	756	760		

1. Jaffrezo and Colin, 1988
2. Harrison and Pio, 1983
3. Arimoto et al., 1985
4. Buat-Menard and Duce, 1986
5. Lindberg, 1982
6. Gatz, 1977
7. Chan et al., 1986
8. Peirson et al., 1973
9. Cawse, 1981
10. Savoie et al., 1987

\* Non-sea sulfate  
 G.M. Geometric mean  
 A.M. Arithmetic mean  
 Med. Median  
 S.D. Geometric standard deviation

cloud processes). The remaining soluble species ( $\text{SO}_4^{2-}$ , K, Ca, Zn, and Mg) showed an intermediate behavior. Earlier data at the same site of the relationship between scavenging ratio and particle mass median diameter (MMD), which showed a minimum in the scavenging ratio for  $\text{MMD} = 1$  to  $2 \mu\text{m}$  (reported as Figure 6-1), were judged to be supportive of the above interpretation.

A significant effort in NAPAP in the 1980s was devoted to development of wet removal characterizations that directly reflected the cloud physics, attachment, reaction, and precipitation processes (Hales, 1991). The PLUVIUS II models, prepared under the auspices of NAPAP, was a reactive storm model based on multi-phase material balance, and served as the basis for the development of the one-dimensional RADM Scavenging Module, RSM. A parallel activity in NAPAP was DOE's PRECP (Processing of Emissions by Clouds and Precipitation) field measurements program which comprised a series of six individual intensive field studies with the objective of systematically measuring scavenging characteristics for different classes of storm systems important to regional acid deposition. In these, studies, the emphasis was on *in situ* aircraft measurements. What follows is a brief review of such research field studies. It is based substantially on Hales (1991). In the context of precipitation scavenging studies, it is useful to bear in mind that pollutant particles, on average, undergo a number of repeated cycles in and out of non-precipitating clouds before finally being removed by precipitation.

*In situ* aircraft measurements in clouds and precipitation are of crucial importance in mechanistic/diagnostic studies. Current technology permits continuous aircraft measurements of NO, NO<sub>2</sub>, NO<sub>y</sub>, HNO<sub>3</sub>, PAN, SO<sub>2</sub>, O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, liquid water content (LWC), and size-segregated aerosol and cloud/rain droplet concentrations with quite high sensitivity and precision. In addition, filter samples and cloudwater samples can provide mass concentrations of the major ions in aerosols and droplets at a temporal resolution of a few minutes. Ground monitoring of precipitation in recent studies has included use of the NAPAP-developed Computer-Controlled Automated Rain Sampler (CCARS) which is a combination rain gauge and sequential precipitation chemistry sampler, controlled and monitored by a programmable microprocessor. Such samplers permit capture of statistically valid footprints (multiple sequential event samples) of deposition during the course of a storm. Upper-air meteorological measurements with fine vertical resolution of wind

1 components, temperature and moisture are also important. These can be made using radar  
2 profilers and doppler radars.

3 Field studies have been conducted in and below point-source plumes (meso- $\gamma$  scale)  
4 and urban plumes (meso- $\beta$  scale). In the former, precipitation scavenging of S and N  
5 compounds was found to be minimal (Granat and Soderland, 1975; Dana et al., 1976;  
6 Drewes and Hales, 1982), indicating low precipitation scavenging efficiency for SO<sub>2</sub> and  
7 NO<sub>x</sub> from fresh plumes. Hales and Dana (1979) found appreciable removal of S and N  
8 compounds from the urban plume of St. Louis by summer convective storms. Patrinos and  
9 Brown (1984), Patrinos (1985) and Patrino et al. (1989) found efficient scavenging of these  
10 compounds from the urban plumes of Philadelphia and Washington, DC by frontal storms.  
11 H<sub>2</sub>O<sub>2</sub> data in rain showed considerable spatial variability in the plumes.

12 The major regional-scale field studies include OSCAR (Oxidation and Scavenging by  
13 April Rains, April 1981), PRECP (mid-1980s), and the DOE-FBS (Frontal Boundary  
14 Study). OSCAR (Chapman et al., 1987) included a nested array of ground level sampling  
15 (an extended regional precipitation chemistry network in northeastern United States, with an  
16 embedded high-density network in northeast Indiana) as well as three research aircraft. The  
17 focus was on scavenging by extratropical cyclonic storms. The aircraft made clear air  
18 measurements before and after frontal passage, as well as measurements within the storm,  
19 in the vicinity of the high-density network. Measurements were made during four storms.  
20 OSCAR data have been used for regional model development and evaluation.

21 The six PRECP studies, conducted between 1984 and 1988, were targeted at  
22 scavenging measurements in different types of storm systems. Three studies were focussed  
23 on convective storms (II, V, and VI) in summer, and the other three on extratropical  
24 cyclonic and frontal storms during other seasons; five were conducted east of the  
25 Mississippi River, and one in the Oklahoma-Kansas-Colorado area. All of them included  
26 two or more research aircraft, and all also included at least limited area precipitation  
27 chemistry networks (PRECP IV had three multiscale networks ranging from a coastal "rain-  
28 band" network to a truly regional scale network). The network in PRECP VI was a highly-  
29 density network within an 80-km RADM grid cell, designated to provide information about  
30 regional sub-grid scale variability. Two of the studies were conducted jointly with other  
31 meteorology-focussed measurement programs; PRECPII with the NSF PRESTORM study,

1 and PRECP IV with the NSF-NASA-NOAA Genesis of Atlantic Lows Experiment  
2 (GALE). Such synergism resulted in particularly strong meteorological data in these two  
3 studies. PRECP I was intended to be an exploratory study, but generated a database of  
4 which at least one storm has been extensively studied (Saylor, 1989). PRECP VI, on the  
5 other hand was designed as the grand finale aimed at generating a definitive database for  
6 evaluation of the RADM Scavenging Module, but failed to meet its main objective owing  
7 to the extreme drought of the summer of 1988.

8 Overall, the studies have developed a substantial database of mechanistic-diagnostic  
9 information suitable for diagnostic model studies. PRECP II definitively demonstrated the  
10 cloud venting phenomenon transporting boundary layer pollutants to considerable heights in  
11 the free troposphere (Dickerson et al., 1987). PRECP III provided a significant new  
12 mechanistic insight regarding scavenging in orographically enhanced storms, e.g., the  
13 observation of an unexpected entrainment mechanism that occurs as orographic lifting  
14 occurs, and which enhances chemical wet removal appreciably (Hales, 1991). PRECP V,  
15 focussed on studying vertical profiles of chemical species in and around convective storms,  
16 resulted in one study (Daum et al., 1990) which showed that while  $\text{SO}_2$  was more  
17 concentrated in the lower parts of the ABL,  $\text{H}_2\text{O}_2$  was concentrated near the top,  
18 underscoring the importance of mixing in facilitating aqueous-phase of  $\text{SO}_2$  by  $\text{H}_2\text{O}_2$ . The  
19 same study also found that in the low- $\text{NO}_x$  background,  $\text{H}_2\text{O}_2$  was correlated with humidity.

20 The Frontal Boundary Study (DOE) was conducted in fall 1989 as part of a global  
21 study of the fate of energy-related pollutants. The focus was on pollutant redistribution and  
22 removal by stable frontal storms occurring subsequent to pollution episodes associated with  
23 high-pressure stagnation. Aircraft soundings ahead of, within, and following the passage of  
24 the front showed considerable spatial variability in precipitation amount and composition  
25 (Hales, 1991).

26 The data of the above studies constitute a substantial mechanistic-diagnostic database  
27 for model evaluation. In addition to these research studies, a number of research-grade  
28 precipitation chemistry networks were also operated in the 1980s. They include the  
29 Canadian CAPMON, and the U.S. MAP3S and UAPSP, as well as the shorter-term EPRI-  
30 OEN and the EPA-ME35. Applications of the research network measurements for source-  
31 receptor pathway studies are discussed by Hales et al. (1987).



### 3.6.2.1 Overview of SO<sub>2</sub> and NO<sub>x</sub> Wet Scavenging

Hales (1991) has presented a useful overview of our understanding of SO<sub>2</sub> and NO<sub>x</sub> wet scavenging based on field measurements which is very pertinent here, and is recapped below. SO<sub>x</sub>: SO<sub>2</sub> is emitted principally from point sources. It is moderately soluble in water, and its solubility decreases with increasing acidity of the solution. It is not efficiently scavenged from concentrated fresh plumes, but this efficiency improves as the plumes dilute. It is essentially insoluble in ice and cold snows, but tends to be more efficiently scavenged by wet slushy snow and snows composed of graupel formed by rimming of supercooled cloud water. Only a small fraction of the SO<sub>2</sub> emission is removed as unreacted S(IV) which constitutes about 20% of S in precipitation in the eastern U.S. in cold seasons (significantly in the form of hydroxymethane sulfonate ions), and virtually none in summer (high acidity of droplets). Sulfate removal is also small from fresh plumes (not much there), but increases substantially with plume dilution as more is formed in the plume. It is scavenged efficiently by clouds and rain. Roughly 1/3 of the S emitted annually in North America is believed to be removed by precipitation.

NO<sub>x</sub>: Point sources are a relatively smaller contributor of NO<sub>x</sub>, but still quite substantial. Both NO and NO<sub>2</sub> have low solubility in water. Virtually no NO<sub>x</sub> is removed from fresh plumes. HNO<sub>3</sub> formed by gas-phase oxidation of NO<sub>2</sub> is very soluble in water and is the principal source of NO<sub>3</sub><sup>-</sup> in precipitation. NO<sub>3</sub>, N<sub>2</sub>O<sub>5</sub>, and HO<sub>2</sub>NO<sub>2</sub> are also believed to be significant intermediates. Since all of the intermediates are secondary products, NO<sub>x</sub> scavenging increases with plume dilution and oxidation. Mesoscale studies show much variation in the efficiency of wet scavenging of SO<sub>x</sub> and NO<sub>x</sub>, depending on storm type and history of plume chemistry. About 1/3 of the anthropogenic NO<sub>x</sub> emissions in the U.S. are estimated to be removed by wet deposition. The distinct seasonal character of SO<sub>x</sub> wet deposition is absent in the case of NO<sub>x</sub> wet deposition. Some likely reasons are as follows: HNO<sub>3</sub> has a strong affinity for ice as well as liquid water; its formation has no direct dependence on H<sub>2</sub>O<sub>2</sub> which peaks in summer; and, there are mechanisms for the formation of HNO<sub>3</sub> in low winter sunlight.

## **3.7 PHYSICAL AND CHEMICAL CONSIDERATIONS IN PARTICULATE MATTER SAMPLING AND ANALYSIS**

### **3.7.1 Size Cut-Point For Separating Fine and Coarse Particulate Matter**

#### **3.7.1.1 Background**

In 1979 EPA scientists, in a paper entitled "Size Considerations for Establishing a Standard for Inhalable Particles" recommended that total suspended particulate matter (TSP), as defined by the high volume sampler, be replaced by the fraction obtained with a sampler having a precise upper cut-point (originally 15  $\mu\text{m}$ , but later changed to 10  $\mu\text{m}$ ); and that "a second particle size cut-point of  $\leq 2.5 \mu\text{m}$  diameter be incorporated in the air sampling devices" (Miller et al., 1979). This study found that "the existence of a bimodal distribution with fine and coarse modes has been clearly demonstrated by.... mass-size distribution studies and by number distribution studies. These size distribution studies suggest 1 to 3  $\mu\text{m}$  as the most appropriate range for a cut-point for fine and coarse aerosols. However, practical considerations of reducing plugging of impactor orifices indicate that 2.5  $\mu\text{m}$  is a more appropriate cut-point, especially for particle size fractionating devices such as the dichotomous sampler" (Miller et al, 1979).

The cut-point of 2.5  $\mu\text{m}$ , which has been used in many studies since 1979, was chosen not because it was ideal but because it was the smallest cut-point deemed feasible for a dichotomous sampler at that time. Current technology has demonstrated the feasibility of dichotomous samplers with cut-points at 1  $\mu\text{m}$ , or even lower if desired. Impactor and cyclone technology can also be used for cut-points below 2.5  $\mu\text{m}$ . Therefore, it is appropriate at this time to review existing data on size distribution of ambient aerosols so that policy makers may consider whether a change to a smaller cut-point should be considered. This is especially important in view of the possibility of a major increase in both research measurements, exposure assessment, and regulatory monitoring of fine particles, as well as of  $\text{PM}_{10}$ .

#### **3.7.1.2 Size Measurements**

Information on the size of fine and coarse particles comes from two basic techniques, (1) particle-counting techniques that measure the size of individual particles and convert the particle number distribution to a particle volume distribution and (2) particle-collecting

1 techniques that use aerodynamic separation, collection of material in specific size ranges,  
2 and gravimetric or chemical analysis to determine the total mass or the mass of specific  
3 components in the size ranges collected. Particle counting has the potential advantages of  
4 not causing as much disturbance to the gas/particle equilibrium. However, considerable  
5 care must be taken to avoid heating the sample or diluting it with clean or drier air than  
6 that present in the atmosphere. With particle counting techniques it may also be possible to  
7 avoid problems of particle bounce. However, several expensive and complex instruments  
8 are required to cover the desired range of 0.001 to 100  $\mu\text{m}$ . Because sizes can be measured  
9 very precisely, the size ranges covered can be very small and an almost continuous function  
10 of number versus size can be obtained.

11 Particle collecting techniques have the advantage of obtaining size-differentiated  
12 samples for chemical analysis. The equipment used is simpler and less expensive.  
13 However, aerodynamic separation does not provide as distinct a classification by size.  
14 Large particles may bounce from their intended collection surface and be counted in smaller  
15 size ranges. Also, the requirement for long sampling times may result in averages of  
16 distributions that change with time. Particle collection techniques provide a limited number  
17 of size cuts and yield discontinuous functions of mass versus particle size.

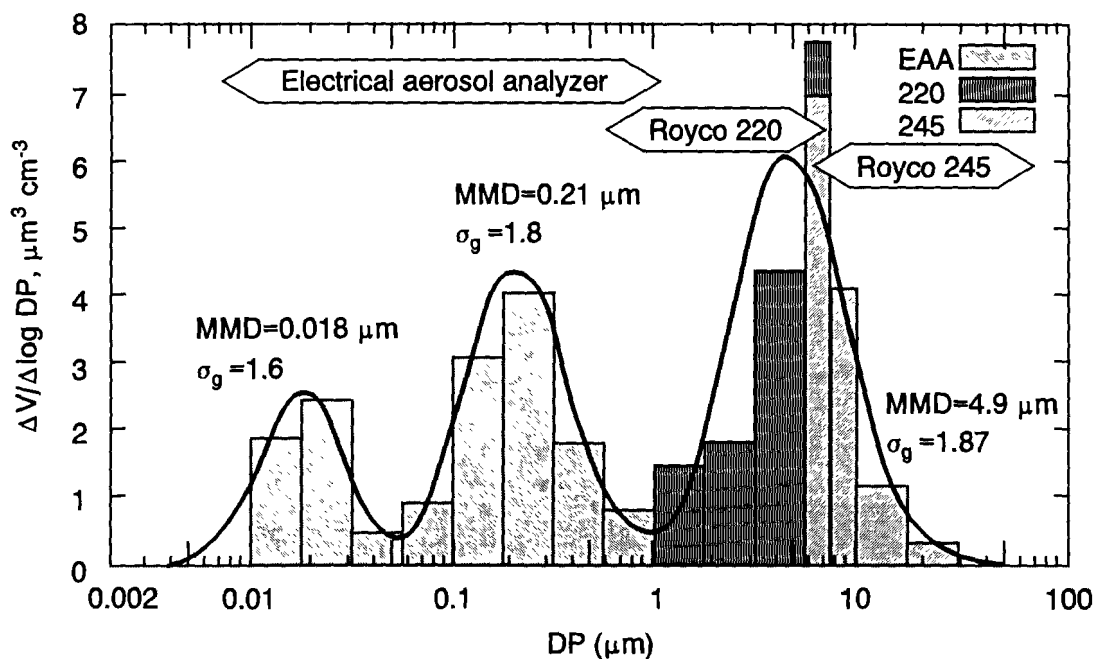
18 Both techniques, however, clearly indicate the natural division of ambient air particles  
19 into fine and coarse modes with a minimum between 1.0 and 3.0  $\mu\text{m}$  diameter. Size  
20 distributions obtained with particle counting techniques tend to show a lower, broader, and  
21 more distinct minimum than distributions obtained with particle collection techniques such  
22 as impactors. The position of the minimum between the accumulation and coarse mode  
23 may vary from study to study. The peak of the fine particle mode tends to increase in size  
24 with increasing concentration and with increasing relative humidity. Several good reviews  
25 of particle size distribution are available: on physical properties of sulfur aerosols (Whitby,  
26 1978), on the size distribution of urban aerosols (Lippmann, 1980) on sizes of particulate  
27 sulfate and nitrate in the atmosphere (Milford and Davidson, 1987); and on the size  
28 distribution of coarse mode aerosol (Lundgren and Burton, 1995).

### 3.7.1.3 Appropriate Display of Size-distribution Data

Size-distribution data, if not properly displayed, can give misleading information on the position and shape of peaks and valleys and can lead to incorrect conclusions, especially in regard to the position, width, and separation of fine and coarse modes. For this reason many workers use a histogram display obtained as follows. The mass, number, surface, or volume in each size range is divided by the difference of the logarithms of the diameters at the upper  $D_i$  and the lower  $D_{i-1}$  ends of the size range, and plotted as rectangles of width  $\log D_i - \log D_{i-1}$  and height, i.e.  $\text{mass} / (\log D_u - \log D_l)$  on a log diameter scale. This is normally shown as  $\Delta C / \Delta \log D_p$ ,  $dM/d \log D_p$ , or normalized, for example, as  $\Delta M/M \cdot \Delta \log D_p$ . Such histogram plots are especially useful for impactor data, which normally yield fewer size intervals than particle-counting techniques. Examples of such displays are shown in Figure 3-13 (Wilson et al., 1977) and Figure 3-14 (John et al., 1990).

It is frequently desirable to draw a smooth line through the data in order to identify modes and the mass mean diameters (MMD) and widths ( $\sigma_g$ ) of modes. This can be done by fitting the data to two or more lognormal distributions, as was done in Figure 3-13 (also see Dzubay and Hasan, 1989; and Whitby-DISFIT (TSI, 1993); or by using an inversion process such as originally developed by Twomey, as was done in Figure 3-14 (John et al., 1990; Winklmayr et al., 1989). In this type of presentation the area in each rectangle or the area under a portion of a curve is proportional to the mass in that size range (or the quantity of any other parameter plotted on a linear scale). Plotting mass per impactor stage versus impactor stage number, or drawing lines connecting the midpoints of size range at the heights of the mass in each size range, does not provide such quantitative information. Once the characteristics of the impactor have been demonstrated, and once good fits to lognormal distributions have been obtained, repeated measurements of the same species may be shown by curves fitted to inversion or lognormal distributions such as the example in Figure 3-15 (John et al., 1990).

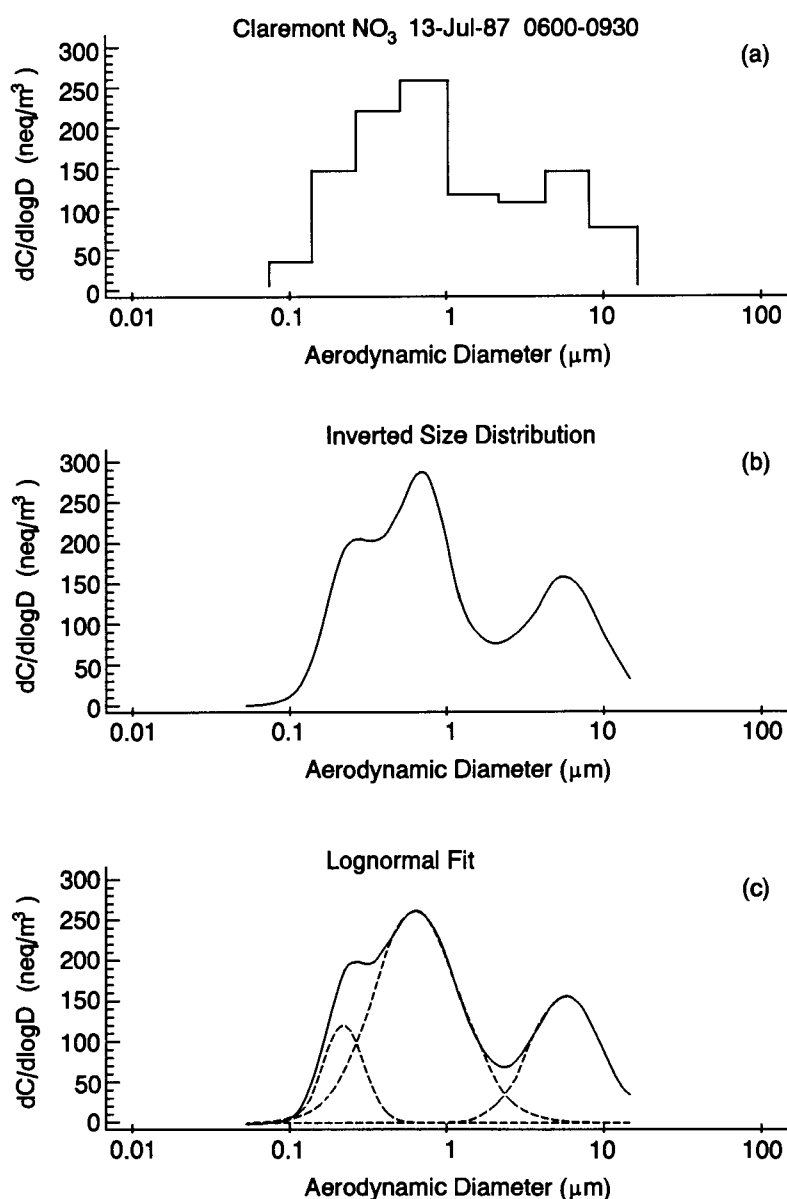
In impactor measurements, the maximum size of the upper stage and the minimum size of the lower stage (or after filter) are not well defined. Therefore, an arbitrary choice must be made in order to define the  $\Delta \log D_p$ . This choice can have a remarkable influence on the perceptions of the positions, height, and width of modes. A particularly



**Figure 3-13.** An example of histogram display and fitting to log-normal functions for particle-counting size distribution data. Instruments used and the range covered by each are shown. Counts are combined into reasonably-sized bins and displayed. Lognormal functions, fitted to the data, are shown with geometric mean sizes (MMD) of each mode and the width ( $\sigma_g$ ) of each mode. Data taken from a study of fine sulfate and other particles generated by catalyst equipped cars as part of a cooperative study by EPA and General Motors Corporation. Note the clear separation of the nuclei mode (MMD = 0.018  $\mu\text{m}$ ), the accumulation mode (MMD = 0.21  $\mu\text{m}$ ) and coarse mode (MMD = 4.9  $\mu\text{m}$ ). Fine particles, as defined by Whitby (1988), include the nuclei and accumulation mode.

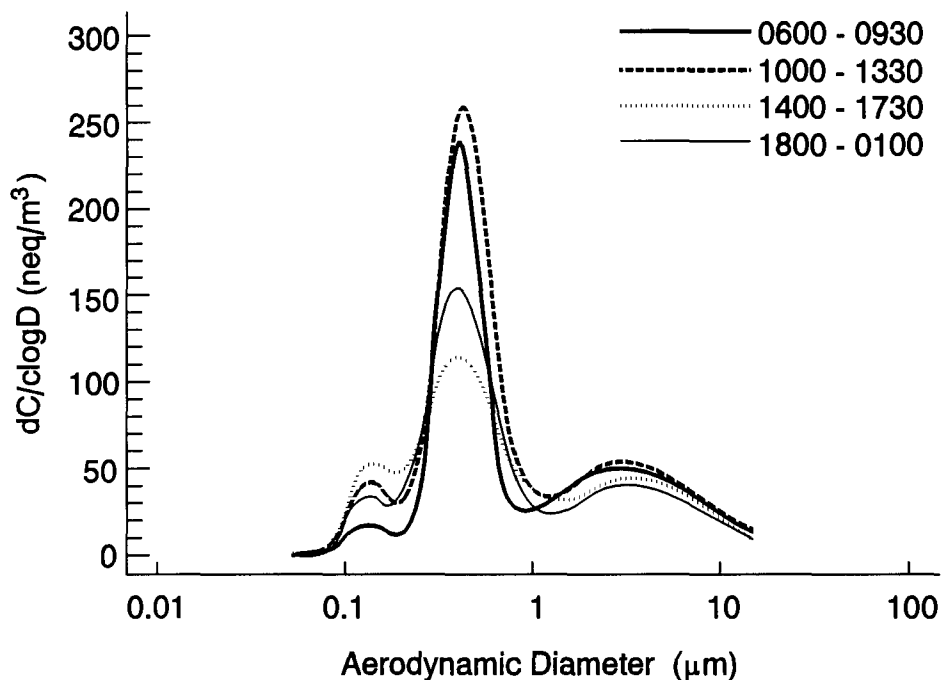
Source: Wilson et al., 1977.

dramatic example is shown in Figure 3-16, from Šega and Fugaš (1984). The authors chose 0.1  $\mu\text{m}$  for the lower limit and 20  $\mu\text{m}$  for the upper limit, suggesting a bimodal distribution with a fine mode MMD at about 1.5  $\mu\text{m}$ , and a coarse mode MMD at about 10.5  $\mu\text{m}$ . However, if 0.4  $\mu\text{m}$  is chosen for the lower limit and 10  $\mu\text{m}$  for the upper limit, the display suggests a fine mode MMD of about 0.7  $\mu\text{m}$  and a coarse mode MMD of about 8  $\mu\text{m}$ .



**Figure 3-14.** An example of an effective display of impactor data: (a) histogram showing mass found on each impactor stage and upper and lower cut points of each stage, (b) inverted size distribution, (i.e., a smooth distribution that would give the observed distribution considering the actual efficiency of each stage; cut points are not exact; each stage allows some large particles, which it should collect, to pass through to the next stage and collects some small particles which it should pass on to the next stage), (c) the solid line is the distribution obtained by fitting a sum of several lognormal functions to the inverted distribution. The dashed lines show the lognormal functions obtained from the fitting process.

Source: John et al., 1990.

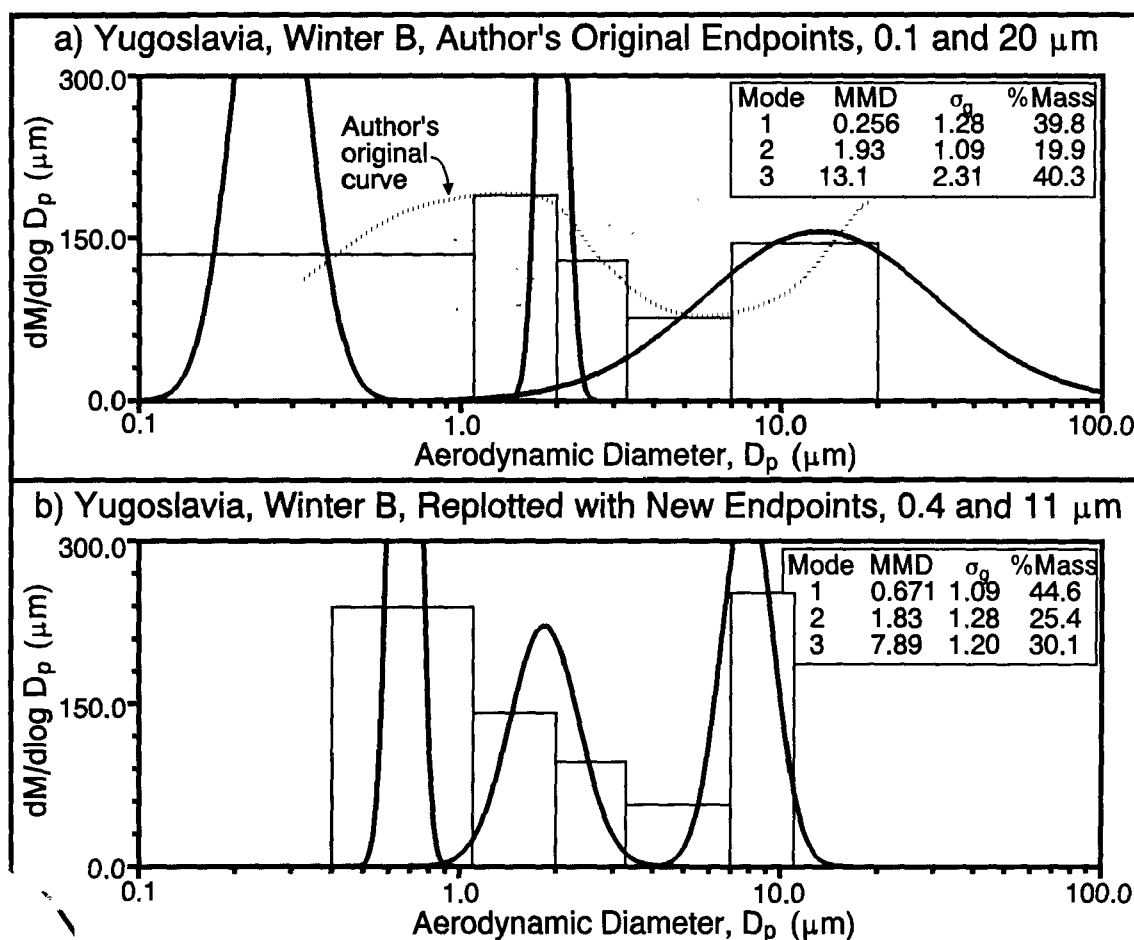


**Figure 3-15. Size distributions of sulfate, Long Beach, June, 1987, showing use of fitted log-normal distributions to describe diurnal variations in size and concentration.**

Source: John et al., 1990.

#### 3.7.1.4 Comparison of Particle-counting and Particle-collection Techniques

Unfortunately, there have been few efforts to compare results of the two particle-sizing techniques. One such effort is shown in Figure 3-17 (Durham et al., 1975). The differences between the two techniques, as evident in the figure, are qualitatively observed in individual studies using either of the two techniques. Particle counting techniques usually give a lower and wider minimum. Typically particle counting leads to volume distributions plotted versus geometric size (or more properly, geometric size inferred from mobility or optical size); whereas impactor separations give mass versus aerodynamic size. In Figure 3-17 both geometric and aerodynamic scales are given. This figure illustrates the problems involved in defining particle "size" and serves as a reminder that each particle sizing technique gives a different "size". The upper scale, used for impactor data, is given in aerodynamic diameter.

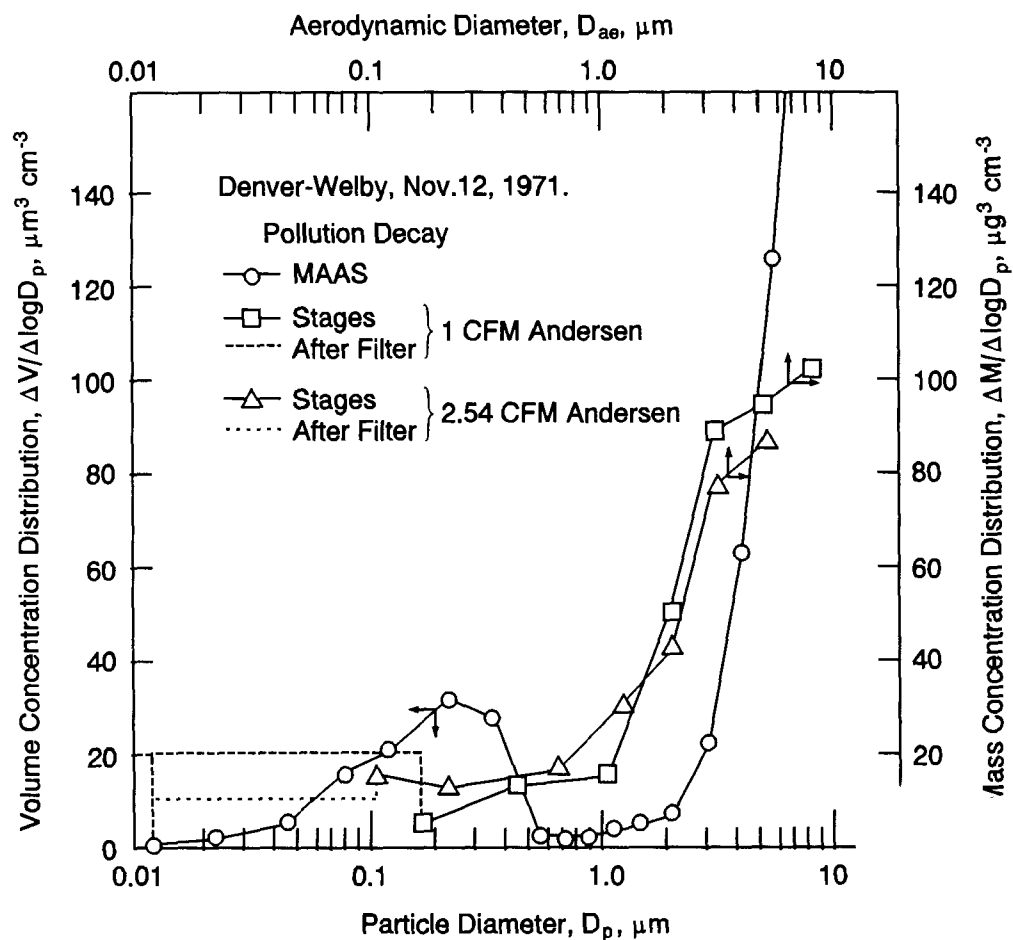


3-16. Effect of changing endpoints. This example of impactor data shows how the lack of a well-defined upper and lower size limit can affect the perception of location of fine and coarse particle modes. The curve drawn by authors of the report, and a histogram with an upper limit of 20  $\mu\text{m}$  and a lower limit of 0.1  $\mu\text{m}$  diameter, are shown in Figure 4a. In Figure 4b a histogram with a lower limit of 0.4  $\mu\text{m}$  and an upper limit of 10  $\mu\text{m}$  is shown. Notice how the author's free hand curve and histogram suggest a fine particle MMD around 1.5  $\mu\text{m}$  diameter. A quite different idea of the location of the modes is given when different endpoints are chosen and when the data is fitted to a 3-lognormal mode distribution. Much of the material found between 1.0 and 5.0  $\mu\text{m}$  is probably smaller particles caught on the glass fiber impactor stages which have very poor separation efficiencies.

Source: Šega and Fugaš, 1984.

- 1 The aerodynamic diameter of a particle is the diameter of a particle of density,  $\rho=1.0$ ,
- 2 which would behave similarly with respect to impaction as the particle in question. For





**Figure 3-17.** These size distributions, obtained during an EPA study of the Denver brown cloud represent one of the few efforts to compare particle-counting and particle-collection size-distribution measurements. Note that impactor data is given in aerodynamic diameter and particle-counting data is given in geometric diameter derived from the number distribution and estimated density.

Source: Durham et al., 1975.

spheres, the aerodynamic diameter,  $D_a$ , equals  $\sqrt{\rho} D_p$ , where  $\rho$  is the density of the particle and  $D_p$  is the geometric diameter. Since coarse particles are expected to have a greater density than fine particles, converting the volume, geometric-size distribution to a mass, aerodynamic-size distribution would increase the apparent size of the volume distribution above  $1 \mu\text{m}$  and widen the minimum. For small particles, below  $0.5 \mu\text{m}$ , or at reduced pressures where the mean free path of the gas molecules is of the same order, or larger than the particle diameter, the Stokes diameter, which is more closely related to the diffusion

coefficient, is a more useful parameter. The relationships between Stokes, aerodynamic and geometric diameter are discussed in Section 3.1.7.1.

The particle size distribution shown on the bottom of the graph was derived from a combination of a mobility counter and several optical counters. The "mobility size", obtained from the electrical aerosol analyzer (EAA) in earlier studies and the differential mobility analyzer (DMA) in more recent studies is dependent on the particle shape but not the density. For irregularly shaped particles the "mobility" size gives the Stokes diameter, which is the geometric diameter of a sphere with the same aerodynamic drag. For a sphere the Stokes diameter and the geometric diameter are the same. By comparing the mobility or Stokes diameter to the aerodynamic diameter it is possible to measure the density of spherical particles (Stein et al., 1994).

The "optical" size of a particle depends on the particles shape and refractive index, and on the characteristics of the optical counter. The amount of light scattered by a particle at a wavelength near the particle size varies rapidly with changes in size, wavelength, refractive index, and scattering angle. Therefore, several different optical counters may be needed to cover the range of atmospheric particle sizes. Because of non-linearities in the response of laser or narrow wavelength optical counters to size changes it is especially difficult to measure particles in the 0.5 to 1.0 size range (Hering and McMurray, 1991; Kim, 1995). Since the amount of scattered light depends strongly on the refractive index it would be useful to calibrate optical counters with particles of the same refractive index as those in the atmosphere. Hering and McMurray (1991) used a differential mobility analyzer to select particles of a uniform geometric diameter. The light scattering of these monodispersed atmospheric particles, as measured by a Particle Measuring System LAS-X optical counter, was compared to that of spheres of polystyrene latex (a substance frequently used to calibrate optical counters) and oleic acid of the same geometric diameter. The atmospheric aerosols scattered less light than polystyrene latex sphere (refractive index =  $1.9 - 0.0i$ ), but about the same amount of light as oleic acid spheres (refractive index =  $1.46 - 0.0i$ ) of the same geometric size. Relating the variety of sizes measured by particle counters and impactors, and combining them into a single size indicator, is a major task which has not yet been adequately addressed.

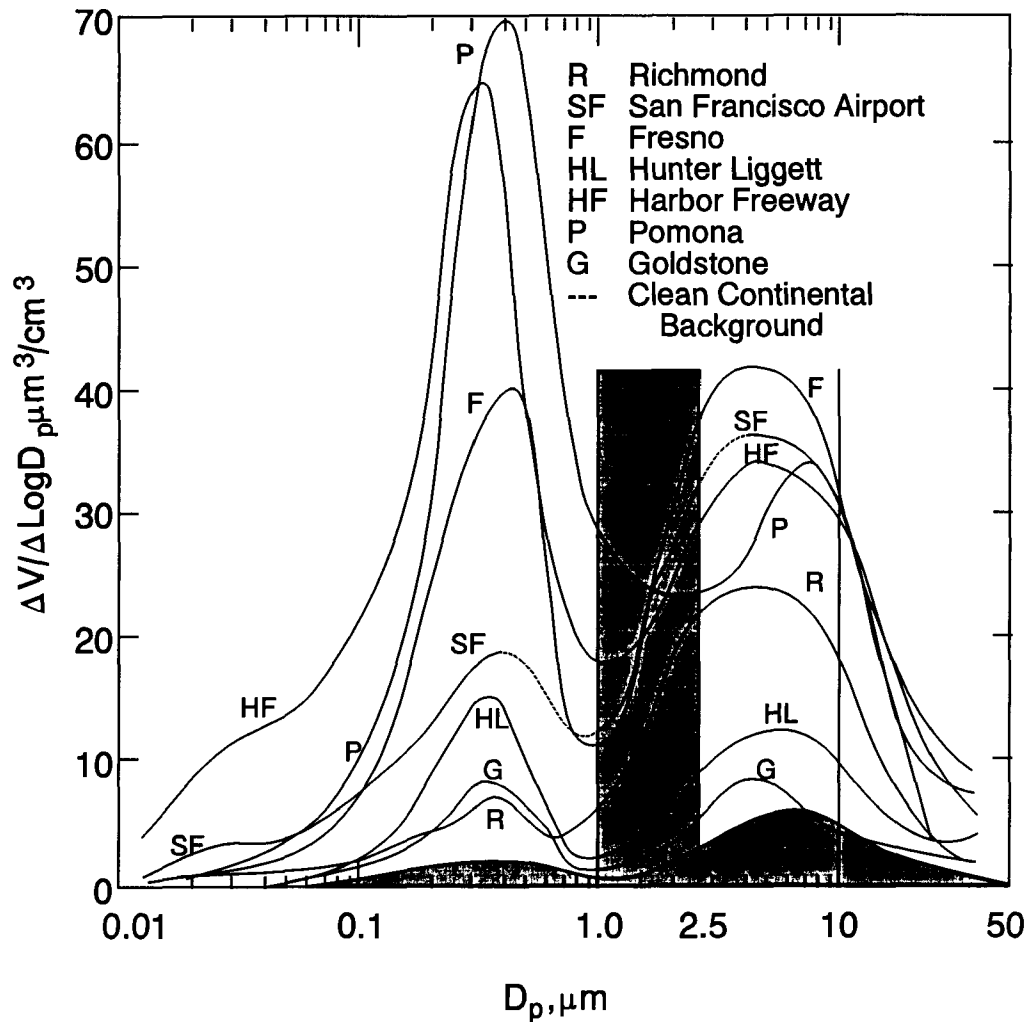
1 The greater width of the coarse modes, as measured by the impactor in Figure 3-17,  
2 may be attributed to the use of glass fiber filter paper for the impactor surface. It is now  
3 recognized that the use of glass fiber filter material, as contrasted to a flat surface, causes a  
4 severe reduction in the effectiveness of the cut. Large particles bounce off the glass fiber  
5 (Vanderpool et al., 1987) giving much reduced collection efficiencies; whereas fine particles  
6 penetrate into the fiber and some are captured in stages that should have near zero collection  
7 efficiencies (Rao and Whitby, 1978). Many studies that used the Anderson High Volume  
8 Fractionating Sampler also used glass fiber filters. The use of glass fiber filters as impaction  
9 collection surfaces causes any given size range to contain both larger and smaller particles  
10 than predicted and thus tends to spread out the modes and fill in the minima. An example of  
11 the smoothing effect of glass fiber collection surfaces, and especially the collection of fine  
12 particles on upper stages, can be seen in Figure 3-16. Nevertheless, the bimodal nature of  
13 the ambient aerosol is still captured.

### 15 **3.7.1.5 Review of Size Distribution Data**

#### 16 ***Early Studies***

17 In 1978, when EPA scientists debated the best cut-point to separate fine particles from  
18 coarse particles, there was limited information available. Particle-counting data from  
19 California studies had been summarized by Whitby and Sverdrup (1980) and are shown in  
20 Figure 3-18. With the exception of one distribution from Pomona, all distributions showed a  
21 minimum near 1  $\mu\text{m}$  and indications of significant amounts of coarse particle material  
22 between 1.0 and 2.5  $\mu\text{m}$ . (The region between 1 and 2.5  $\mu\text{m}$  will be referred to as the  
23 intermodal region.) Other studies of size distribution (McMurry et al., 1981) in the  
24 Southeastern United States, provided similar information (Figure 3-19).

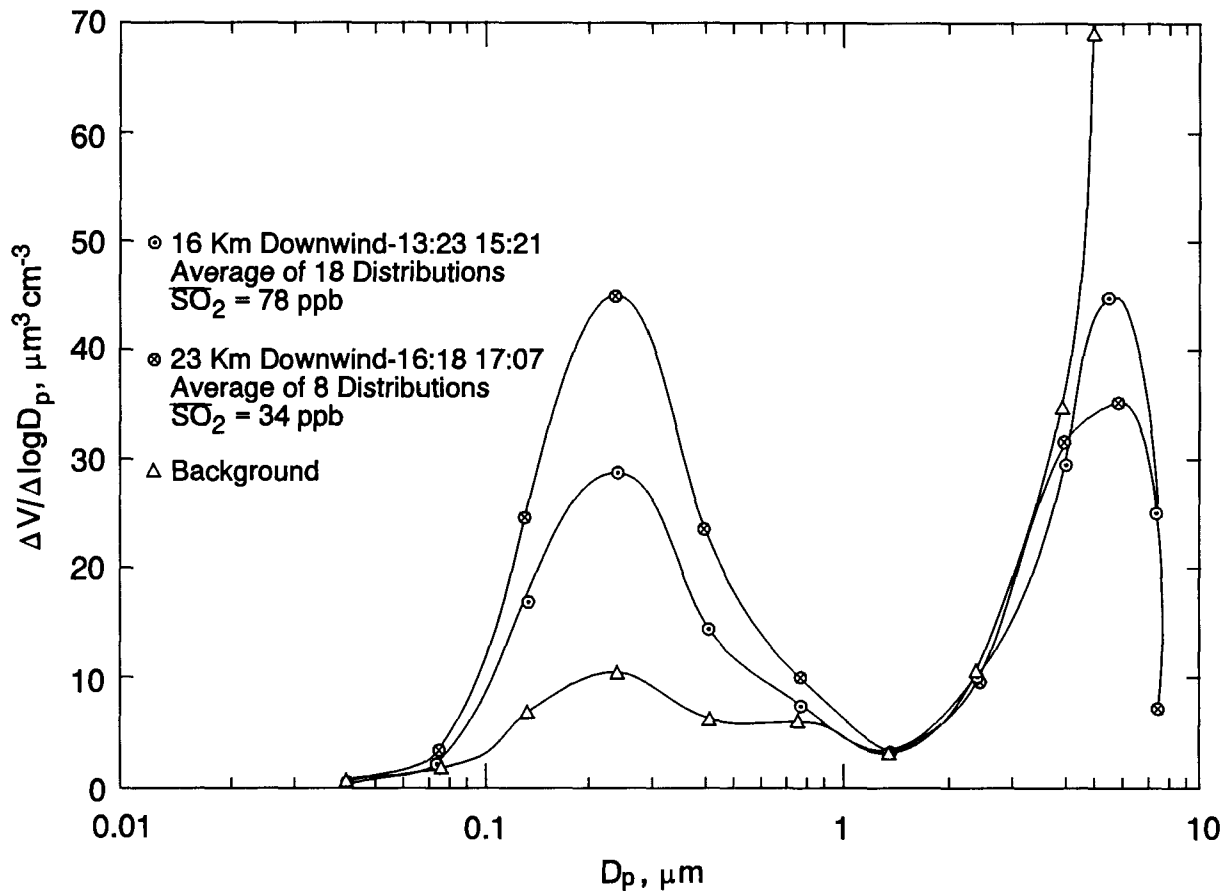
25 Results from several impactor studies were also available, some of which suggested two  
26 modes. However, much of the impactor data were considered unreliable in regard to the  
27 existence and position of modes (Whitby et al., 1974). However, one of the more extensive  
28 and reliable studies available (Patterson and Wagman, 1977) provided confirmation of the  
29 Whitby bimodal observations. In this study, mass and composition measurements were made  
30 for four different levels of visibility. The histograms for mass, sulfate, and iron for two  
31 levels of visibility are shown in Figure 3-20. It is clear that the major portion of the fine



**Figure 3-18.** Grand average volume-size distributions from the Aerosol Characterization Experiment (ACHEX) in 1972. A size distribution for clean continental aerosol is shown for comparison. Note that with the exception of the Pomona size distribution, all distributions show a distinct minima near 1.0  $\mu\text{m}$  diameter. A line has been added at 1.0  $\mu\text{m}$ , 2.5  $\mu\text{m}$ , and 10  $\mu\text{m}$  diameter to indicate how much of the coarse particle mode is observed between 1.0 and 2.5  $\mu\text{m}$  diameter.

Source: Whitby and Sverdrup, 1980.

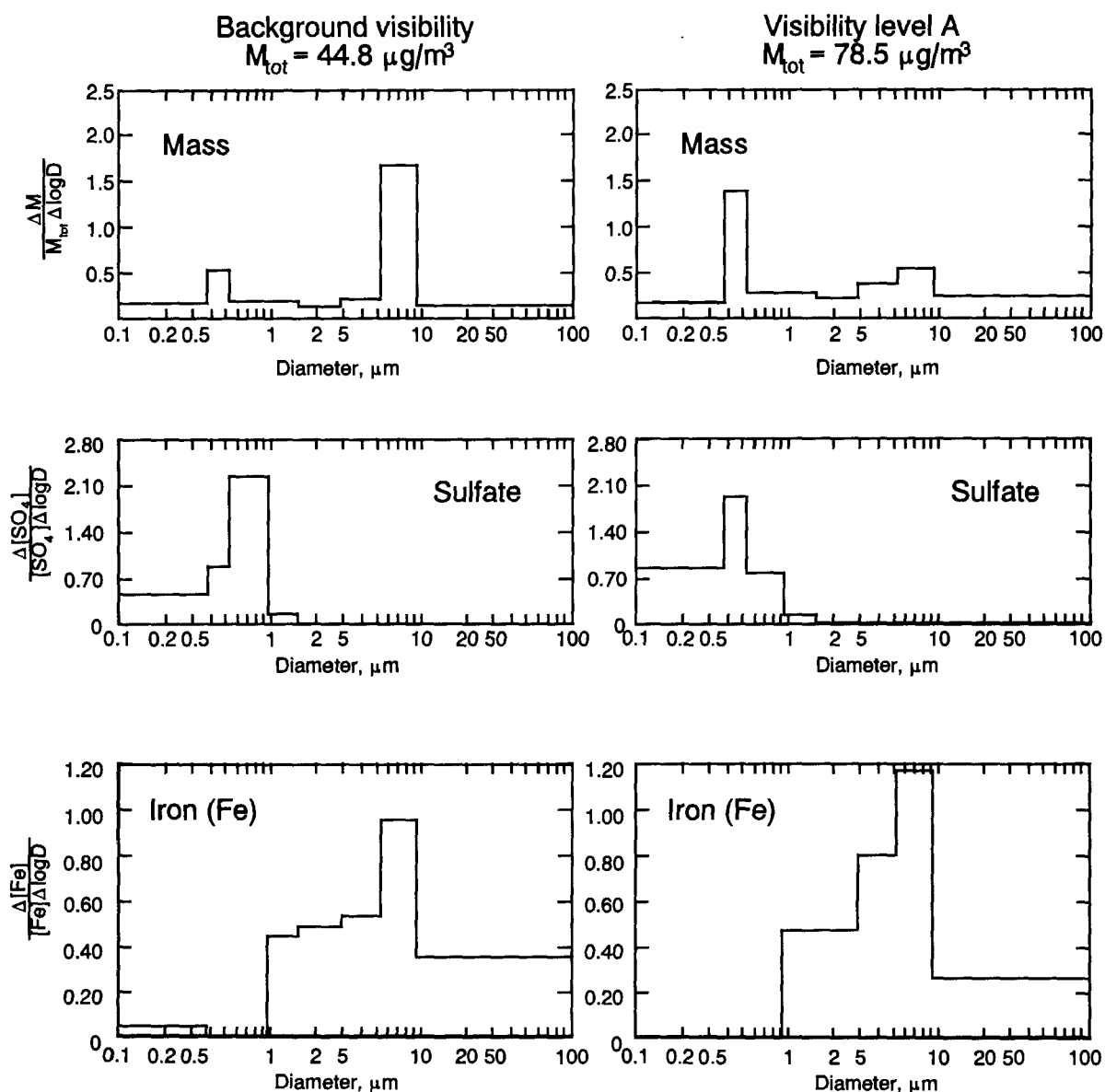
- 1 mass is below 0.6  $\mu\text{m}$  and the major portion of the coarse mass is greater than 3  $\mu\text{m}$  in
- 2 diameter. These impactor data, coupled with the more extensive number-size distributions
- 3 data of Whitby and Sverdrup (1980) led to a preference for a 1  $\mu\text{m}$  cut-point but an



**Figure 3-19. Volume-size distribution taken in the midwestern U.S. near the Cumberland Power Plant in Tennessee. Note that coarse mode decreases and fine mode increased as the mobile sampling van moved downwind farther from urban influence but allowing more time for reaction as the power plant plume mixed with background air and  $SO_2$  was converted to sulfate and  $NO_x$  to nitrate.**

Source: McMurry et al., 1981.

- 1 acceptance of 2.5  $\mu m$  on the assumption, then considered to be the case, that 2.5  $\mu m$
- 2 represented the minimum cut-point that was attainable with a dichotomous sampler (Miller et
- 3 al., 1979).



**Figure 3-20.** Examples of size distribution histograms for total mass, sulfate, and iron obtained at two visibility levels using an Anderson impactor. Arbitrary choice of 0.1 and 100 for lower and upper limits cause the extreme rectangles to be long and low. Note the separation into fine and coarse modes in mass and that sulfate and iron clearly belong in the fine and coarse mode respectively.

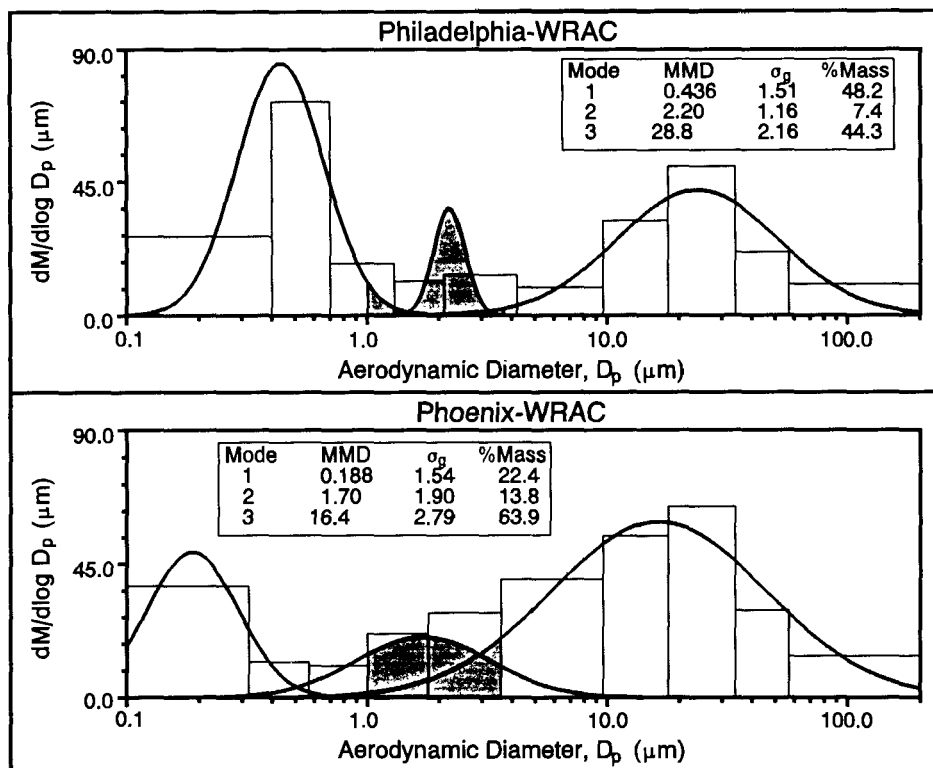
Source: Patterson and Wagman, 1977.

## Recent Work

In the intervening 15 years, there has been very little additional work in which particle-counting techniques, covering the entire size range, have been used to measure ambient aerosols. Most of the particle-counting studies have focused on fine and ultrafine particles, diameter  $< 1.0 \mu\text{m}$ . There have however been a number of impactor studies that provide insight into the size of the fine and coarse modes and into what material is found between them.

There are only a few impactor size distribution studies that cover the full size range from  $0.01$  to  $100 \mu\text{m}$  (Lundgren and Hausknecht, 1982; Lundgren et al., 1984; Burton and Lundgren, 1987; Vanderpool et al, 1987). Lundgren and co-workers used a mobile unit, the wide range aerosol classifier (WRAC), to measure mass-size distribution in ten size ranges from  $< 0.4$  to  $> 50 \mu\text{m}$ . Two distributions, averages for Philadelphia and Phoenix, are shown in Figure 3-21. Both clearly indicate a fine particle mode with an MMD near  $0.5 \mu\text{m}$  for Philadelphia and  $0.3 \mu\text{m}$  for Phoenix. Both show a coarse particle mode with an MMD near  $20 \mu\text{m}$  in diameter. However, there is a significant amount of material found in the intermodal region,  $1$  to  $2.5 \mu\text{m}$ . Although the intermodal mass is not a significant fraction of the total suspended particulate mass or even of TSP, as would be measured by a high-volume sample (upper cut-point around  $25 \mu\text{m}$ ), it does represent a major portion of the coarse fraction of  $\text{PM}_{10}$ .

The existing size-distribution data were recently reviewed by Lundgren and Burton (1995), with emphasis on the coarse mode. They concluded that the coarse mode could be reasonably well described by a lognormal distribution with a mass mean diameter (MMD) of  $15$  to  $25 \mu\text{m}$  and a mode spread ( $\sigma_g$ ) of approximately two. This allows one to calculate, for a freshly-generated coarse mode aerosol, that about  $1\%$  of the mass would be less than  $2.5 \mu\text{m}$  and only about  $0.1\%$  would be less than  $1.0 \mu\text{m}$  in diameter. This conclusion is confirmed by data from Whitby in which a wind change allowed a measurement of fresh coarse mode aerosol (National Research Council, 1979). As can be seen in Figure 3-22, the intermodal mass,  $1.0$  to  $2.5 \mu\text{m}$ , was not affected, even though the mass at  $20 \mu\text{m}$  increased substantially.

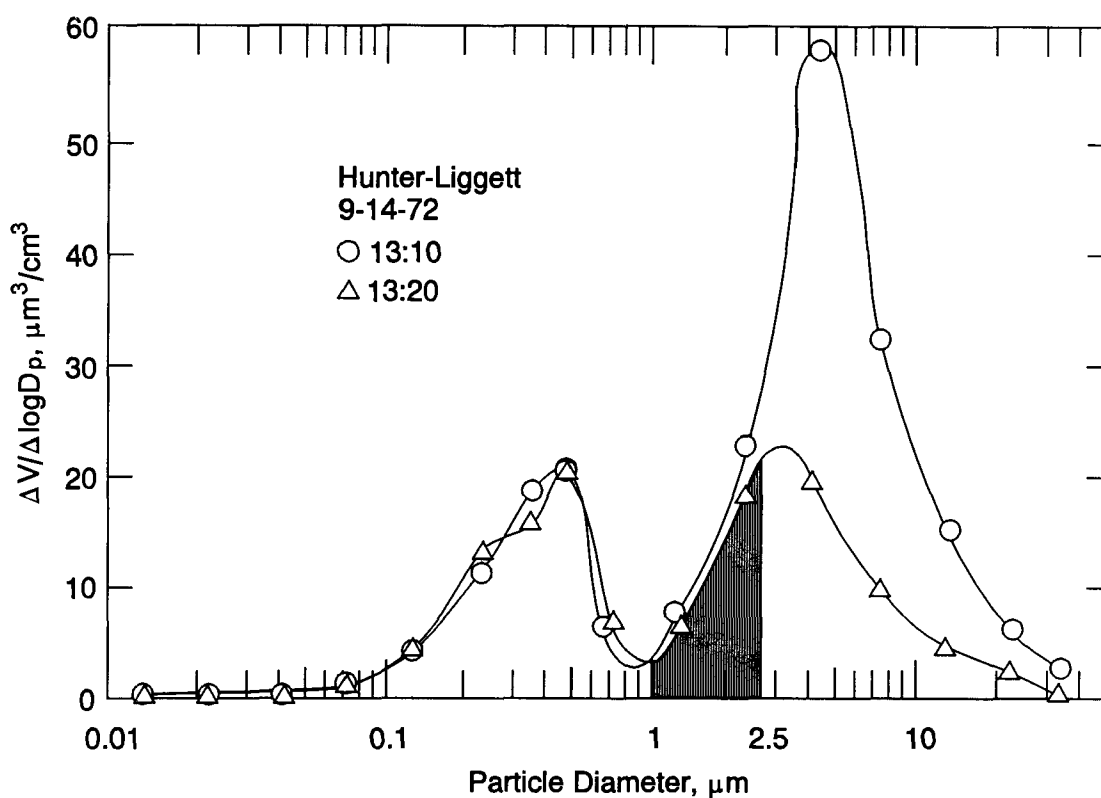


**Figure 3-21. Impactor size distribution measurement generated by Lundgren et al. with the Wide Range Aerosol Classifier: (a) Philadelphia and (b) Phoenix. Note the much larger, small size tail to the coarse mode in the dryer environment of Phoenix.**

Source: Lundgren et al., EPA Report.

Another extensive set of studies covering the full size range, but limited to the Chicago area, has been reported by Noll and coworkers (Lin et al., 1993, 1994). They used an Anderson impactor for smaller particles and a Noll Rotary Impactor for larger particles. Results of Lin et al. also indicate a bimodal mass distribution. For the shorter time interval measurements (8 or 16 h), the average MMD for the fine mode was  $0.42 \mu\text{m}$ , with a  $\sigma_g$  around two. The average MMD of the coarse mode was  $26 \pm 8 \mu\text{m}$ , with a  $\sigma_g$  varying from 2.0 to 3.5. As shown in Figure 3-23, the results of Noll and coworkers (Lin et al., 1993, 1994) also suggest that some coarse mode material is found in the intermodal region, 1.0 to  $2.5 \mu\text{m}$ .





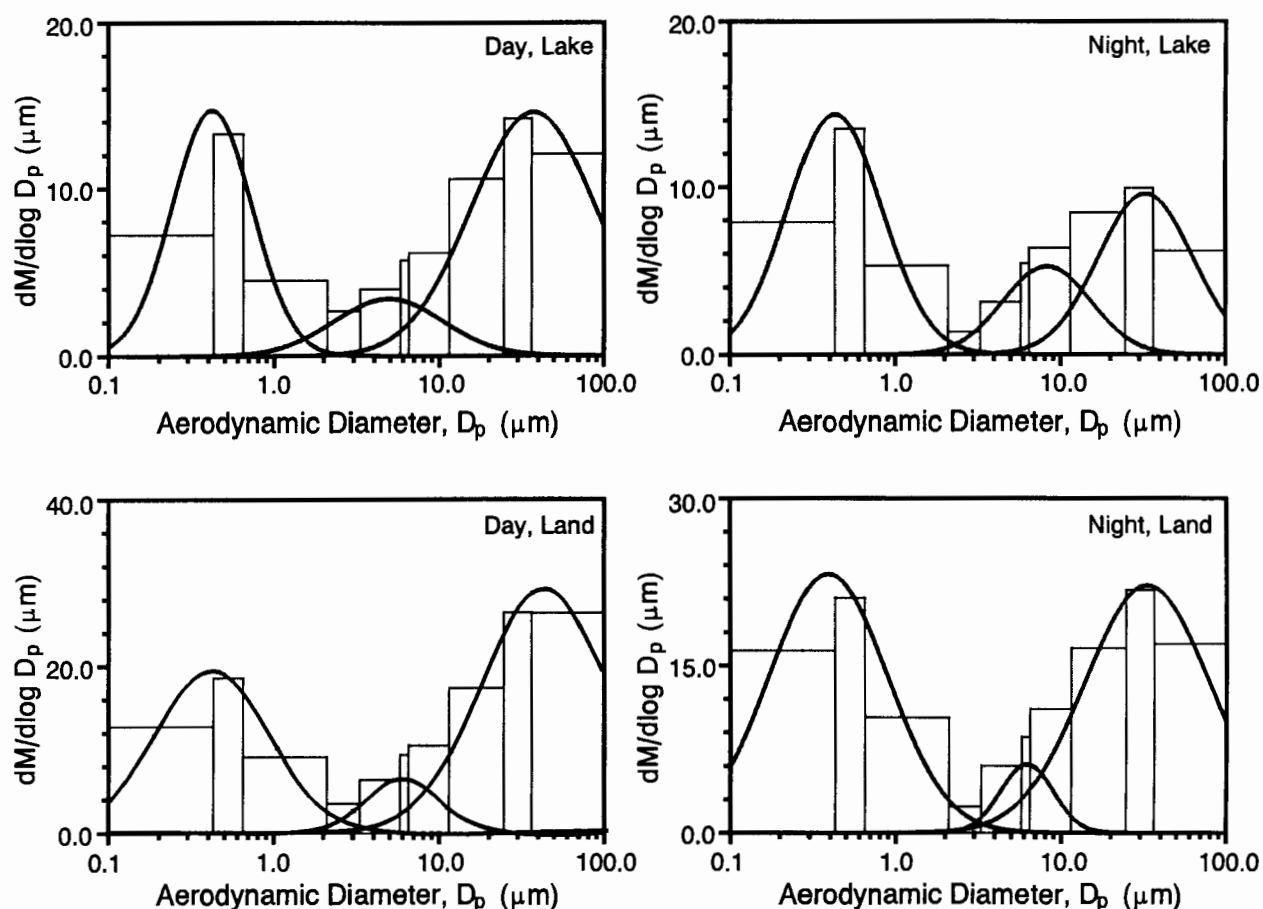
**Figure 3-22.** Example of aged and fresh coarse mode particle size distributions. A sudden wind change brought fresh wind-blown dust to the sampler, operated as part of the South Coast Air Quality Study. Note that there is only a very small change in the intermodal mass, 1.0 to 2.5  $\mu\text{m}$  diameter, although there is a major increase in the mass between 2.5 and 10  $\mu\text{m}$  in diameter.

Source: National Research Council, 1979.

#### 1 3.7.1.6 Intermodal Region

##### 2 *Coarse mode*

3 The question then arises, what portion of the coarse mode material found in the  
 4 intermodal region is real and what portion is artifact? As discussed in Section 3.3.3.2.4, the  
 5 optical size may differ from the geometric or aerodynamic size. Optical counters are  
 6 normally calibrated with latex particles, or other particles of a specific refractive index.  
 7 Atmospheric particles with different refractive indices would be incorrectly sized if the



**Figure 3-23. Size distributions reported by Noll from the Chicago area using an Anderson impactor for the smaller particles and a Noll Rotary Impactor for the larger particles.**

Source: Lin et al., 1993.

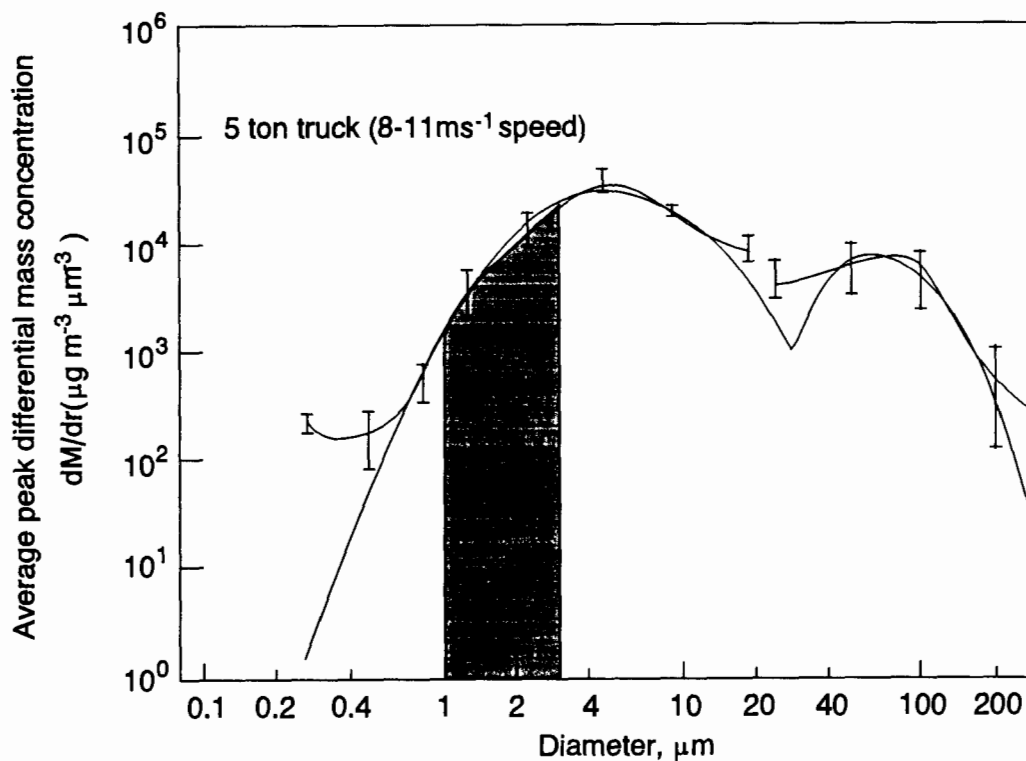
1 difference in refractive index resulted in a difference in the amount of light scattered by the  
 2 particles (Wilson et al., 1988; Liu et al., 1992; Hering and McMurry, 1991). For particle  
 3 counters using lasers, particles of different sizes within the 0.5 to 1.0  $\mu\text{m}$  range may give the  
 4 same light scattering (Hering and McMurry, 1991; Kim 1995).

5 In the case of impactors, it is possible that it an artifact may arise from particle bounce,  
 6 from fragmentation of larger agglomerates, or from loosening of material from other surfaces  
 7 by impacting particles. The problem of particle bounce in impactors has been treated  
 8 theoretically and practically in many studies (Wang and John, 1987, 1988). Most workers  
 9 coat the coarse particle stages with a grease or oil to reduce bounce. However, as the

1 surface becomes covered with aerosols, a particle may impact another particle instead of the  
2 surface and either bounce to a lower stage or cause deagglomeration and reentrainment of  
3 previously collected particles (John et al., 1991; John and Sethi, 1993). As impactor  
4 collection plates become loaded or as inlet upper size cut surfaces become dirty, the  
5 magnitude of the effect increases (Ranade et al., 1990; John and Wang, 1991). One result is  
6 a lowering of the effective cut point of the inlet and the impactor stages. Thus, it is  
7 uncertain how much of the mass found in the intermodal size range is real and how much is  
8 due to artifacts.

9 There are several reasons to believe, however, that some of the intermodal mass may  
10 be real. For example, Lundgren and Burton (1995) point out that the lifetime of particles in  
11 the atmosphere is a strong function of their aerodynamic size. Thus, while freshly generated  
12 coarse mode aerosol may have a MMD of 20  $\mu\text{m}$ , with only 1% below 2.5  $\mu\text{m}$ , as the  
13 aerosol ages the larger particles will rapidly fall out, leaving a distribution enriched with  
14 particles in the small-size tail of the distribution.

15 A second explanation has to do with the possible multimodal nature of dust generated  
16 by wind or vehicular traffic. A study by the U.S. Army (Pinnick et al., 1985) measured the  
17 size distribution of dust generated by heavy vehicles driven on unpaved roadways in the arid  
18 southwestern United States. A variety of light-scattering instruments were used and were  
19 recalibrated for the refractive index of the soil particles. The occurrence of strong surface  
20 winds (gusts of 15 to 20  $\text{m s}^{-1}$ ) during the study permitted, in addition to the vehicular-  
21 generated dust, some measurements of windblown dust. There were some differences  
22 between sandy soil and silty soil, and between dust generated by vehicular traffic and by  
23 wind. However, all situations produced a bimodal size distributions. The upper mode had  
24 an MMD that ranged from 35 to 53  $\mu\text{m}$ , with  $\sigma_g$  from 1.37 to 1.68. Of particular interest,  
25 however, was a second mode having an MMD that varied from 6.2 to 9.6  $\mu\text{m}$ , with a  $\sigma_g$   
26 from 1.95 to 2.20. (One measurement in silty soil had an MMD of 19.4  $\mu\text{m}$ .) The MMDs  
27 of the smaller coarse particle modes are significantly smaller than those coarse mode MMD's  
28 observed by Lundgren or Noll. An example of vehicular generated dust is shown in  
29 Figure 3-24. Note that the differential mass is plotted on a logarithmic scale. These results  
30 suggest that in arid areas, significant soil material, generated by traffic or wind, may be  
31 found in the intermodal region.



**Figure 3-24.** Size distribution of dust generated by driving a truck over an unpaved test track. "Error bars" show the range of distributions from individual tests. The curves shown are log-normal fits to the average distribution. The original data was plotted as log radius but has been replotted versus log diameter. The shaded bar between lines at diameters of 1.0 and 2.5  $\mu\text{m}$  indicate how the smaller size mode of this dust can contribute to the intermodal mass found in arid areas (see Figure 9b).

Source: Pinnick et al., 1985.

1 A third reason for believing that the intermodal mass is real has to do with the relative  
 2 size efficiency of particle removal equipment used on power plants and other large industrial  
 3 facilities. Older control devices, which may still be used in some applications, allow  
 4 significant particle mass to escape. Overall mass efficiencies are approximately 80% for  
 5 cyclones and 94% for scrubbers. Modern control devices have very high overall  
 6 efficiencies, 99.2% for electrostatic precipitators (ESP) and 99.8% for baghouses. However,  
 7 all of these devices have efficiencies for coarse particles that decrease with decreasing size.

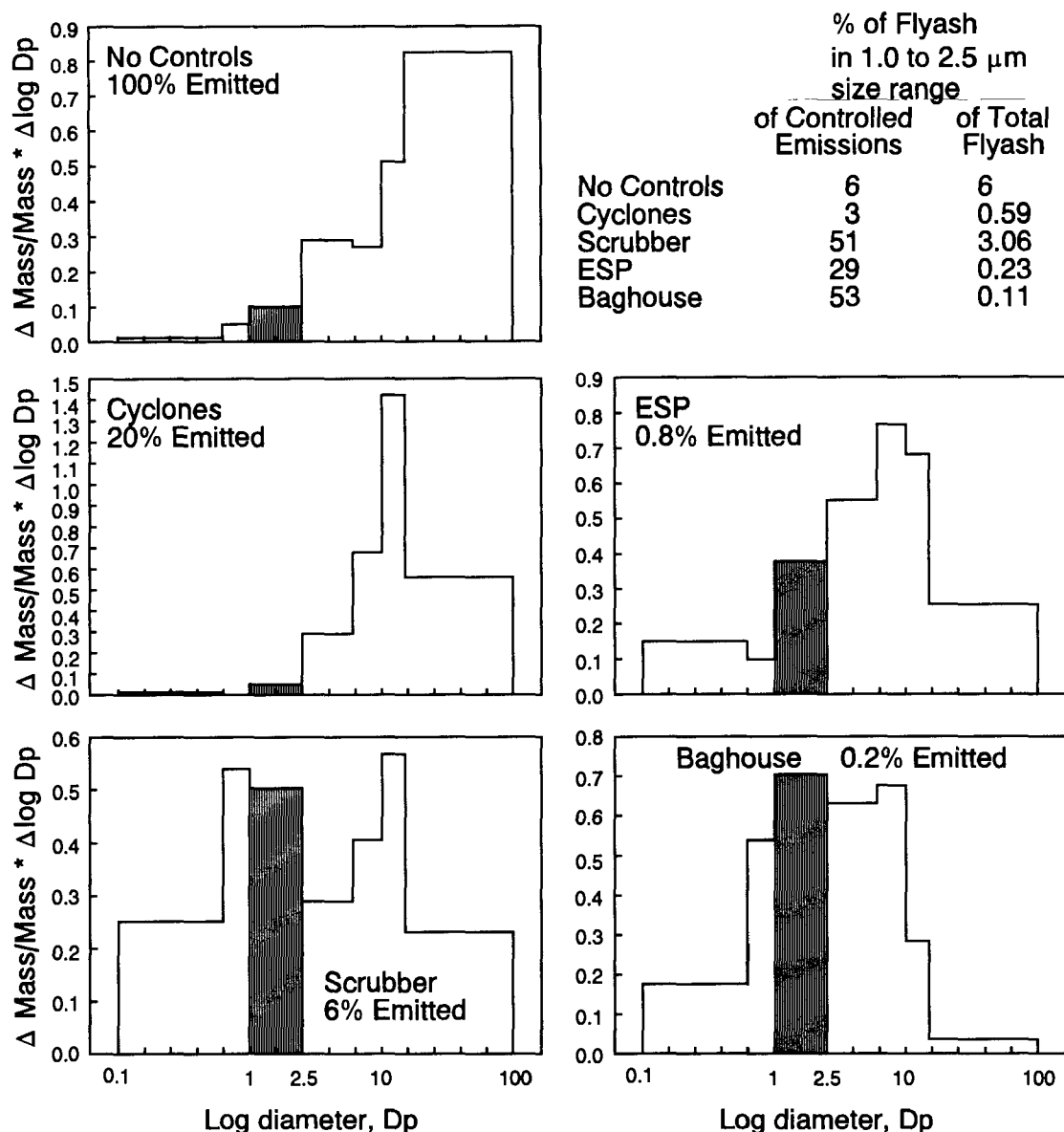
Efficiencies typically reach a minimum between 0.1 and 1  $\mu\text{m}$  and increase for particles smaller than 0.1  $\mu\text{m}$ . Thus, although most of the particulate mass is captured, the particles that do escape are in the smaller size range. Data from U.S. EPA, plotted in Figure 3-25, (U.S. Environmental Protection Agency, 1993) show the size distribution of fly ash from a pulverized coal power plant and the size distribution of the material escaping from the various control devices. The small-size tail of the coarse mode escapes preferentially and likely contributes material in the intermodal region.

Cheng et al. (1985) reported experimental measurements from an atmospheric fluidized-bed coal combustor. Size distribution measurements, made downstream of a cyclone and again downstream from baghouse filtration of the material leaving the cyclone, are shown in Figure 3-26 (Cheng et al., 1985). Electron microscope photographs confirmed a fine particle mode of spherical particles between 0.1 and 0.25  $\mu\text{m}$ , presumably formed from evaporation and condensation of volatile species from the coal matrix; and irregular-shaped chunks from the coarse mode with a peak concentration between 1 and 3  $\mu\text{m}$  in diameter.

A fourth reason comes from a study of the size of particles collected in various types of samplers. Burton et. al (1995) used two techniques to measure the size of individual particles collected on filters. Particles with diameters between 1 and 2.5  $\mu\text{m}$  were found to account for 18 to 20% of the coarse fraction of  $\text{PM}_{10}$ .

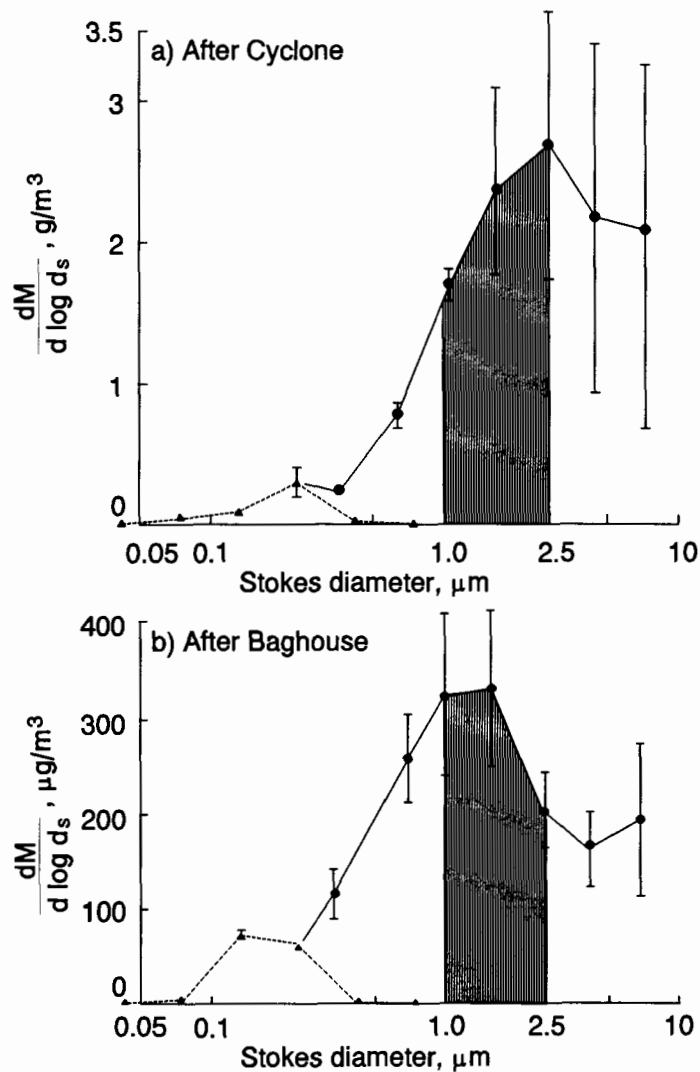
A fifth piece of evidence comes from studies in which measurements are made of the elemental composition of  $\text{PM}_{2.5}$  and  $\text{PM}_{10}$  or the coarse fraction of  $\text{PM}_{10}$ . Elements representative of soil type material have been found in the  $\text{PM}_{2.5}$  fraction. In a study in Philadelphia that used dichotomous samplers, an amount of soil-type material equal to 5% of the coarse mode fraction of  $\text{PM}_{10}$  was found in the  $\text{PM}_{2.5}$  fraction (Dzubay et al., 1988). Since the virtual impactor used in the dichotomous sampler minimizes particle bounce and reintrainment, this would appear to be the small-size tail of the coarse mode in the 1 to 2.5  $\mu\text{m}$  size range. Similar results have been reported from the IMPROVE network (Eldred et al., 1995). Elemental analysis suggested that soil-derived material, equal to 20% of the coarse fraction of the  $\text{PM}_{10}$  sample, was found in the  $\text{PM}_{2.5}$  sample.

Thus, one can conclude that coarse mode material is found in the intermodal region. There are reasons to suspect that a portion of this material is an artifact but that a portion is real coarse mode material having an aerodynamic diameter between 1.0 and 2.5  $\mu\text{m}$ . In



**Figure 3-25.** Size distribution of emissions from a pulverized-coal power plant and the particle size distributions remaining after several types of control devices (EPA, AP-42, 1993).

- 1 either event, this can lead to a misunderstanding of the source of the particles, to
- 2 inappropriate control strategies, or to exposure studies that fail to differentiate correctly
- 3 between fine and coarse particles.



**Figure 3-26.** Size distributions from a fluidized-bed pulverized coal combustor, a) after initial clean up by a cyclone collector, and (b) after final clean up by a baghouse.

Source: Cheng et al., 1985.

### ***Fine Mode***

This section discusses the source of fine mode material found in the intermodal region. Early particle-counting data suggested that, with a few exceptions, significant mass of fine mode material would not be found above 1  $\mu\text{m}$  (see Figures 3-13, 3-18, 3-19, and 3-20). However, impactor studies, on some occasions, have observed significant mass on stages with a cut point of 1  $\mu\text{m}$ . In some instances, the MMD of the fine mode was as large as 1  $\mu\text{m}$  (John et al., 1990). The change in relative humidity produced by a few degrees

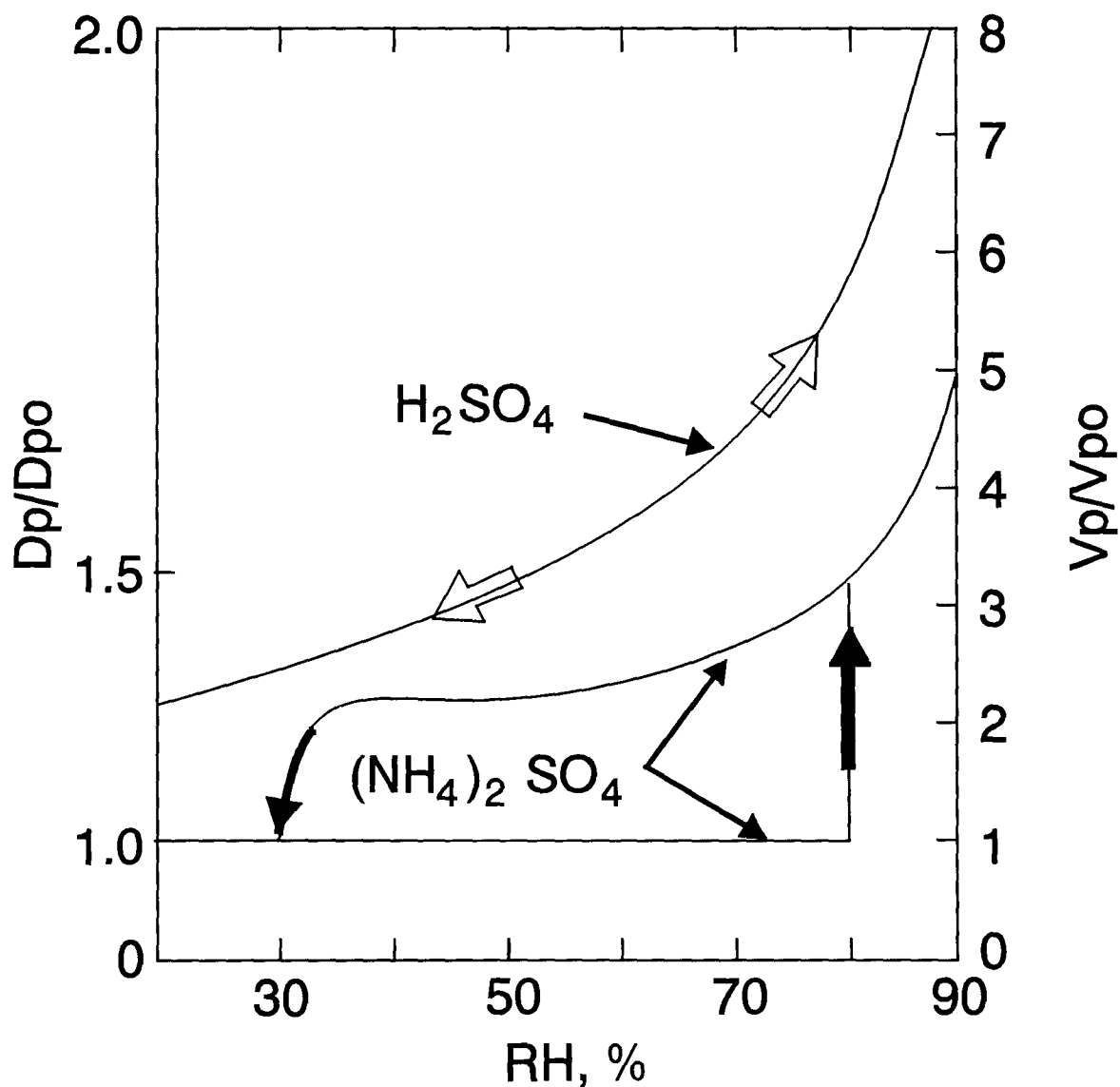
change in temperature can significantly modify the MMD of an ambient aerosol size distribution. As the RH approaches 100%, accumulation mode aerosols, with dry sizes below  $1.0\ \mu\text{m}$  in diameter, may grow larger than  $2.5\ \mu\text{m}$  in diameter, be rejected by  $\text{PM}_{2.5}$  samples, and be counted as coarse particles.

Before examining additional field data demonstrating the effect of relative humidity on particle size, it is useful to review some basic information on the interaction of water vapor with the components of fine particles. Sulfuric acid ( $\text{H}_2\text{SO}_4$ ) is a hygroscopic substance. When exposed to water vapor a  $\text{H}_2\text{SO}_4$  droplet will absorb water vapor and grow in size until an equilibrium exists between the liquid water concentration in the  $\text{H}_2\text{SO}_4$  solution droplet and the water vapor concentration in the air. The amount of water in the sulfuric acid droplet will increase and decrease smoothly as the RH increases and decreases. Ammonium sulfate,  $(\text{NH}_4)_2\text{SO}_4$ , however, is deliquescent. If initially a crystal in dry air, it will remain a crystal until a certain RH is reached; at this point it will absorb water and become a solution droplet. The RH at which this happens,  $\approx 80\%$  RH in the case of  $(\text{NH}_4)_2\text{SO}_4$ , is called the deliquescent point. At RH's above the deliquescent point the  $(\text{NH}_4)_2\text{SO}_4$  droplets are hygroscopic, gaining or losing water reversibly as the RH increases or decreases. If the RH decreases below the deliquescent point the solution droplet becomes supersaturated and unstable to crystallization. However, sub-micron sized droplets will remain supersaturated until a significantly lower RH, known as the crystallization or efflorescent point is reached. The crystallization point decreases with decreasing droplet size and decreasing purity (Whitby, 1984). Thus, for a deliquescent substance, a plot of droplet diameter or water content as a function of RH will have two lines, one for increasing RH and another for decreasing RH. An example of this phenomena, known as hysteresis, is shown in Figure 3-27. Table 3-15 shows the RH at the deliquescent and crystallization points for some compounds found in the atmosphere.

Much experimental and theoretical effort has gone into understanding this process. The basic theory was elucidated by Hänel (1976). Much experimental work has been done on atmospheric species (e.g., Tang and Munkelwitz, 1977, 1993; Richardson and Spann, 1984).

Ammonium nitrate,  $\text{NH}_4\text{NO}_3$ , because of its volatility, is difficult to handle but has been studied successfully by Richardson and Hightower (1987). The aerosol equilibria models





**Figure 3-27.** 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% RH, hygroscopic growth of ammonium sulfate solution droplets at RH greater than 80%; and hysteresis as the droplet remains supersaturated as the RH decreases below 80% RH until the crystallization point is reached.

Source: National Research Council, 1979.

**TABLE 3-15. RELATIVE HUMIDITY OF DELIQUESCENT AND CRYSTALLIZATION FOR SEVERAL ATMOSPHERIC SALTS<sup>a</sup>**

Compound	Deliquescence	Crystallization <sup>c</sup>
(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	79.9 ± 0.5	37 ± 2
NH <sub>4</sub> HSO <sub>4</sub>	39.0 ± 0.5	
NH <sub>4</sub> NO <sub>3</sub>	61.8	
NaCl	75.3 ± 0.1	42

<sup>a</sup>Taken from Tang and Munkelwitz (1993) unless otherwise indicated.

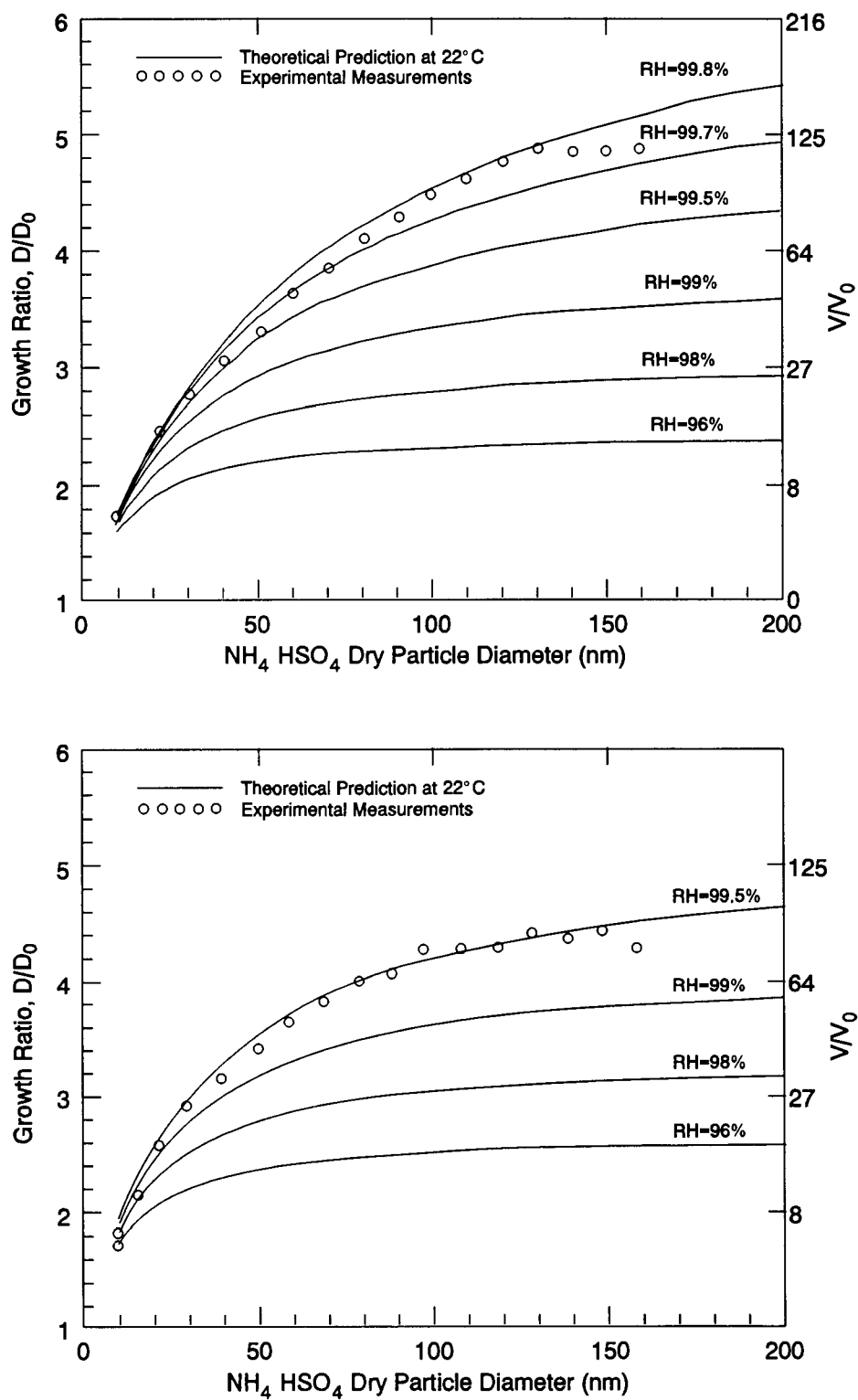
<sup>b</sup>Tang and Munkelwitz (1977).

<sup>c</sup>Shaw and Rood (1990) and references therein.

developed by Seinfeld and co-workers allow calculation of the water content of bulk solution as a function of relative humidity. (Kim et al., 1993a,b).

The water content of a sub-micron sized droplet, and therefore its size, depends not only on the dry size but is a result of a balance between surface tension and solute concentration (Li et al., 1992). Pure water is in equilibrium with its vapor when the RH equals 100% and is therefore, stable, i.e. the rate of evaporation equals the rate of condensation. The water in a solution will be in equilibrium with water vapor at a lower water vapor concentration because the presence of solute molecules or ions lowers the rate of evaporation. Therefore, a solution will absorb water and become more dilute, increasing the water vapor concentration needed for equilibrium until the solution water vapor concentration required for equilibrium matches the ambient water vapor concentration or RH. As the droplet size decreases the surface tension increases and the vapor pressure of water required to maintain equilibrium increases. Therefore, the smaller the dry size of the particle, the less the amount of growth as RH increases.

Theoretical calculations of the growth of various sizes of ammonium sulfate particles and an experimental verification of such calculations, using a simulation of the humidification process in the human lung, are shown in Figure 3-28. Note the very rapid increase in the amount of water and in the diameter of the aerosol particle as the relative humidity approaches 100% RH. Considering the difficulty of measuring relative humidity accurately between 99 and 100%, theory and experiment are in reasonable agreement. As can be seen

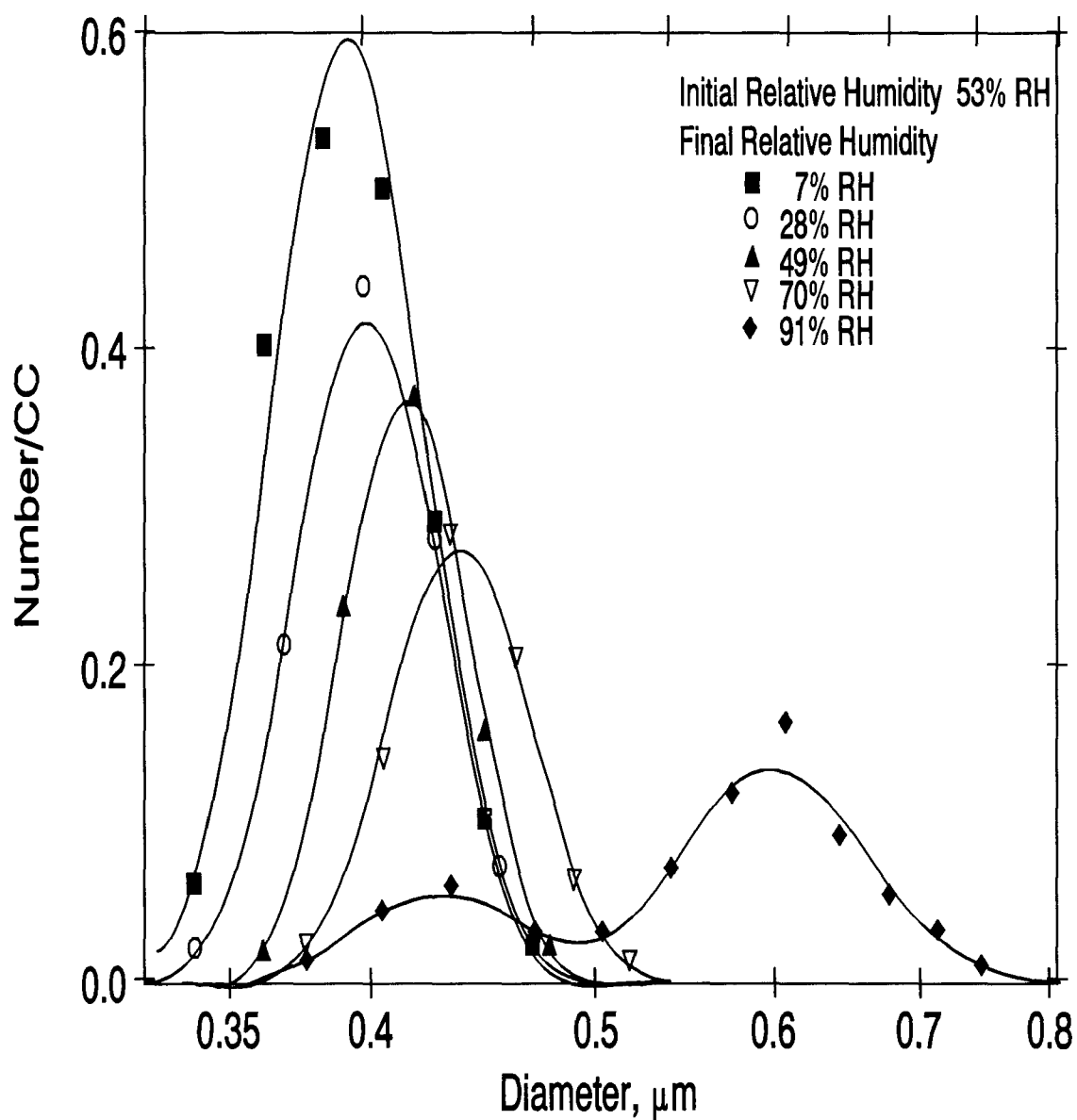


**Figure 3-28.** Theoretical predictions and experimental measurements of growth of  $\text{NH}_4\text{HSO}_4$  and  $(\text{NH}_4)_2\text{SO}_4$  particles at RH between 95 and 100% RH.

Source:

1 the effect of surface tension is most important for particles with dry size less than 100 nm  
2 (0.1  $\mu\text{m}$ ). This phenomena may be of importance in considering the biological effect of  
3 water-soluble pollutants. Accumulation mode particles will be diluted when exposed to  
4 humidification in the lungs. Ultrafine or nuclei mode particles will not be diluted as much.  
5 In the atmospheric aerosol the number distribution will almost always be dominated by  
6 particles below 100 nm (see Section 3.2.1). However, aerosols generated in the laboratory  
7 for exposure studies probably lack the smaller particles found in the atmosphere. This  
8 provides a hypothesis for the difference in effects observed in epidemiological studies and  
9 laboratory exposure studies. The importance of this more concentrated, ultrafine droplet  
10 component of the atmospheric atmosphere may have been neglected because most of the  
11 experimental studies of hygroscopicity have used near-micron-sized particles. However, in  
12 the modeling of deposition of hygroscopic particles, workers, such as Martonen (1993), have  
13 corrected the experimental curves of particle size as a function of RH, based on  
14 measurements of near micron-sized particles, to account for the effects of surface tension on  
15 ultrafine particles.

16 In addition to the laboratory studies discussed above there are some measurements on  
17 the effect of RH changes on atmospheric aerosol. McMurray and co-workers have made use  
18 of a Tandem Differential Mobility Analyzer (TDMA) system (Rader and McMurry, 1986) to  
19 measure the change in particle size with changes in relative humidity at Claremont, CA, as  
20 part of the Southern California Air Quality Study (SCAQS) (McMurry and Stolzenberg,  
21 1989) and at the Grand Canyon National Park, AZ, as part of the Navajo Generating Station  
22 Visibility Study (Zhang and McMurray, 1993; Pitchford and McMurry, 1994). One mobility  
23 analyzer is used to isolate a narrow size distribution. After humidification the size  
24 distribution of this fraction is measured. An example is shown in Figure 3-29. Note that  
25 Figure 3-29 is a number size distribution not a mass size distribution. Particle growth with  
26 increasing RH is evident. However, between 70 and 91% RH the distribution splits into  
27 less-hygroscopic and more-hygroscopic components. Pitchford and McMurry (1994)  
28 attribute this splitting to external mixing, i.e. there are two relatively distinct classes of  
29 particles, both containing some soluble and some non-soluble material, with the more  
30 hygroscopic component containing significant more soluble and hygroscopic material. A  
31 summary of the results of these studies is given in Table 3-16 (Zhang and McMurray, 1993).



**Figure 3-29.** Tandem Differential Mobility Analyzer measurements of the sensitivity of particle size to relative humidity at Claremont, CA. Particle number concentrations varied during the measurement, therefore changes in relative size with humidity are meaningful but changes in number concentration are not.

Source: McMurry and Stolzenberg, 1989.

TABLE 3-16. SUMMARY OF HYGROSCOPIC GROWTH FACTORS

1987 SCAQS, Claremont, CA		
Dry Size ( $\mu\text{m}$ )	More hygroscopic peak $\frac{D_p(90 \pm 3\% \text{ RH})}{D_p(0\% \text{ RH})}$	Less hygroscopic peak $\frac{D_p(87 \pm 2\% \text{ RH})}{D_p(0\% \text{ RH})}$
0.05	$1.14 \pm 0.05$	$1.03 \pm 0.03$
0.2	$1.23 \pm 0.08$	$1.02 \pm 0.02$
0.4	$1.63 \pm 0.11$	$1.04 \pm 0.05$
0.5	$1.59 \pm 0.08$	$1.07 \pm 0.03$
1990 NGS Visibility Study, Grand Canyon, AZ		
Dry Size ( $\mu\text{m}$ )	More hygroscopic peak $\frac{D_p(89 \pm 4\% \text{ RH})}{D_p(0\% \text{ RH})}$	Less hygroscopic peak $\frac{D_p(89 \pm 4\% \text{ RH})}{D_p(0\% \text{ RH})}$
0.05	$1.36 \pm 0.08$	$1.14 \pm 0.10$
0.10	$1.42 \pm 0.08$	$1.17 \pm 0.09$
0.20	$1.49 \pm 0.11$	$1.17 \pm 0.10$
0.30	$15.1 \pm 0.09$	$1.14 \pm 0.10$
0.40	$1.43 \pm 0.10$	$1.07 \pm 0.03$

Values are mean  $\pm$  standard deviations.

1 The difference in growth rates may be due both to size and to variation in composition as a  
2 function of size. The lower growth factor for 0.2  $\mu\text{m}$  particles in Claremont relative to the  
3 Grand Canyon may be due to a higher concentration of non-soluble organic material in  
4 Claremont.

5 Some experimental examples of the significant effect of relative humidity on ambient  
6 aerosol size distributions are shown in Figure 3-30 (Lowenthal et al., 1995). In this work,  
7 supported by the Electric Power Research Institute, impactor collection and ion  
8 chromatographic analysis were used to measure sulfate size distributions over short enough  
9 periods to demonstrate the effects of changing relative humidities. The results suggest that  
10 the lognormal distribution is preserved as relative humidity increases, but that the MMD  
11 increases. This effect is especially pronounced as the relative humidity approaches 100%.

12 There are also studies of the behavior of ambient aerosols as the relative humidity is  
13 reduced by heating the sampled air. Shaw and Rood (1990) report a study using a heated  
14 integrating nephelometer in which crystallization RHs of 4 to 67% were observed. Similar  
15 studies in Washington, D.C. by Fitzgerald et al. (1982) found no evidence of crystallization  
16 or efflorescence when RH was reduced to 30% RH.

17 Further experimental evidence of the effect of decreasing relative humidity on aerosol  
18 size distribution is provided by impactor data reported by Berner (1989). One impactor  
19 sampled aerosol in its humidified state directly from the atmosphere. The inlet of a second  
20 impactor was warmed  $\approx 7^\circ\text{C}$  above the ambient temperature of  $\approx 5^\circ\text{C}$  in order to  
21 evaporate most of the particle-bound water before collecting the aerosol. The water and  
22 other volatile material in both the "wet" and the "dry" samples would evaporate in the  
23 laboratory prior to weighing the impactor stages. As can be seen in Figure 3-31 in the  
24 ambient air most of the non-volatile mass was above 1.0  $\mu\text{m}$  with significant amounts above  
25 2.5  $\mu\text{m}$ . However, after heating the size of the aerosol was reduced so that most of the non-  
26 volatile mass was below 1.0  $\mu\text{m}$ . Berner treated the distributions as monomodal and derived  
27 growth factors of 4.9 for fog and 4.1 for haze. If the observations are treated as  
28 multimodal, good bimodal, or as shown in Figure 3-31, trimodal fits are obtained. This  
29 splitting into "more" and "less" hygroscopic modes at high relative humidity has been  
30 observed by McMurry and co-workers (McMurry and Stolzenberg, 1989; Zhang and  
31 McMurry, 1993) (Figure 3-29) and Lowenthal et al., (1995) (Figure 3-30). In some cases,

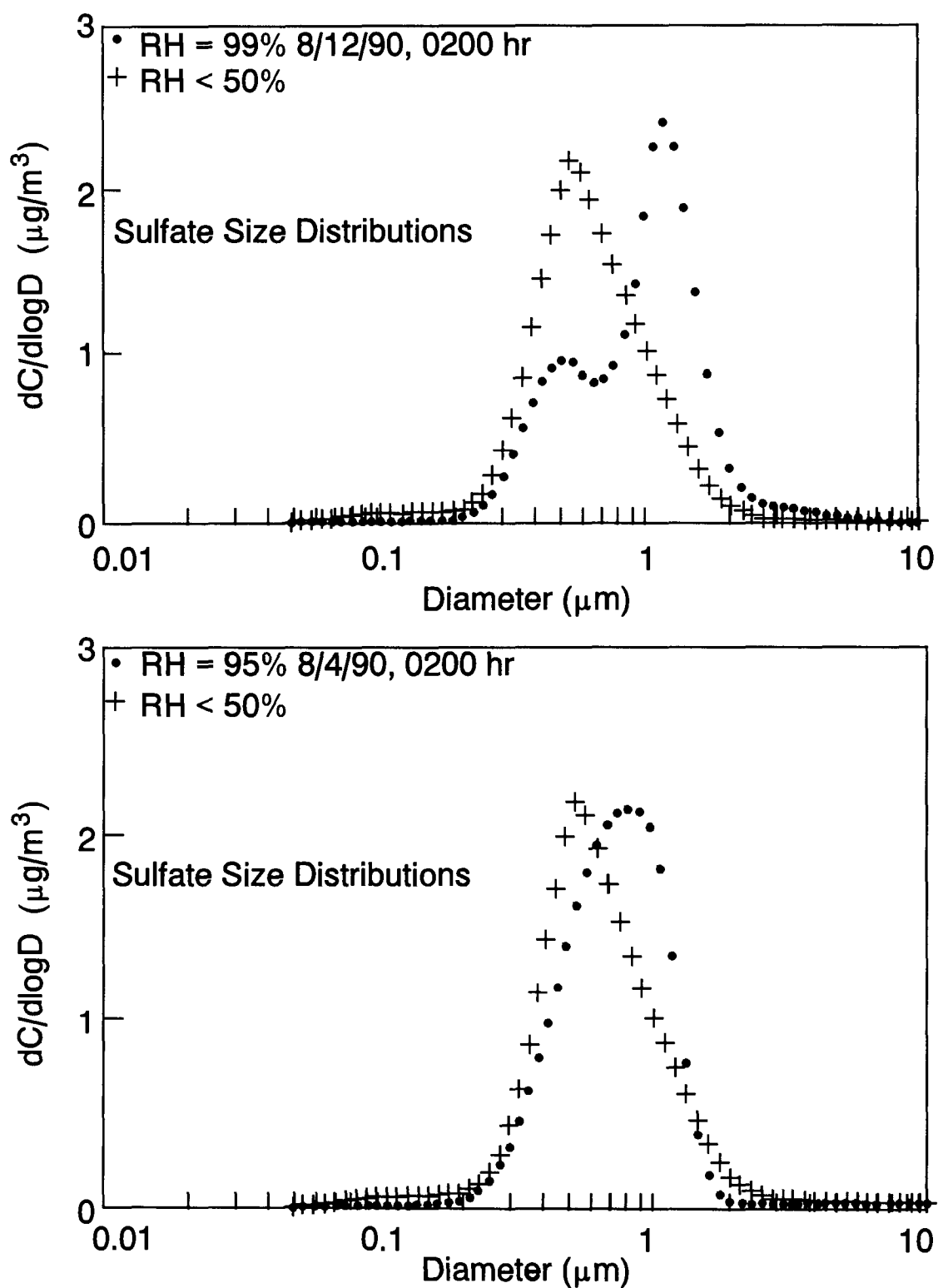
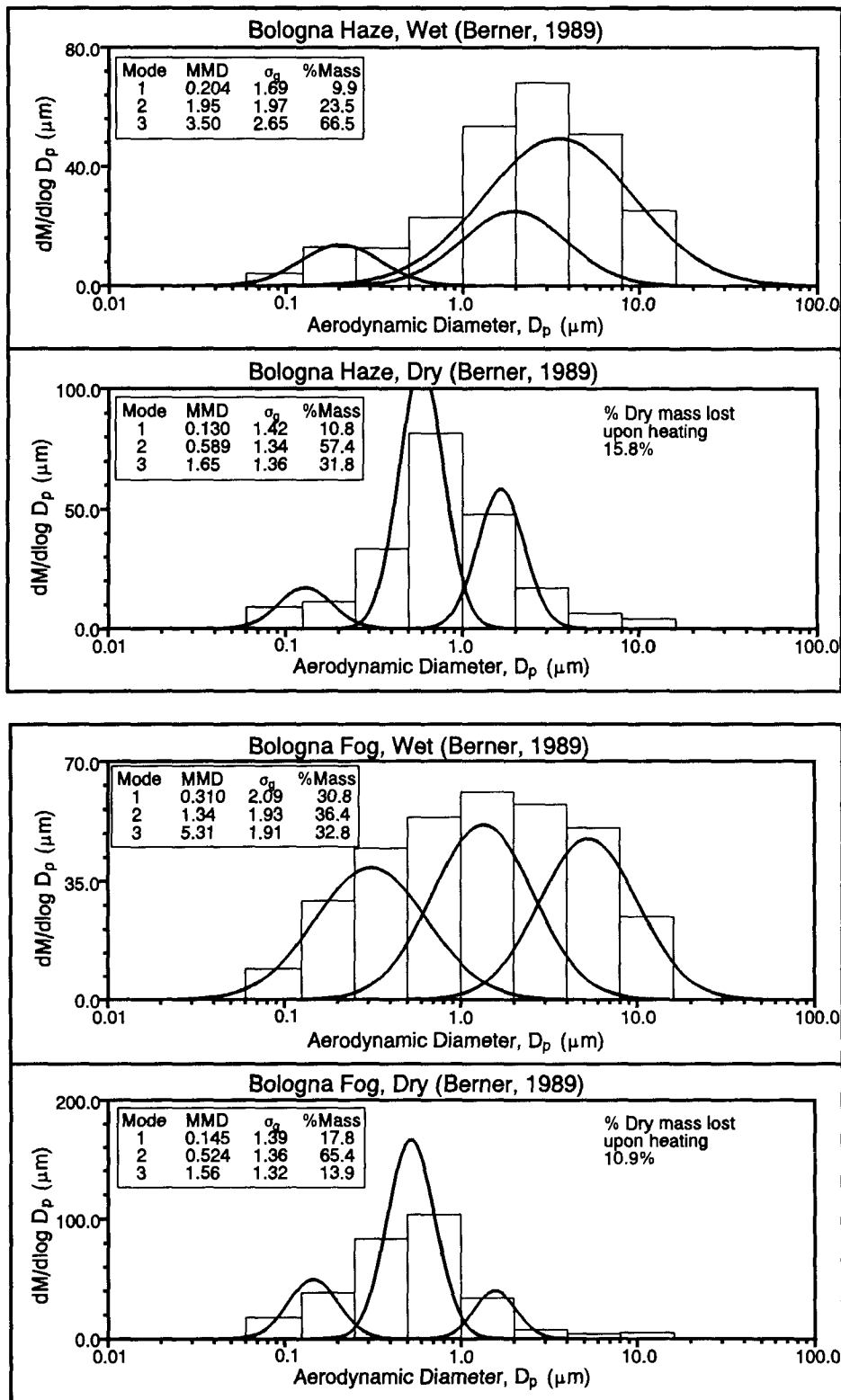


Figure 3-30. Example of growth in particle size due primarily to increases in relative humidity from Uniontown, PA.

Source: Lowenthal et al., 1995.





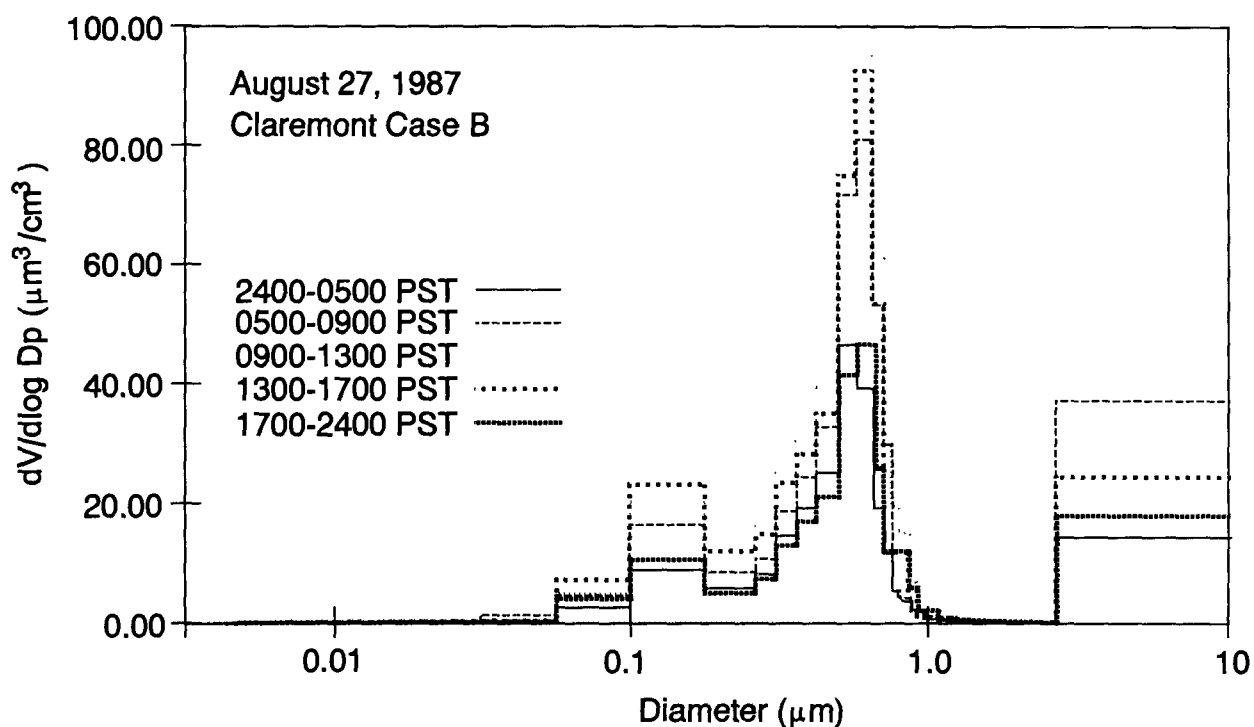
**Figure 3-31. Mass size distribution of non-volatile aerosol material. The aerosol was collected at ambient conditions, "wet", or after evaporation of water, "dry". A - haze; B - fog.**

Source: Berner, 1989.

1 reported by Pitchford and McMurray (1994), splitting into three modes of varying  
2 hygroscopicity was observed. However, the separation into two "more" hygroscopic modes  
3 may represent, as suggested by Berner, variations in relative humidity extremes during  
4 different parts of the overnight sampling period.

5 In measuring light scattering with the integrating nephelometer, the aerosol community  
6 has been very concerned about the difference in relative humidity and temperature in the  
7 ambient air and in the volume of air in which particle scattering is actually measured (Covert  
8 et al., 1972; Fitzgerald et al., 1982). Temperature differences between the measurement  
9 volume and ambient air of 1 or 2 °C can change the relative humidity and change the  
10 observed light scattering. Great efforts have been made to minimize this temperature  
11 difference. However, researchers have not been nearly as careful in considering temperature  
12 and relative humidity effects when measuring size distribution, either with impactors or  
13 particle counters, even though effects have been reported in the early literature (Wagman  
14 et al., 1967; Sverdrup et al., 1980).

15 A recent paper by Cass and coworkers (Eldering et al., 1994) provides some insight  
16 into how differences in RH resulting from heating can cause differences between  
17 particle-counting distributions and impactor distributions. Particle size distributions were  
18 obtained by counting particles by mobility (electrical aerosol analyzer) and light scattering  
19 (optical particle counter). An example is shown in Figure 3-32. Almost no particles were  
20 found between 1.0 and 2.5  $\mu\text{m}$  diameter. When these particle number data were converted  
21 to total expected light scattering, they agreed with measurements made by a heated, but not  
22 an unheated, integrating nephelometer; and when converted to expected mass, agreed with  
23 filter measurements of dry mass. Eldering et al. (1994) conclude that even the moderate  
24 heating occurring in mobility and optical counters was enough to change the size of the  
25 particles, especially when the ambient air was close to 100% RH. It seems likely that most  
26 particle counting systems produce some heating of the aerosol, and thus some reduction of  
27 the measured particle size from that existing in the ambient air. On the other hand, if  
28 particle-size measuring devices were located in air conditioned or heated trailers or  
29 laboratories, the temperature of the sampled air would be changed and the measured particle  
30 size distribution would be different from that existing in the ambient air (Sverdrup et al.,  
31 1980).



**Figure 3-32.** Example of particle-counting volume distribution obtained in Claremont, CA. Compare to Figures 3-14 and 3-31. Heating of the sampled air by the mobility and optical counters are believed to have resulted in a distribution representative of a lower than ambient relative humidity.

Source: Eldering et al., 1994.

During the high relative humidities that occur at nighttime, growth of hygroscopic components can result in the growth of some fine mode aerosol to diameters greater than  $1.0 \mu m$  and perhaps even above  $2.5 \mu m$ . As can be seen in Figure 3-28, dry ammonium sulfate particles having a dry diameter of  $0.5 \mu m$  will grow to  $\approx 2.5 \mu m$  at a relative humidity between 99 and 100%. When the relative humidity actually reaches 100%, the particles will continue to grow to maintain the relative humidity at 100%, and eventually become fog droplets that are large enough to be collected in the fraction larger than  $2.5 \mu m$ . Ammonium sulfate particles with dry sizes greater than  $0.5 \mu m$  would also grow into the larger than  $2.5 \mu m$  size range.

The addition of water to hygroscopic particles, discussed in the previous section, is a reversible process. Particles absorb water and grow as RH increases; as RH decreases some

of the particle-bound water evaporates and the particles shrink. However, the large amount of liquid water associated with hygroscopic particles at high relative humidity provides a medium for liquid phase transformation process. A number of atmospheric process, which convert SO<sub>2</sub> to sulfate or NO<sub>x</sub> to nitrate, can take place in water solutions but not in the gas phase. These processes are not reversible but lead to an accumulation of sulfate or nitrate and lead to an increase in the dry size of the particle. Of course as more sulfate or nitrate is added to the particle it will absorb more water so that the wet size will also increase.

The first observation and clear discussion of these combined effects of relative humidity on growth and SO<sub>2</sub> conversion to sulfate are given by Hering and Friedlander (1982) as shown in Table 3-17. Using a low pressure impactor, they observed that days with higher relative humidity had higher sulfate concentration and higher MMD's compared to days with lower relative humidity. Hering and Friedlander (1982) named the small mode the condensation mode and suggested that it was formed by the gas phase conversion of SO<sub>2</sub> to sulfate and subsequent nucleation, coagulation, and growth by condensation. They named the larger mode the droplet mode. They discussed possible mechanisms for formation of this mode. They ruled out coagulation as being too slow. Reactions in fog droplets were ruled out on the basis that fog has too few particles per unit volume to give the number of particles found in the droplet mode. They concluded that growth occurred due to reaction of SO<sub>2</sub> in the liquid water associated with the particle.

**TABLE 3-17. COMPARISON OF SULFATE CONCENTRATION AND MASS MEAN DIAMETERS OF AEROSOLS FOR DAYS WITH HIGHER AND LOWER RELATIVE HUMIDITY**

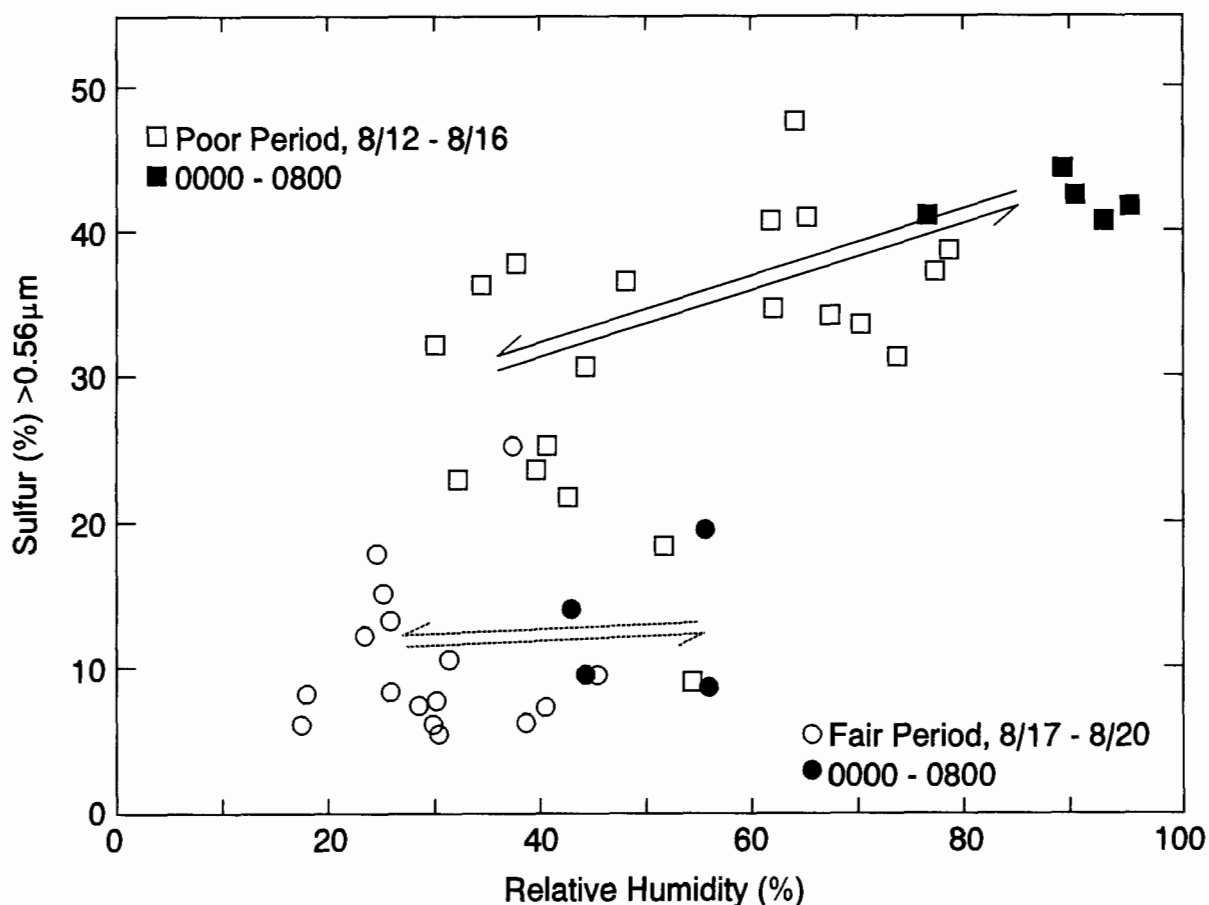
	Low RH Days	High RH Days
Minimum RH, %	17 - 35	26 - 66
Maximum RH, %	45 - 68	69 - 100
Sulfate Concentration, $\mu\text{g}/\text{m}^3$	3 - 9	3 - 52
Mass Mean Diameter, $\mu\text{m}$	$0.20 \pm 0.02$	$0.54 \pm 0.07$

In a series of papers McMurray and co-workers make use of the aerosol growth law, originally developed by Heisler and Friedlander (1977), to study the mechanism and rates of

sulfate formation in ambient air (McMurry et al., 1981; McMurry and Wilson, 1982, 1983). They were able to apportion growth to condensation and droplet mechanisms and observed droplet growth in particles up to 3  $\mu\text{m}$  in diameter.

A process of aerosol growth due to increasing relative humidity (Figure 3-33) has also been utilized by Cahill et al. (1990) to explain observations of sulfate size changes during the 1986 Carbonaceous Species Methods Comparison Study in Glendora, CA. Cahill used a DRUM sampler to measure sulfate in nine size ranges. By tracking the mass of sulfate in the 0.56 to 1.15  $\mu\text{m}$  size range Cahill et al. could follow the expansion and contraction of aerosol particles containing sulfate. Because of the relative high time resolution of the DRUM sampler (4 h except for an 8-h increment each night from midnight to 8 a.m.), Cahill et al. (1990) could follow this process as the relative humidity increased during the night and decreased during the day. This data indicates that during the "Poor Period" (low visibility) particles grow as relative humidity increases. However, they did not return to the smaller size observed during the "Fair Period" (good visibility). This could be due to a combination of growth due to reaction of  $\text{SO}_2$  to sulfate within the particles or failure of the droplet to crystallize thus maintaining particle-bound water in a supersaturated state.

John et al. (1990), in studies in the Los Angeles area, observed a number of sulfate size distributions with MMD near 1.0  $\mu\text{m}$ . A histogram of the sulfate MMDs from his study is shown in Figure 3-34. John et al. (1990) have provided a qualitative explanation to account for these large MMDs for fine mode aerosol. In analyzing their data John et al. plotted sulfate mass as a function of sulfate MMD and found two distinct regions, as shown in Figure 3-35. Distributions with particles near 0.2  $\mu\text{m}$  diameter are probably still dry; the particles have not reached their deliquescent point. As the relative humidity increases they reach their deliquescent point and grow rapidly into the 0.5 to 0.7  $\mu\text{m}$  size range. During the formation of fog, the hygroscopic particles act as fog condensation nuclei, and with relative humidity at 100%, grow into 1 to 10  $\mu\text{m}$  fog droplets. Sulfur dioxide dissolves in the fog droplets and is rapidly oxidized to sulfate by atmospheric oxidants such as  $\text{H}_2\text{O}_2$  or  $\text{O}_3$ , or by catalysis by Fe or Mn. These particles lose some of their water as the relative humidity decreases below 100% RH, but will have substantially more sulfate than prior to activation. Similar processes occur in clouds (Swartz, 1984).



**Figure 3-33.** Relative humidity versus sulfur, during the 1986 Carbonaceous Species Methods Comparison Study, for particles with  $D_p > 0.56 \mu\text{m}$ . The approximate trajectories followed during each day by the  $D_p > 0.56 \mu\text{m}$  sulfur size fraction are shown for period P and period F. Note that even when the humidities are low, 30 to 50 %, the period P aerosols remain coarser by a factor of three than those of period F. The water content incorporated in the aerosols during the 0000- to 0800-h time periods is lost only slowly, giving a strong hysteresis effect in sulfur size.

Source: Cahill et al., 1990.

- 1 In an analysis of data from the IMPROVE network Cahill and co-workers (Eldred et
- 2 al., 1995) report that 20% of the total sulfate is found in the coarse fraction of  $\text{PM}_{10}$ .
- 3 Studies in Philadelphia using dichotomous samplers have also reported that 20% of the total
- 4 sulfate is found in the coarse fraction (Dzubay et al., 1988). Cahill and coworkers suggest

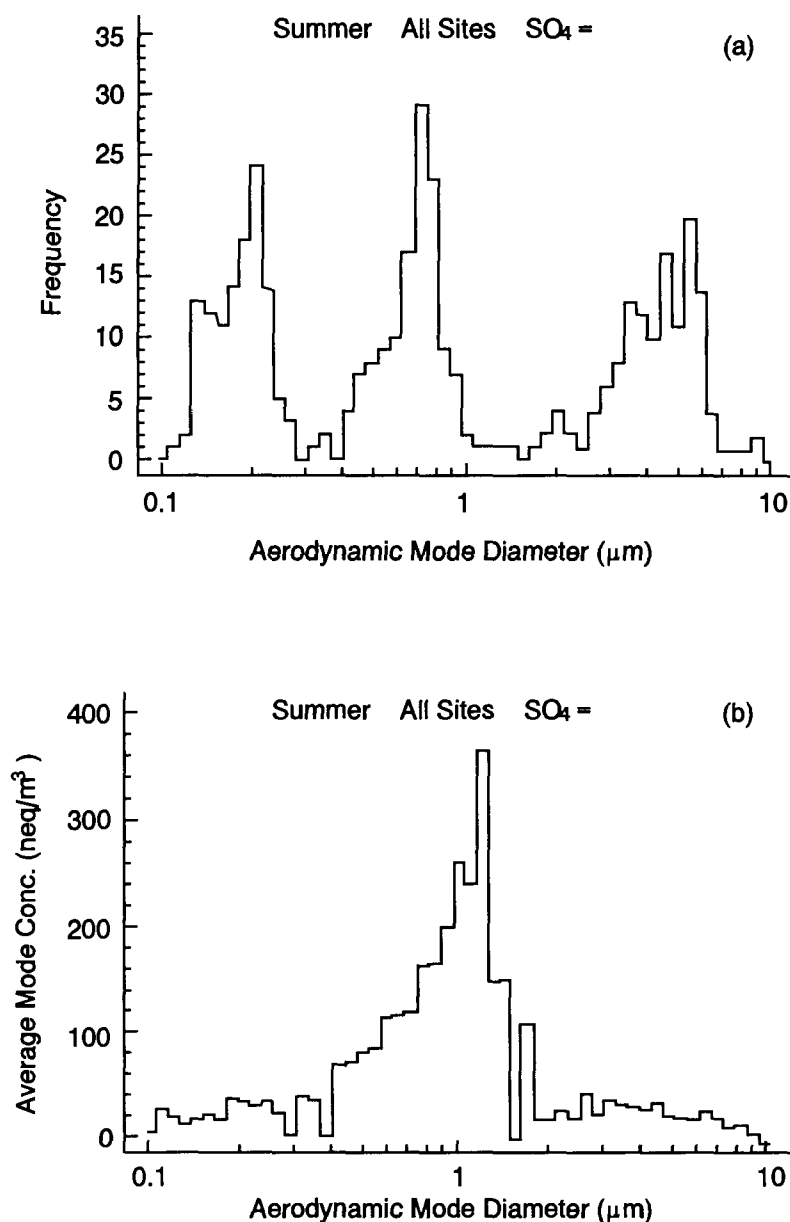
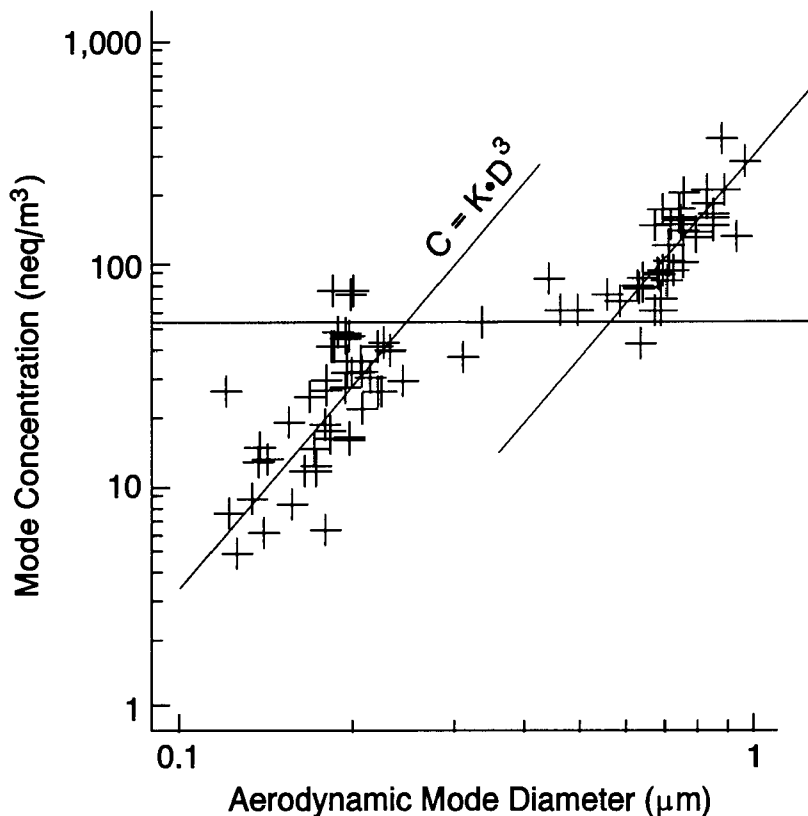


Figure 3-34.

Data from the South Coast Air Quality Study (John et al., 1990). Plots show (a) frequency of sulfate modes of various sizes as a function of mode mass mean diameter (MMD) and (b) average sulfate mode concentration as a function of mode MMD. Note that although there are only a few instances when the MMD is near 1.0  $\mu\text{m}$  diameter, it is these situations that give rise to the highest sulfate concentrations. Modes with MMDs above 2.5  $\mu\text{m}$  diameter may be due to collection of fog droplets containing sulfate or reaction of  $\text{SO}_2$  in liquid droplets of NaCl due to NaCl sea spray droplets in which  $\text{SO}_2$  has dissolved and reacted to form sulfate and release HCl gas.

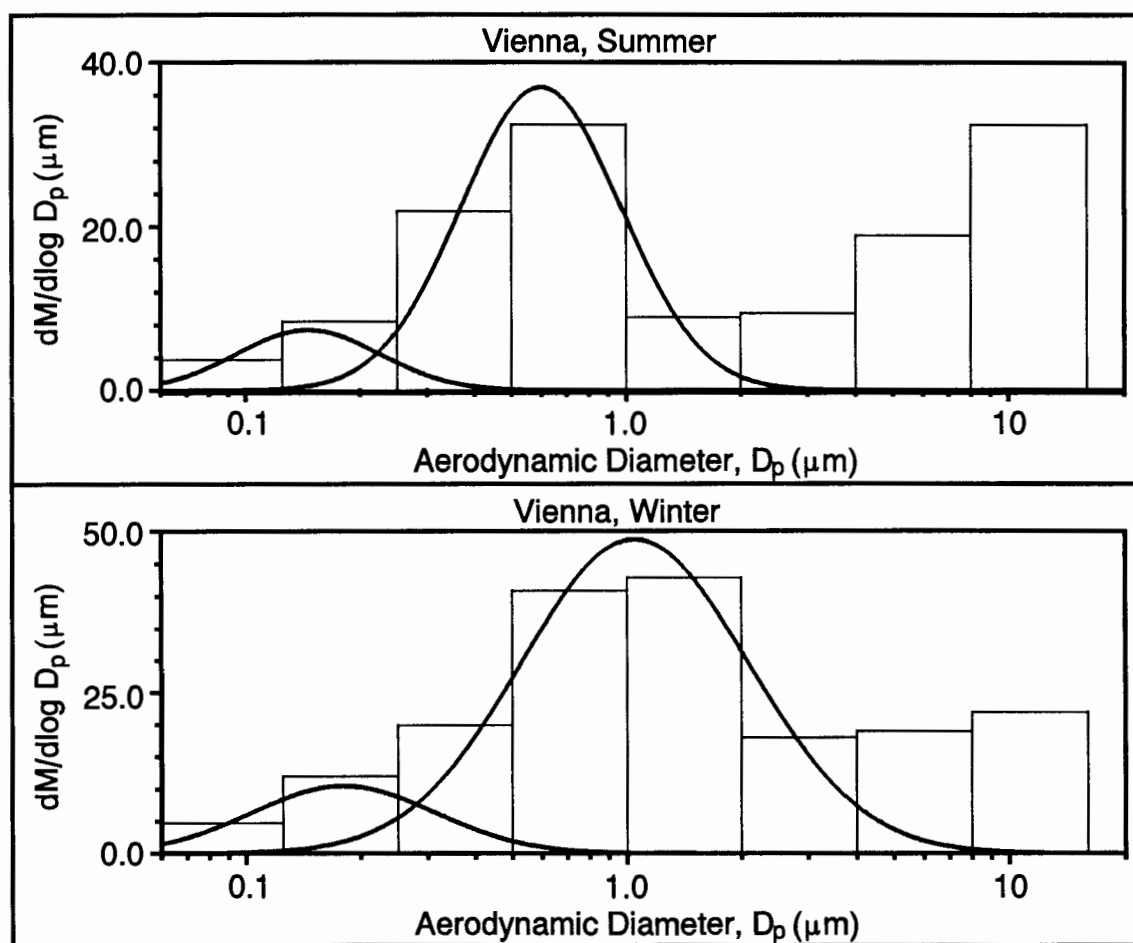


**Figure 3-35.** Log-log plot of sulfate mode concentration versus mode diameter from Claremont during summer SCAQS (John et al., 1990). The solid lines have slopes corresponding to mode concentration increasing with the cube of the mode diameter. A transition between the two modes is believed to occur at approximately the sulfate mode concentration indicated by the horizontal dashed line.

1 that sulfate particles may grow larger than 2.5  $\mu\text{m}$  in diameter and thus be sampled in the  
 2  $\text{PM}_{10}$  fraction but not the  $\text{PM}_{2.5}$  fraction. It is possible for  $\text{SO}_2$  to react with basic  
 3 carbonatecoarse particles to form a sulfate coating or to dissolve in wet NaCl particles, from  
 4 oceans, lakes, or salt placed on streets to dissolve ice, and be converted to sulfate with the  
 5 release of HCl. However, there is substantial evidence that some fine sulfate, and therefore  
 6 possibly other fine mode material, may be found in the size range above 1.0  $\mu\text{m}$  and even  
 7 above 2.5  $\mu\text{m}$  diameter, due to the growth of hygroscopic particles at very high relative  
 8 humidity.



1 A similar process probably accounts for the large size of the fine mode observed in  
 2 Vienna (Berner et al., 1993). Winter and summer size distribution are shown in Figure 3-36.  
 3 Berner et al. reported that fog occurred during the night time during the winter study. In  
 4 this European study, as in American studies, instances of fine mode size distributions with  
 5 MMDs near or above  $1\ \mu\text{m}$  seem to occur only when fog or very high relative humidity  
 6 conditions have been present.



**Figure 3-36.** Typical results of size-distribution measurements taken with a Berner impactor in a Vienna street with heavy automotive traffic (Berner et al., 1993): (a) measurements taken during summer at three different elevations, (b) measurements taken during winter at three different elevations, fog was frequently present during the winter sampling period.

### 3.7.1.7. Conclusions

This review of atmospheric particle-size-distributions was undertaken to provide information which could be used to determine what cut-point; 1.0  $\mu\text{m}$ , 2.5  $\mu\text{m}$ , or something in between; would give the best separation between the fine and coarse particle modes. The data do not provide a clear or obvious answer. Depending on conditions, a significant amount of either fine or coarse mode material may be found in the intermodal region between 1.0 and 2.5  $\mu\text{m}$ . However, the analysis does demonstrate the important role of relative humidity in influencing the size of the fine particle mode and indicates that significant fine mode material is found above 1.0  $\mu\text{m}$  only during periods of very high relative humidity.

Thus, a PM<sub>2.5</sub>  $\mu\text{m}$  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  $\mu\text{m}$  in diameter. A PM<sub>1.0</sub>  $\mu\text{m}$  sample will prevent misclassification of coarse mode material as fine but under high RH conditions will 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  $\mu\text{m}$ . However, reducing the RH by heating will result in loss of semivolatile components such as ammonium nitrate and semivolatile organic compounds. No information was found on techniques designed to remove particle-bound water without loss of other semivolatile components.

## 3.8 SUMMARY

- The scales of transport of most interest with respect to atmospheric aerosols are the  $\beta$ - and  $\alpha$ -mesoscales, which have been emphasized in this section.
- Field measurements and model evaluations of transport and dispersion on these scales are quite limited. Quantitative simulations of transport processes on these scales are believed to be subject to considerable error.
- The main sources of this error are believed to be related to sub-grid-scale processes related to plumes, clouds, complex terrain and complex mesoscale flow systems.

1 Routine surface meteorological measurements are extensive enough, but upper level  
2 measurements are too coarse.

- 3
- 4 • New multi-scale models currently under development are expected to provide
- 5 substantially finer spatial resolution where most needed, as well as special treatment
- 6 of some of the remaining sub-grid-scale effects (e.g., plume-in-grid treatment for
- 7 major point source emissions). Transport simulation should be much improved in
- 8 these new models.
- 9
- 10 • Meteorology influences particulate air quality in a variety of other ways also (Sloane,
- 11 1983). Over a period of a week or so, air masses stagnating in high pressure cells
- 12 over source regions may develop considerable haze which may then be transported
- 13 over a long range (Gillani and Husar, 1976; Samson, 1977). Also, UV radiation,
- 14 temperature and humidity are well known to be important factors in atmospheric
- 15 chemistry and aerosol formation.
- 16
- 17 • The primary focus in this section has been on field measurements related to two
- 18 important transformation processes: gas-to-particle conversion (particle formation),
- 19 and growth of hygroscopic particles in humid air, clouds, and fogs.
- 20
- 21 • Another major focus has been on transformations in plumes of major point sources
- 22 and urban-industrial complexes which are the carriers of most particles of
- 23 anthropogenic origin.
- 24
- 25 • Field measurements of homogeneous gas-phase and heterogeneous aqueous-phase
- 26 chemistry are reviewed for sulfur, nitrogen, and organic compounds.
- 27
- 28 • Gas-phase chemistry in ( $\text{NO}_x$ ) plumes depends principally on plume dilution with
- 29 background hydrocarbons and oxidants, and on sunlight. Large diurnal and seasonal
- 30 variations exist in the rates of oxidation of  $\text{SO}_2$  to sulfate and  $\text{NO}_2$  to inorganic
- 31 nitrate. For  $\text{SO}_2$ , the gas-phase rate in diluted point-source plumes varies typically
- 32 between 1 and 3%  $\text{h}^{-1}$  during summer midday conditions in the eastern United States,
- 33 and up to about 1%  $\text{h}^{-1}$  in the cleaner conditions of southwestern United States. In
- 34 urban plumes, the upper limit appears to be closer to 5%  $\text{h}^{-1}$  under the more polluted
- 35 conditions. For  $\text{NO}_2$ , the rates appear to be about three times faster for both types of
- 36 plumes. Winter rates are about an order of magnitude lower, on average.
- 37 Conversion rates in the background are comparable to the peak rates in diluted
- 38 plumes. Neutralization of  $\text{H}_2\text{SO}_4$  formed from  $\text{SO}_2$  oxidation increases with plume
- 39 age and background  $\text{NH}_3$  concentration. If the  $\text{NH}_3$  concentration is more than
- 40 sufficient to completely neutralize  $\text{H}_2\text{SO}_4$  to  $(\text{NH}_4)_2\text{SO}_4$ , then some of the  $\text{HNO}_3$  may
- 41 be converted to  $\text{NH}_4\text{NO}_3$ , depending also on temperature.  $\text{NH}_4\text{NO}_3$  is observed
- 42 commonly in summer in Los Angeles at Riverside, downwind of a major source of
- 43 ammonia.
- 44
- 45 • Contributions of aqueous-phase chemistry in plumes are highly variable, depending
- 46 on availability of the aqueous phase (wetted aerosols, clouds, fogs, and light rain) and
- 47 the photochemically generated oxidizing agents (particularly  $\text{H}_2\text{O}_2$  in the case of

1 sulfur). In-cloud conversion rates for sulfur can be several fold larger than the  
2 underlying gas-phase rates, and both are low in stable and low-sunlight conditions.  
3 Nitrate in the aqueous phase is due mainly to dissolution of nitric acid formed in the  
4 gas phase during daylight; there are indications of its formation under dark conditions  
5 by heterogeneous processes involving the  $\text{NO}_3$  radical and  $\text{N}_2\text{O}_5$ .  
6

- 7 • Variable amounts of secondary organic aerosols have been observed in urban smog,  
8 particularly in the Los Angeles basin. They are most common on summer days at  
9 downwind sites, and have been observed to comprise as much as 70% of the total  
10 OC. More typically, however, primary OC is dominant.  
11
- 12 • There is considerable recent evidence suggesting that aerosol composition is  
13 externally mixed, at least partially, with "more" hygroscopic and "less" hygroscopic  
14 components co-existing in monodisperse populations. This observation has important  
15 implications concerning the water content of atmospheric particles, and their growth  
16 in humid conditions.  
17
- 18 • One- to three-quarters of the aerosol mass in the eastern United States atmosphere is  
19 estimated to be water-soluble. At  $\text{RH} \geq 75\%$ , the water content of such aerosol in  
20 creases with RH. Also, the critical supersaturation for activation of such aerosol is  
21 relatively insensitive to its chemical composition. The accumulation mode of such  
22 aerosol is expected to be fully activated in convective clouds, but evidently only  
23 partially in stratiform clouds and ground fogs, depending on particle dry size,  
24 concentration, and cooling rate. In stratiform clouds under polluted conditions,  
25 activation efficiency decreases non-linearly with increasing particle concentration.  
26  
27

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## 4. SAMPLING AND ANALYSIS OF PARTICULATE MATTER AND ACID DEPOSITION

### 4.1 INTRODUCTION

Assessment of the risks associated with airborne aerosols implies that measurements be made defining the aerosol characteristics, concentrations and exposures that contribute to, or simply correlate with, adverse health effects. The proper selection of an aerosol sampling or analysis methodology to accomplish these measurements requires that rationales be applied that consider how the resulting data will be applied and interpreted, in addition to the data quality required. As an example, integrated collection of an aerosol sample on a heated substrate may help to stabilize a subsequent measurement technique, but in the process may dramatically change the character of the aerosol as it existed in the air. Similarly, integrated collection of acidic fine aerosols, without selectively removing the larger, more basic particles, will cause neutralization (i.e., modification) of the sample on the substrate. The same logic applies to the selective removal of gas phase components during sampling that might react with the deposited aerosol sample, in a manner inconsistent with naturally occurring transformation processes. The assumption that fixed-location measurements are representative of inhalation exposure implies that the effects of local spatial and temporal gradients are understood and appropriately applied to the sampler siting criteria. Development of relationships between aerosol characteristics and health or ecological responses requires that the aerosol sampling and analysis processes are truly representative and adequately defined.

The application of sampling and analytical systems for aerosols must recognize that particles exist modally as size distributions (see Section 3.3.3), generated by distinctively different source categories and having distinctly different chemistries. The primary reasons for making size-specific aerosol measurements are (a) to relate the in situ aerosol character to the potential deposition sites, and thus toxicity, of the respiratory system, and (b) separation of the size distribution modes to identify sources, transformation process or aerosol chemistry. The interpretation of particle size must be made based on the diameter definition inherent in the measurement process. Since the respiratory system classifies particles of

1 unknown shapes and densities based on aerodynamic diameter, development of aerosol  
2 relationships with health responses requires that sampling techniques either incorporate  
3 inertial aerodynamic sizers or provide mechanisms to accurately convert the measured  
4 diameters (e.g., optical) to an aerodynamic basis. All particle diameters described in this  
5 chapter are aerodynamic, unless otherwise specified.

6 Friedlander (1977a) provided the descriptive matrix shown in Figure 4-1 for placing  
7 measurement techniques that define aerosol characteristics into perspective, in terms of their  
8 particle sizing capabilities, resolution times and chemical identification attributes. This  
9 approach defined these characteristics by resolution (single particle or greater), discretizing  
10 ability, and averaging process. The author notes that the “perfect” aerosol sampler  
11 characterizes particle size with “perfect” resolution, determines the chemistry “perfectly” of  
12 each particle, and operates in real-time with no “lumping” of classes. These characteristics  
13 could be amended in “real-world” terms by suggesting that the “perfect” sampler would also  
14 have minimal cost and operator intervention. Additionally, if the aerosol measurement  
15 design goal is mimicking the respiratory system, physiological averaging characteristics must  
16 be considered. Size-specific, integrated aerosol measurements have improved significantly  
17 and their capabilities are better characterized since the 1987  $PM_{10}$  standard, but a “perfect”  
18 aerosol sampling system has not been devised. As discussed subsequently, the methodologies  
19 required to adequately define the performance specifications of aerosol samplers have yet to  
20 be devised.

21 Many recent developmental efforts in aerosol measurement technologies have addressed  
22 the need to perfect the chemical characterization of reactive or volatile species collected on  
23 filtration substrates. Some of the most significant recent advances in aerosol measurement  
24 technologies have come in the form of analysis system “protocols”, rather than individual  
25 pieces of hardware. Recognizing that there is no single “perfect” sampler, these protocols  
26 attempt to merge several aerosol sampling and analysis technologies into an adaptable and  
27 analytically versatile system. System attributes typically include one or more size-specific  
28 aerosol inlets, subsequent fractionators to separate the fine and coarse particle modes, and  
29 denuders and/or sequential filter packs to selectively account for reactive gas phase species.  
30 Examples include EPA’s Versatile Air Pollution Sampler (VAPS), (Conner et al., 1993), the  
31 Southern California Air Quality Study (SCAQS) sampler, (Fitz et al., 1989) and the

Instrument	Resolution			Quantity Measured (Integrand x $N_{\infty}^{-1}$ )
	Size	Time	Chemical Composition	
Perfect Single Particle Counter Analyzer				$g$
Optical Single Particle Counter				$\int_{v_1}^{v_2} g \, dn_i \, dv$
Electrical Mobility Analyzer				$\int_{v_1}^{v_2} g \, dn_i \, dv$
Condensation Nuclei Counter				$\int g \, dv \, dn_i = 1$
Impactor				$\int_{v_1}^{v_2} g \, dn_i \, dv$
Impactor Chemical Analyzer				$\int_{v_1}^{v_2} g \, n_j \, dn_i \, dv$
Whole Sample Chemical Analyzer				$\int \int g \, n_j \, dn_i \, dv$

Key:

Resolution of single particle level

Discretizing process

Averaging process

**Figure 4-1. Characteristics of aerosol measurement instruments.**

- 1 Interagency Monitoring of PROtected Visual Environments (IMPROVE) sampler, (Malm
- 2 et al., 1994).
- 3 Recognizing that personal exposure concentrations for aerosols may differ from
- 4 classical outdoor, fixed-location measurements has produced much smaller and less obtrusive
- 5 samplers using the same sizing techniques for application indoors, or even worn on the body

1 during normal activities. Miniaturization of aerosol separators stretches the limits of current  
2 technologies to maintain required sampling precisions and accuracies. One of the most  
3 significant limitations imposed by the low flowrates inherent in personal exposure samplers is  
4 the extremely small sample size available for chemical analysis.

5 This chapter briefly describes the technical capabilities and limitations of aerosol  
6 sampling and analytical procedures in Sections 4.2 and 4.3, respectively, focusing on those  
7 that (1) were used to collect data supporting other sections in this document, (2) those  
8 supporting the existing PM<sub>10</sub>, TSP and Pb regulations, (3) those that were used to support  
9 health and welfare response studies, (4) those having application in development of a possible  
10 fine particle standard, and (5) discussing the attributes of several new technologies. The  
11 discussion of aerosol separation technologies is divided between (a) devices used to mimic  
12 the larger particle ( $> 10 \mu\text{m}$ ) penetration rationales for the upper airways, and (b) those  
13 devices generally used to mimic smaller particle penetration ( $< 10 \mu\text{m}$ ) to the sub-thoracic  
14 regions. These device descriptions are followed by sampling considerations for their  
15 applications. The applications of performance specifications to define these measurement  
16 systems for regulatory purposes are discussed, along with a number of critical observations  
17 suggesting that the current specification process does not always assure the accuracy or  
18 representativeness necessary in the field. The EPA program designating PM<sub>10</sub> reference and  
19 equivalent sampling systems is then briefly described, along with a current list of designated  
20 devices. Selected measurement systems used to provide more detailed characterization of  
21 aerosol properties for research studies are discussed, with a focus on the determination of  
22 particle size distributions. Aerosol sampling systems for specialty applications, including  
23 automated samplers, personal exposure samplers and the sampling systems used in aerosol  
24 apportionment studies are briefly described. This chapter is intended to provide supplemental  
25 information to Section 3.3.3 and other discussions of aerosol methodologies in support of the  
26 existing standards and possible development of a "fine particle" standard in the 1 to 3  $\mu\text{m}$   
27 range. An important contribution of the sampling and analytical sections is the extensive  
28 compilation of salient peer-reviewed technical references that can be obtained by the reader  
29 for more detailed information.

## 4.2 SAMPLING FOR PARTICULATE MATTER

### 4.2.1 Background

The development of relationships between airborne particulate matter and human or ecological effects requires that the aerosol<sup>1</sup> measurement process be accurately, precisely and representatively defined. Improvements in sampling methodologies since the 1982 Air Quality Criteria Document for Particulate Matter and Sulfur Oxides<sup>2</sup> was released, have resulted from improved sensor technologies, and more importantly, a better understanding of the aerosol character in situ<sup>3</sup>. Additionally, health studies and atmospheric chemistry research in the past decade have focused more closely on smaller, better-defined aerosol size fractions of known integrity, collected specifically for subsequent chemical characterization.

The system of aerosols in ambient air is a continuum of particle sizes in a gas phase carrier formed as the summation of all size distributions produced by individual sources and secondary transformations. Portions of the composite distributions are often found to exist lognormally (Baron and Willeke, 1993; see also Section 3.3.3). Aerosol systems also exist as a continuum of particle "ages", resulting from loss and transformation mechanisms such as agglomeration, settling, volatilization, gas-particle reaction, and rain-out affecting freshly generated particles. The chemical compositions of the various portions (modes) of the aerosol size distribution are more discreet, and sampling strategies must consider a specific range of sizes for a given chemical class. The constantly changing character of the atmosphere (or indoor air) places a premium on a sampling strategy to remove a representative aerosol sample from the air and protect its integrity until analyzed.

The 1982 Criteria Document provided basic descriptions of many of the aerosol measurement techniques still used today, and these methods will be briefly mentioned here, but not described in detail. This section will highlight the more recent peer-reviewed

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<sup>1</sup>Consistent with recent literature (e.g., see Willeke and Baron, 1993), the term "aerosol" will refer to the continuum of suspended particles and the carrier gas.

<sup>2</sup>U.S. Environmental Protection Agency (1982a), referenced subsequently as an entity as the "1982 PM Criteria Document".

<sup>3</sup>The in situ characteristics of particles in the ambient air medium can be substantially modified by the sampling and analysis processes. For example, a particle counter which draws particles through a restrictive or heated inlet before reaching the sensing volume, may perceive the particle properties (e.g. scattering coefficients, size distributions) differently from those that existed in the ambient.

research on aerosol measurement technologies since 1982 and provide salient points that should be considered in their application. The aerosol sampling section is not intended to be an exhaustive treatise, but is structured to highlight important concepts and technologies relevant to the development of aerosol measurement/response relationships, or supporting existing and potential EPA aerosol regulations. Ancillary reference texts, describing basic aerosol mechanics (e.g., Hinds, 1982; Reist, 1984) and applied aerosol mechanics and measurements (e.g., Willeke and Baron, 1993; Hering, 1989; Lundgren et al., 1979; Friedlander, 1977b, Liu, 1976) should be consulted for more fundamental details.

## **4.2.2 Large Particle Separators**

### **4.2.2.1 Cutpoint Considerations**

The collection of an aerosol sample is defined by the penetration characteristics of the inlet, overlaid on the existing in situ size distribution. Cooper and Guttrich (1981) describe this process mathematically, and estimate the influences of non-ideal penetration characteristics. Miller et al. (1979) described the considerations for the possible selection of 15  $\mu\text{m}$  (designated “inhalable”) as a standard for size-selective particle sampling with upper airway respiratory deposition as the primary consideration. The selection of the most appropriate aerodynamic criteria for ambient aerosol sampling was only partially resolved by the 1987 EPA designation (U.S. Environmental Protection Agency, 1987b) of a 10  $\mu\text{m}$  cutpoint,  $\text{PM}_{10}$  cutpoint. The “ideal”  $\text{PM}_{10}$  inlet was referenced to the thoracic penetration model of Lippmann and Chan (1979). Ogden (1992) noted that the standardization for aerosol cutpoint sizes and separation sharpness is still under debate across settings (ambient air, occupational) and across national and international governmental entities. As shown in Figure 4-2 (from Jensen and O’Brien, 1993), the international conventions for cutpoints have been roughly categorized as Respirable, Thoracic and Inhalable (previously, Inspirable). These cutpoints are related to the penetration, respectively, to the gas exchange region of the lung, the larynx, and the nasal/oral plane. The influences of physiological variables on these cutpoints are described by Soderholm (1989). The British Standard EN 481:1993 describes size fraction definitions for workplace aerosol sampling, and identifies inhalable “conventions” relative to thoracic, respirable, extra-thoracic and tracheobronchial penetration (but not necessarily deposition) in the respiratory system. They define a thoracic cumulative

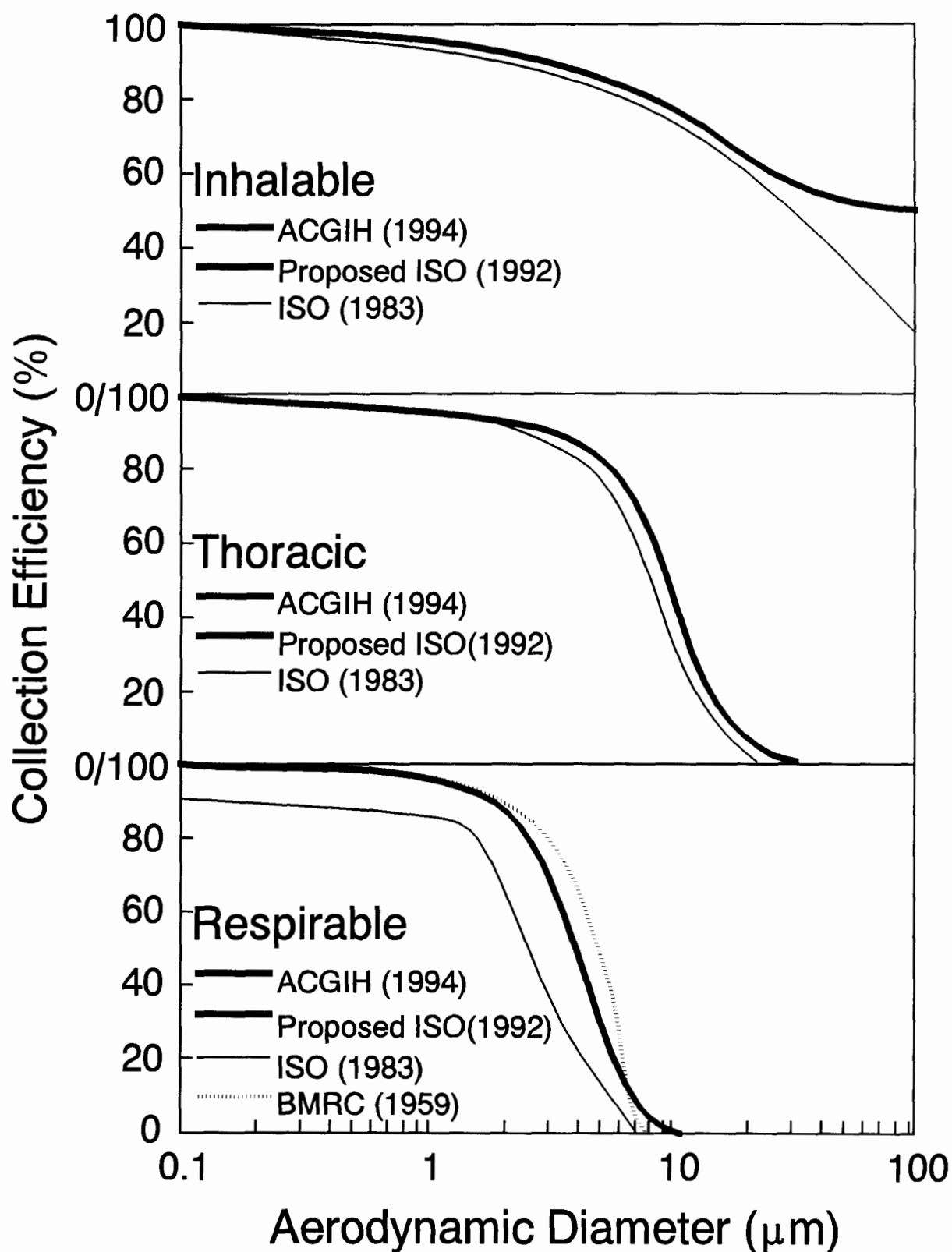


Figure 4-2.

American Conference of Governmental Industrial Hygienists (ACGIH), British Medical Research Council (BMRC), and International Organization for Standardization (ISO) size-selective sampling criteria.

lognormal distribution with a median of  $11.64 \mu\text{m}$  and a geometric standard deviation of 1.5, such that 50% of airborne particles with  $D_a = 10 \mu\text{m}$  are in the thoracic region. The American Conference of Governmental and Industrial Hygienists (ACGIH, 1994) also adopted these convention definitions as applied to chemical substance TLV's. Owen et al. (1992) provides an extensive list of the outdoor and indoor particles by type and source category that are found in or overlap these ranges. Willeke et al. (1992) describe the sampling efficiencies and test procedures for bioaerosol monitors.

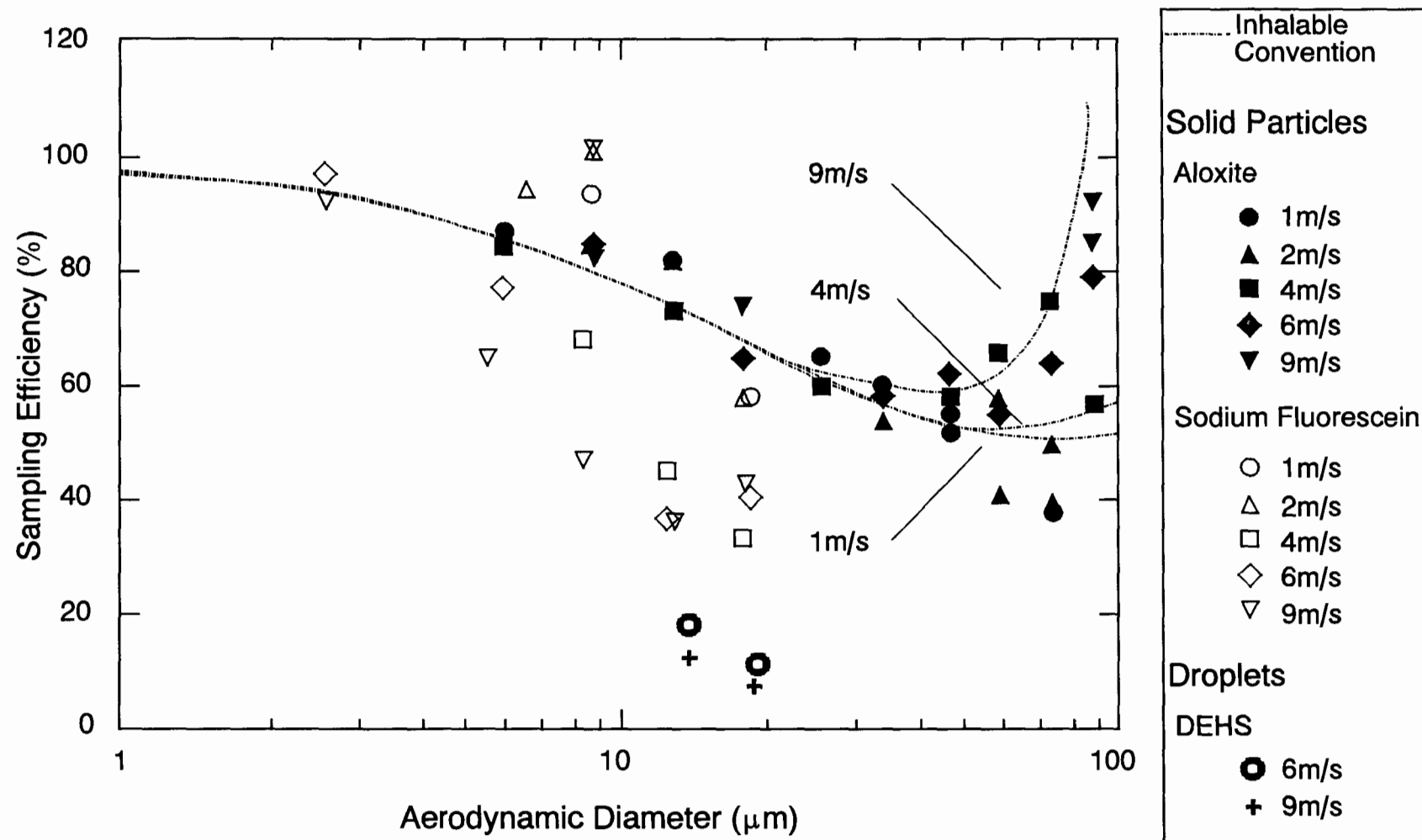
The concept of using an inlet that has the same sampling (penetration) characteristics as portions of the respiratory system has been discussed by a number of researchers, including Lippmann and Chan (1979), Vincent and Mark (1981), Soderholm (1989), Lidén and Kenny (1991) and John (1993). They describe sampler design considerations for matching penetration models for respirable, thoracic and inhalable fractions that have been proposed by a number of governing bodies. Since all models proposed for the same fraction do not necessarily coincide, given the variability and differences in interpretation of respiratory system data, Soderholm (1989) proposed compromise conventions for each fraction. Watson et al. (1983), Wedding and Carney (1983) and van der Meulen (1988) mathematically evaluated the influences of inlet design parameters on collection performance relative to proposed sampling criteria. These analyses suggested that factors such as extremes in wind speed and Coarse particle concentration could pose significant problems in meeting performance specifications.

An analysis of the human head as an aerosol sampler was discussed by Ogden and Birkett (1977), who noted that breathing is an anisokinetic sampling process. The concept of a "total inhalable" fraction that passes the oral and nasal entry planes was refined by Mark and Vincent (1986) with the development of a personal aerosol sampling inlet that mimicked this penetration as a function of aerodynamic size. The inlet was designated the IOM for the Institute for Occupational Medicine in Edinburgh, Scotland, where it was developed with the cutpoint as a function of wind speed and aerosol type shown in Figure 4-3. The total inhalable approach has been adopted by the International Standards Organization (ISO, 1983 and ISO, 1992)<sup>4</sup>, European Committee for Standardization (CEN, 1993) and by the American Conference on Governmental and Industrial Hygienists (ACGIH, 1985; ACGIH,

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<sup>4</sup> A proposed ISO convention is described by Soderholm (1989)





**Figure 4-3. Sampling efficiency of IOM ambient inhalable aerosol sampler for three different types of test aerosol.**

Source: Mark et al. (1992).

1994) for workplace aerosol sampling. The total inhalable fraction using the IOM inlet was selected for a total human exposure study (Pellizzari et al., 1994) to provide the total body burden for metals (lead and arsenic), by the air exposure route.

Similar thoracic penetration conventions have been adopted by ISO, CEN, ACGIH and EPA, each with  $D_{50}$  values of  $10.0\ \mu\text{m}$  (ISO, 1992, CEN, 1993, ACGIH, 1994, and EPA, 1987). The EPA definition was based primarily on the data of Chan and Lippmann (1980). The exact shapes of each efficiency curve were mathematically defined by Soderholm (1989) and are slightly different for each convention.

The respirable conventions have had  $D_{50}$  values ranging from  $3.5$  to  $5.0\ \mu\text{m}$ , but a compromise convention has been accepted internationally by several organizations. It has a  $D_{50}$  of  $4.0\ \mu\text{m}$  (Soderholm, 1989). ISO (1992) calls this the “healthy adult respirable convention”. Lidén and Kenny (1992) discuss the performance of currently available respirable samplers. EPA’s emphasis on the  $2.5\ \mu\text{m}$  cutpoint was more closely associated with separating the Fine and Coarse atmospheric aerosol modes, rather than mimicking a respiratory deposition convention. The exact location of this minimum in the atmospheric size distribution is currently under debate. It is noteworthy that ISO (1992) defines a “high risk” respirable convention which is claimed to relate to the deposition of particles in the lungs of children and adults with certain lung diseases. The respirable “high risk” convention has a  $D_{50}$  of  $2.4\ \mu\text{m}$ , so it could be identified closely with the EPA samplers having a cutpoint of  $2.5\ \mu\text{m}$ .

The  $\text{PM}_{10}$  size fraction has become nearly universal for ambient air sampling in the U.S., with the implementation of the 1987 standard (U.S. Environmental Protection Agency, 1987a). The setting of performance specifications, even with their limitations, has provided a more consistent  $\text{PM}_{10}$  data base, with better definition of the data quality. As additional information becomes available on the sources of biases in aerosol collection methodologies, further characterizations of older methods may be needed to better define the quality of collected data. Factors that affect bias, and especially representativeness, should be identified and their influences determined as a function of particle size. As an example, volatilization losses of nitrates were reported by Zhang and McMurry (1992), while losses for organics were reported by Eatough et al. (1993). Because of the prevalence of these chemical classes in the Fine fraction, the effect of the losses on larger fractions (e.g.,  $\text{PM}_{10}$ ,

TSP) would be proportionately smaller and can now be estimated. The losses of larger particles through aerosol inlet sampling lines (Anand et al., 1992) has a substantial influence on Coarse fraction samples. This was demonstrated for the British smoke shade sampler inlet line by McFarland et al. (1982). Inlet losses would be expected to play only a minor role in sampling the Fine particle fraction. Biases in concentration for samplers with large particle cutpoints are exacerbated by the large amount of mass present near the cutpoints and the steep slope of mass versus aerodynamic size. Thus, small changes in cutpoint can give significant and hard-to-predict mass biases.

#### 4.2.2.1 Total Suspended Particulates (TSP)

The gable roof inlet and sampling system for the TSP high volume sampler have remained essentially unchanged since the sampler's identification as a reference ambient sampling device in 1971 (U.S. Environmental Protection Agency, 1971). The sampling performance (e.g., wind speed and direction sensitivity) was described in detail in the 1982 Criteria Document, and shown by McFarland and Ortiz (1979) to collect particles with aerodynamic diameters exceeding 40  $\mu\text{m}$ . More importantly, its particle collection characteristics were shown to be significantly wind speed (2 to 24 km/hr) and wind direction sensitive. Only minor technical updates have been incorporated in commercially available units, such as in the types of available sequence and elapsed timers (mechanical, electronic) and in the types of flow controllers (mass flow, volumetric). Cassettes are now available that protect the fragile glass or quartz fiber filters during handling and transport. Size fractionating inlets for smaller size cutpoints (e.g., 2.5, 6.0 and 10.0  $\mu\text{m}$ ) and cascade impactors have been developed that can be retro-fitted in place of the gable roof. Similar to the Pb strategy of using the TSP high volume sampler to collect a "total" sample, asbestos sampling utilizes an aerosol inlet that attempts to collect a "total" sample, by using an open-faced filter holder with a conductive inlet cowling. Baron (1993) discusses the potential anisokinetic problems that can occur with such a simple inlet, but notes that the small Stokes number for typical asbestos fibers provides efficiencies close to 100%.

#### 4.2.2.2 Total Inhalable

The toxicity of contaminants such as lead pose health concerns as total body burdens, suggesting that penetration of all aerosols inhaled into the nose and mouth must be considered, rather than just thoracic penetration. The TSP sampler for atmospheric lead is considered (U.S. Environmental Protection Agency, 1978) to more closely capture this larger size fraction than would a  $PM_{10}$  counterpart, but was not specifically designed to mimic inhalability. The ISO “inhalable” draft sampling convention (ISO, 1993) is intended to apply to such situations, defining collection of all particles passing the oral/nasal entry planes. The total inhalable cutpoint is currently available only in a personal sampler version. Mark and Vincent (1986) described the development of an inhalable inlet (designated as the IOM) meeting the ISO (1992), CEN (1993) and ACGIH (1994) conventions for inspirable dust. This inlet was improved by Upton et al. (1992) and tested by Mark et al. (1992) and shown to satisfy the ACGIH criteria for wind speeds of 0.5 and 1.0 m/s.

#### 4.2.2.3 $PM_{10}$

The penetration of ambient aerosols through a size-fractionating inlet to the collection substrate must be characterized over the ranges of operating conditions (typically, meteorology and aerosol types) that may be encountered. The range of conditions currently required by EPA  $PM_{10}$  performance specifications were given in U.S. Environmental Protection Agency (1987b). Ranade et al. (1990) and John (1993) described the required testing, which specifies a controlled flow wind tunnel, mono-dispersed, fluorescently-tagged wet and dry aerosols, and an iso-kinetic nozzle aerosol sampling reference to determine aerodynamic penetration through candidate  $PM_{10}$  inlets.

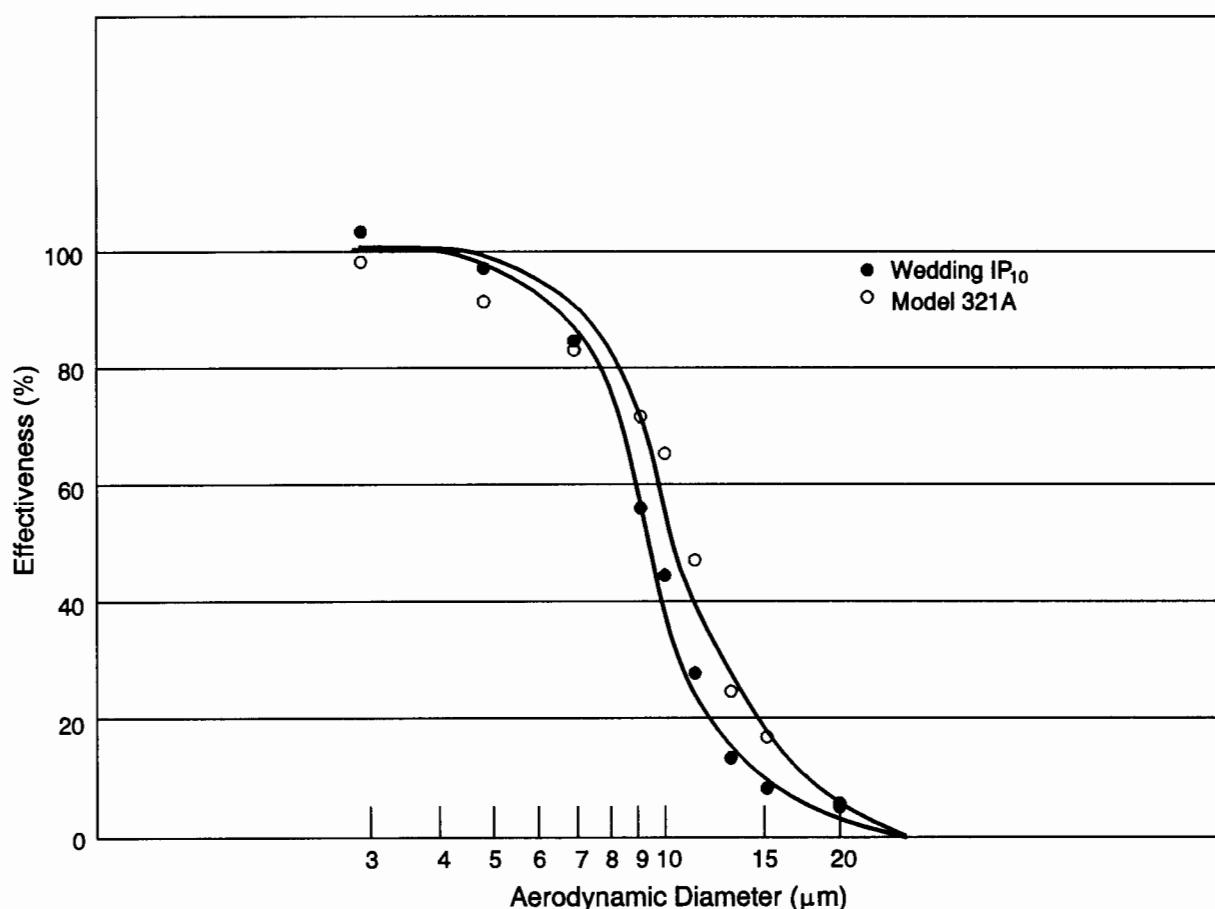
Marple and Rubow (1976) suggested an alternate approach to fluorescent tracer chemistry, using a representative poly-dispersed aerosol and monitoring the size distributions of the challenge aerosol entering and exiting the inlet in a static chamber with an optical particle counter (OPC). Buettner (1990) showed that this technique is only accurate if the OPC particle responses are aerodynamically calibrated to account for factors affecting the optical response, including particle shape and refractive index. Maynard (1993) used this approach to determine the penetration of a respirable cyclone to poly-disperse glass microspheres, using the TSI, Inc. Aerodynamic Particle Sizer. John and Wall (1983) noted that

inaccurate inlet sizing results may be obtained using poly-disperse AC test dust, as the result of agglomeration. Kenny and Lidén (1991) used the APS to characterize personal sampler inlets, and observed that on theoretical grounds, calm air sampling would be expected to provide unity aspiration efficiencies for particles below about 8  $\mu\text{m}$ . Tufto and Willeke (1982) used an OPC to monitor monodispersed aerosols in a wind tunnel setting to determine the performance of aerosol sampling inlets relative to an iso-kinetic nozzle. Yamada (1983) proposed using electron microscopy to determine the size distributions of poly dispersed particles using manual counting techniques before and after a candidate aerosol separator. Penetration data from this technique were found to be significantly less precise and difficult to interpret compared with data for the same separators using fluorometric methods.

The aerosol cutpoint performance of two  $\text{PM}_{10}$  samplers that have met the EPA performance specifications are illustrated (see Figure 4-4) by the data for the Andersen 321A and Wedding  $\text{IP}_{10}$  high volume sampler inlets at 8 km/hr from Ranade et al. (1990). The data show that the cutpoint requirements, defined as a  $D_{50}$  of  $10.0 \mu\text{m} \pm 0.5 \mu\text{m}$  and mimicking a modeled cutpoint sharpness ( $\sigma_g$ ), were met for each of the tested wind speeds. These performance results were verified by repeating the tests in wind tunnels located at two other research facilities. A diagram (U.S. Environmental Protection Agency, 1990) of the two-stage Sierra-Andersen  $\text{PM}_{10}$  high volume sampler inlet with a design flowrate of  $1.13 \text{ m}^3/\text{min}$  is shown in Figure 4-5. The buffer chamber of this inlet serves to dampen the influences of variable wind speeds and directions. Aerodynamic separation occurs as the particle-laden air stream passes through two sets of acceleration nozzles, which deposit the particles larger than  $\text{PM}_{10}$  on internal collection surfaces. The  $\text{PM}_{10}$  fraction is typically collected by a glass fiber filter. An oiled impaction shim was incorporated into the first stage fractionator of the 321A to minimize reentrainment of deposited particles during field sampling. This modified version (Sierra-Andersen 321B) was designated as an EPA reference method for  $\text{PM}_{10}$  in 1987. A subsequent single-stage fractionator (Sierra-Andersen 1200) was developed<sup>5</sup> and designated as an EPA reference method, with a  $D_{50}$  of  $9.5 \mu\text{m}$  and a hinged design to facilitate cleaning and oiling of the oiled impaction shim.

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<sup>5</sup>Graseby-Andersen, Inc., Atlanta, GA.



**Figure 4-4. Liquid particle sampling effectiveness curves with solid particle points superimposed for the Wedding IP<sub>10</sub> (●) and the Andersen Samplers Model 321A inlets at 8 km/h.**

1 A diagram of the cyclone-based Wedding<sup>6</sup> PM<sub>10</sub> high volume sampler inlet (U.S.  
 2 Environmental Protection Agency, 1990) with a design flowrate of 1.13 m<sup>3</sup>/min is shown in  
 3 Figure 4-6. This inlet uses an omni-directional cyclone to accelerate the particle-laden air  
 4 stream to deposit particles larger than PM<sub>10</sub> on an oiled collection surface. Two additional  
 5 turns are made to alter the flow into a downward trajectory toward the collection filter. A  
 6 brush is used to clean the deposited aerosol from the absorber surface through an access port.  
 7 This inlet was designated as an EPA reference method for PM<sub>10</sub> in 1987.

<sup>6</sup>Wedding and Associates, Fort Collins, CO.

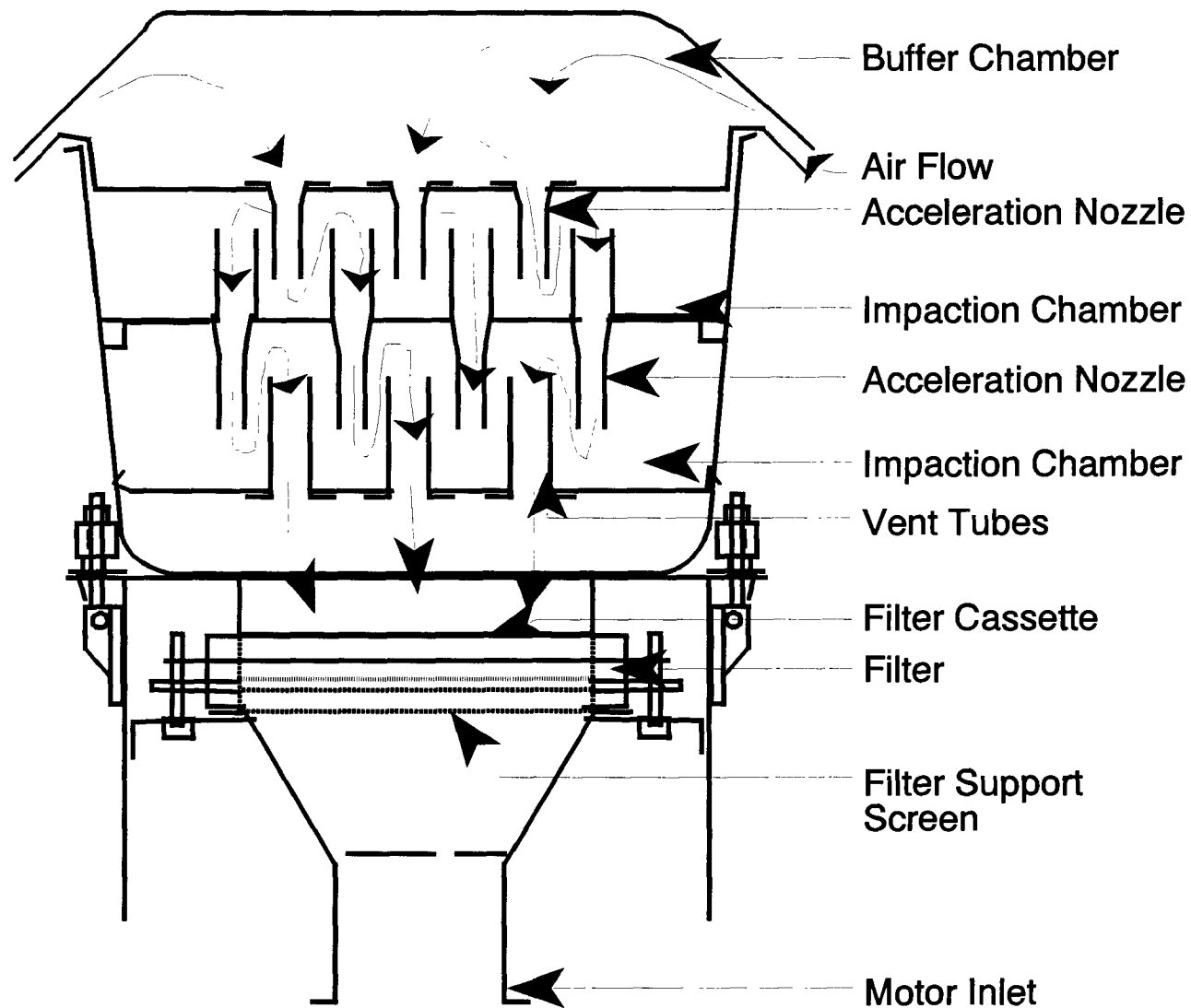


Figure 4-5. Andersen sampler.

1 The aerosol collection performances for 16.67 lpm PM<sub>10</sub> inlets for the dichotomous  
2 sampler are described by Wedding et al. (1982) and McFarland and Ortiz (1984), and  
3 illustrated by the penetration data in Figure 4-7. The variability of the performance as a  
4 function of wind speed for the Andersen 321A PM<sub>10</sub> inlet is shown in Figure 4-8 from data  
5 by McFarland et al. (1984). This is a dramatic improvement over the variability shown by  
6 the TSP high volume sampler (McFarland and Ortiz, 1979) for the same speed range. An  
7 attempt to simplify the complexity and improve the availability of wind tunnels to test PM<sub>10</sub>  
8 inlets was addressed by Teague et al. (1992), who describe a compact tunnel 6 m long by  
9 1.2 m high that is capable of testing inlets against the EPA PM<sub>10</sub> specifications.

10 Watson and Chow (1993) noted that the EPA PM<sub>10</sub> performance specifications allowed  
11 a tolerance range around the D<sub>50</sub> that permitted inlets to be undesirably “fine tuned” to  
12 provide a cutpoint on the lower or upper end of the range. Since a significant amount of  
13 mass in the atmospheric aerosol may be associated with particles in the allowable tolerance  
14 range, a “reduction” in reported concentrations could be achieved by simply using a lower  
15 (e.g., 9.6 μm) cutpoint inlet that is still within the acceptable D<sub>50</sub> range. The biases  
16 between acceptable samplers have been apparent in the data from field aerosol comparison  
17 studies (e.g., Rodes et al., 1985; Purdue et al., 1986; Thanukos et al., 1992). Most of the  
18 reported biases between samplers were less than 10%, although differences of up to 30%  
19 were reported. The data suggested that the high volume sampler PM<sub>10</sub> inlets based on  
20 cyclonic separation (Wedding, 1985) were consistently lower, while those based on low  
21 velocity impaction (McFarland et al., 1984) were consistently higher. Sweitzer (1985)  
22 reported results of a field comparison of these two high volume sampler types at an industrial  
23 location, and reported average biases of 15%. It was noted that this amount of bias was  
24 unacceptable for compliance monitoring and more stringent performance requirements should  
25 be used. Rodes et al. (1985) observed that the PM<sub>10</sub> concentration data from the  
26 dichotomous sampler (regardless of the inlet design) gave the most predictable results.

27 Wang and John (1988) were critical of the EPA PM<sub>10</sub> performance specification on  
28 allowable particle bounce (U.S. Environmental Protection Agency, 1987b), stating that the  
29 criteria can lead to a 30% overestimation of mass under worst-case conditions. In a related  
30 paper, John et al. (1991) reported that although reentrainment by air flow alone of particles  
31 deposited in an aerosol inlet is typically negligible, reentrainment caused from subsequent



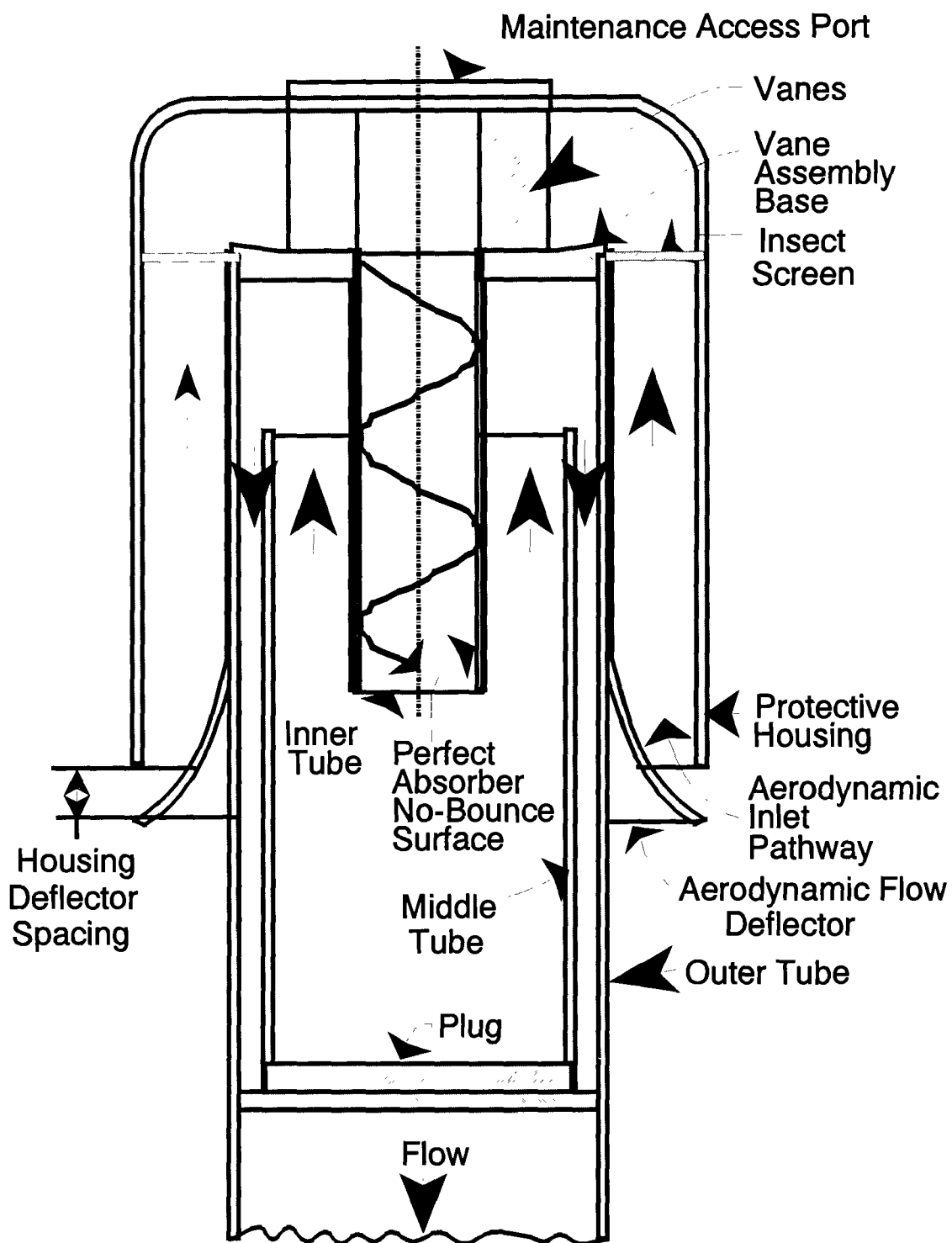
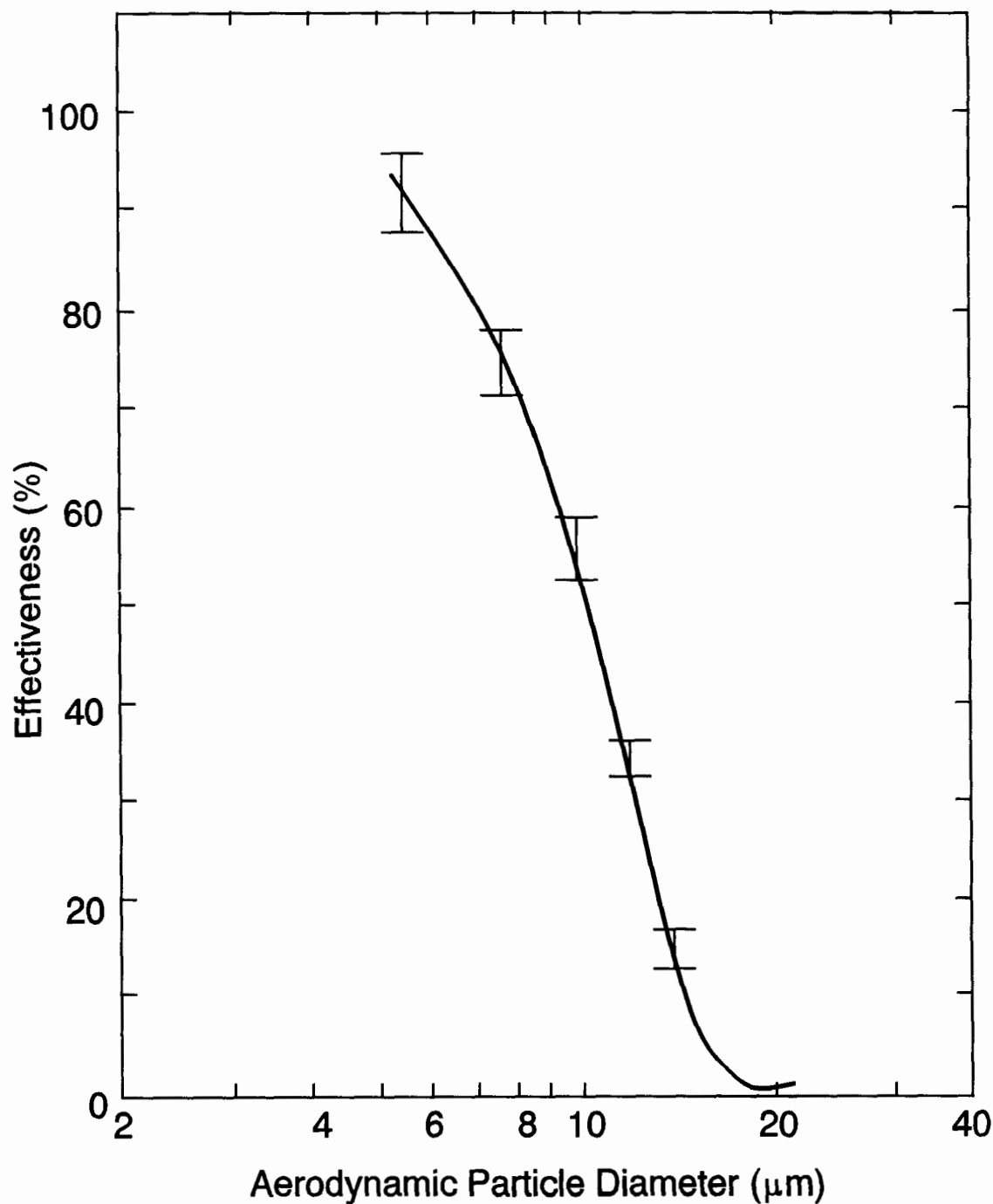
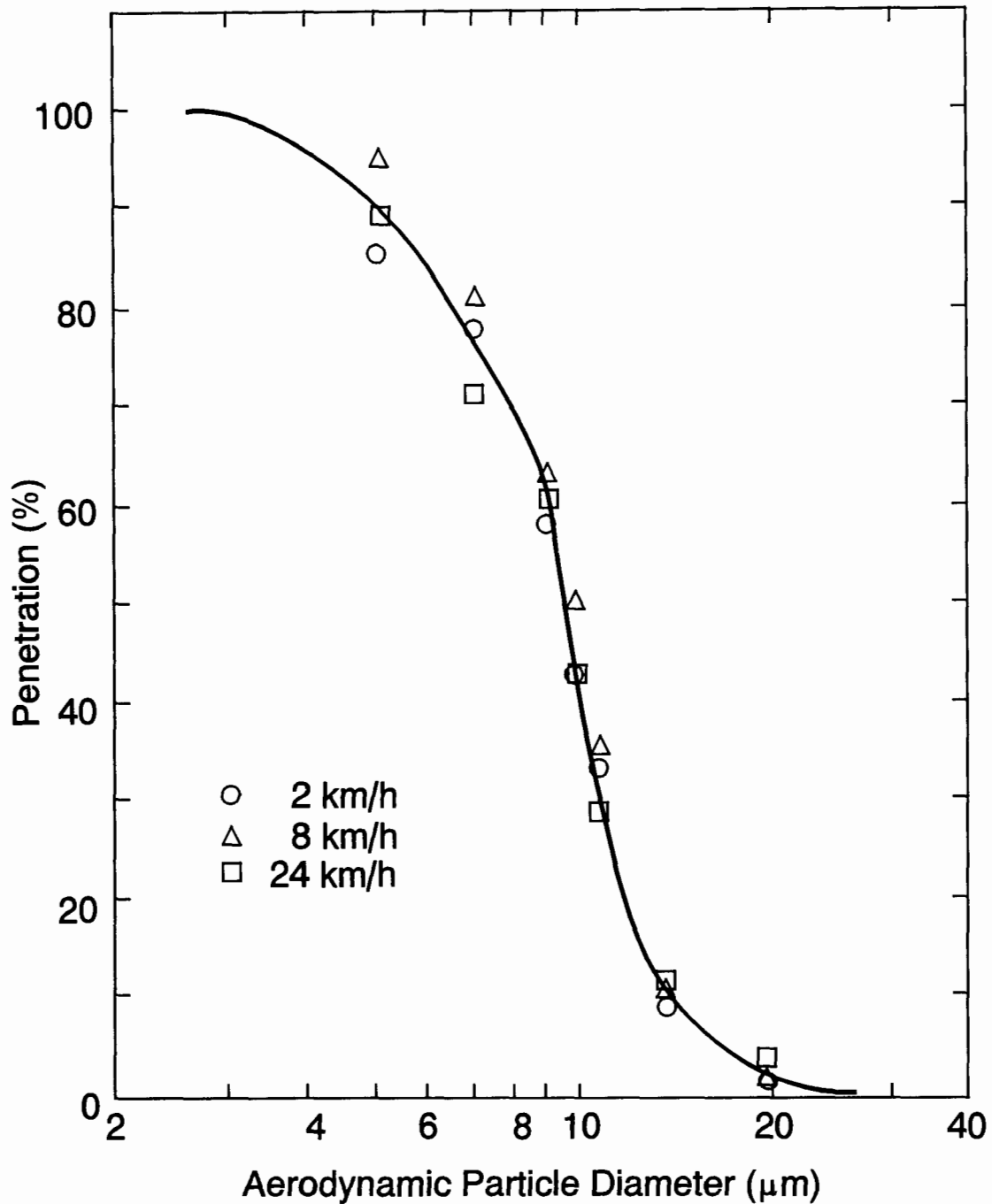


Figure 4-6. Sampling characteristics of two-stage size-selective inlet for liquid aerosols.



**Figure 4-7. Penetration of particles for 16.67 1 pm PM<sub>10</sub> inlets.**

- 1 particle “bombardment” can be substantial. John and Wang (1991) suggested that particle
- 2 loading on oiled deposition surfaces can bias the collection 2.2%/gram deposited, and
- 3 strongly suggested that a periodic cleaning schedule should be required for PM<sub>10</sub> inlets.



**Figure 4-8. Collection performance variability as a function of wind speed.**

1        The EPA PM<sub>10</sub> performance specification program should be considered successful  
2        (John, 1993) in providing consistent aerosol collection results during field sampling. As  
3        noted by Thanukos et al. (1992), the cases of greatest concern were those where the  
4        measured concentrations were near an exceedance level. A review of the current PM<sub>10</sub>

performance requirements and possible amendments of the existing specifications may be appropriate, given the information base now available.

### 4.2.3 Fine Particle Separators

#### 4.2.3.1 Cutpoint Considerations

Although a particle separation at 2.5  $\mu\text{m}$  has been utilized by the dichotomous sampler for a number of years, the 1987 standard reassessment (U.S. Environmental Protection Agency, 1987a) did not specifically require routine monitoring for Fine particles. It has become apparent (see Chapter 14) that certain health and ecological responses are most strongly correlated with fine particles, significantly smaller than 10  $\mu\text{m}$ , and their related chemistry. Since the mass of a particle is proportional to the cube of its diameter, larger particles (especially above 10  $\mu\text{m}$ ) can totally dominate the mass of  $\text{PM}_{10}$  and TSP samples. The 2.5  $\mu\text{m}$  cutpoint generally occurs near a minimum in the mass distribution, minimizing mass concentration differences between samplers with cutpoint biases. The development of control strategies based on mass concentrations from a smaller cutpoint standard must be carefully constructed, especially if large particle interference problems (e.g., particle bounce) cannot be appropriately minimized. This issue was highlighted by an EPA workshop in May, 1994 that focused on the implications of introducing a "fine" particle standard and possibly changing the current 2.5  $\mu\text{m}$  cutpoint for fine fraction sampling to 1.0  $\mu\text{m}$ . A background paper by Lundgren and Burton (1994) notes that the size fraction less than 1.0  $\mu\text{m}$  typically contains only 0.1% of the total aerosols by mass for particles less than 100  $\mu\text{m}$ , while the less than 2.5  $\mu\text{m}$  fraction contains  $\sim 1\%$ . By comparison, it was estimated that at least 50% of the aerosol particles by number are less than 1.0  $\mu\text{m}$ , while at least 80% are less than 2.5  $\mu\text{m}$ .

Practical considerations would be the time and expense required to develop inlets with 1.0  $\mu\text{m}$  cutpoints that meet required specifications and retrofit existing samplers. Given the body of data available at 2.5  $\mu\text{m}$ , a focused effort may prove practical that defines the characteristics of the particle mass and chemistry between 1.0 and 2.5  $\mu\text{m}$ . This would add to the technical knowledge base, allow interpretive corrections between cutpoints to be made, and permit continued sampling at 2.5  $\mu\text{m}$  with a minimum of additional resources. Compositional analysis of the  $\text{PM}_{2.5}$  to  $\text{PM}_{10}$  coarse fraction at eastern U. S. sites show that

1 more than one half of anthropogenically -produced sulfates would be lost by adoption of a  
2 1.0  $\mu\text{m}$  cutpoint during the important summer haze period (Eldred et al., 1995). Similar  
3 losses would also be suggested at some California sites.

#### 4 5 **4.2.3.2 Virtual Impactors**

6 The dichotomous sampler utilizes virtual impaction to separate the Fine and Coarse  
7 fractions into two separate flowstreams (see Novick and Alvarez, 1987). The calibration of a  
8 nominal 2.5  $\mu\text{m}$  impactor, including wall loss data, is shown in Figure 4-9 (from Loo and  
9 Cork, 1988). A virtual impactor has been designed with a 1.0  $\mu\text{m}$  cutpoint (Marple et al.,  
10 1989), and for cutpoints as small as 0.12  $\mu\text{m}$  (Sioutas et al., 1994). After applying a cross-  
11 channel correction factor for the Coarse mode, the mass concentrations of each fraction and  
12 total (using a  $\text{PM}_{10}$  inlet) can be determined gravimetrically. An inherent consideration with  
13 virtual separation is contamination of the Coarse fraction by a portion of the Fine fraction,  
14 equivalent to the ratio of the Coarse channel flow to the total flow (typically 10%). This can  
15 influence subsequent chemical and physical characterizations, if significant differences exist  
16 between the chemistry of each fraction (e.g., acidic Fine fraction and basic Coarse fraction).  
17 Stevens et al. (1993) utilized this limited addition of Fine particles to the Coarse fraction to  
18 advantage in the SEM analysis of samples collected on Nuclepore filters. The current  
19 separator design provides a relatively sharp cutpoint with minimal internal losses. Keeler  
20 et al. (1988) showed that the growth of Fine aerosols at elevated relative humidities can  
21 significantly alter the ratio of Fine to Coarse collection for the dichotomous sampler. During  
22 early morning periods when the humidity approached 100%, an apparent loss of up to 50%  
23 of the Fine mass (to the Coarse channel) was observed. They commented that analyzing  
24 only the fine fraction of the measured aerosol may not be appropriate, especially for short  
25 integration intervals.

26 A high volume (1.13  $\text{m}^3/\text{min}$ ) virtual impactor assembly was developed by Marple, Liu  
27 and Burton (1990) that can be placed on an existing high volume sampler to permit larger  
28 total collections than the dichotomous sampler for chemical speciation by size fraction. By  
29 placing a number of virtual impactors in parallel, a separation can be achieved at higher  
30 flows, while reducing the total pressure drop. Marple et al. (1993) provide a list of

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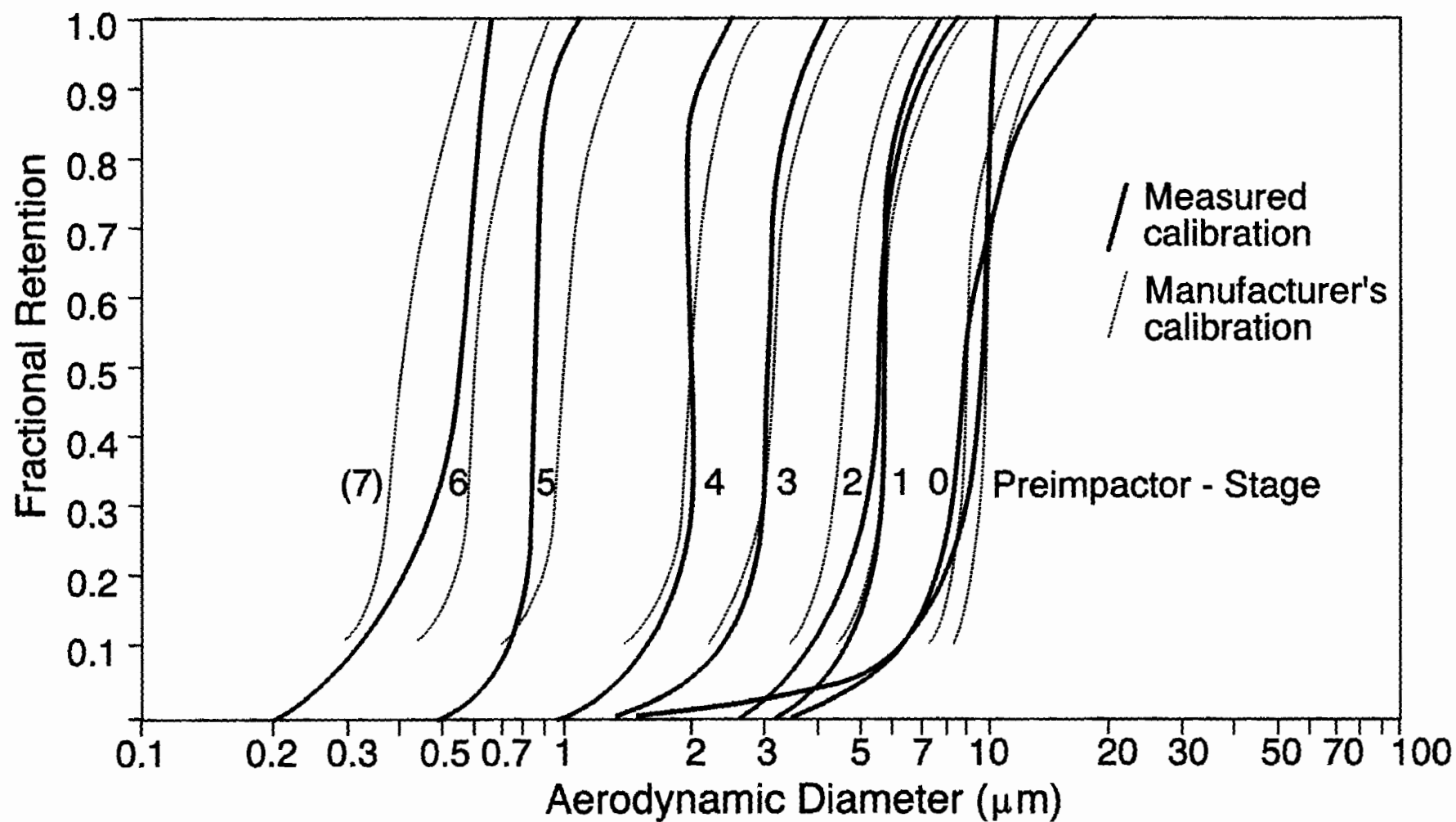


Figure 4-9. Calibration of a 2.5  $\mu\text{m}$  impactor.

commercially available virtual impactors by flowrate and available cutpoints. They also note that virtual separators inherently concentrate the particles in the Coarse fraction (typically by a factor of 10), making them useful as pre-concentrators for sensors with marginal sensitivities. John et al. (1983) found that an oiled Nuclepore filter with a nominal 8  $\mu\text{m}$  porosity could provide a  $D_{50}$  cutpoint of 2.5  $\mu\text{m}$ , similar to that of a virtual impactor, if operated at the appropriate face velocity.

#### 4.2.3.3 Cyclones

Cyclones have been used as aerosol separators in personal exposure sampling in occupational settings for many years. Lippmann and Chan (1979) summarized the cyclones for sampling aerosol sizes below 10  $\mu\text{m}$ , and note that the aerosol penetration through a cyclone can be designed to closely mimic respiratory deposition. An intercomparison of three cyclone-based personal exposure samplers under occupational conditions (concentrations typically  $> 1 \text{ mg/m}^3$ ) was described by Groves et al. (1994). They reported that even though the cyclones were reportedly design to mimic similar respirable conventions, biases as large as a factor of two were noted, possibly attributable to over-loading problems. Marple et al. (1993) provided a list of commercially available air sampling cyclones, by sampling flowrate and  $D_{50}$  range. Cyclones can be used individually or in a cascade arrangement to provide a size distribution. Bartley and Breuer (1982) describe methods to reduce biases when using a 10 mm (diameter) personal air sampling cyclone, especially as related to cutpoint shifts caused by flowrate changes. Saltzman (1984) provided a similar analysis for atmospheric sampling cyclones. Sass-Kortsak et al. (1993) observed that substantial uniformity-of-deposition problems can occur on the filters downstream of personal sampling cyclones. Wedding (1983) used a cyclone within a high volume aerosol inlet to provide a  $\text{PM}_{10}$  cutpoint for ambient sampling that did not allow penetration of particles greater than 10.0  $\mu\text{m}$ .

The simplicity of cyclones has prompted their use as inlets and subsequent separators in samplers designed to fractionate the aerosol sample for chemical analysis. The “Enhanced Method” employed by EPA for sampling acidic aerosols, uses a glass cyclone with a 2.5  $\mu\text{m}$  cutpoint as the sampler inlet (EPA, 1992). The percent collection as a function of aerodynamic diameter is shown in Figure 4-10 (Winberry et al., 1993). Hering et al. (1990)

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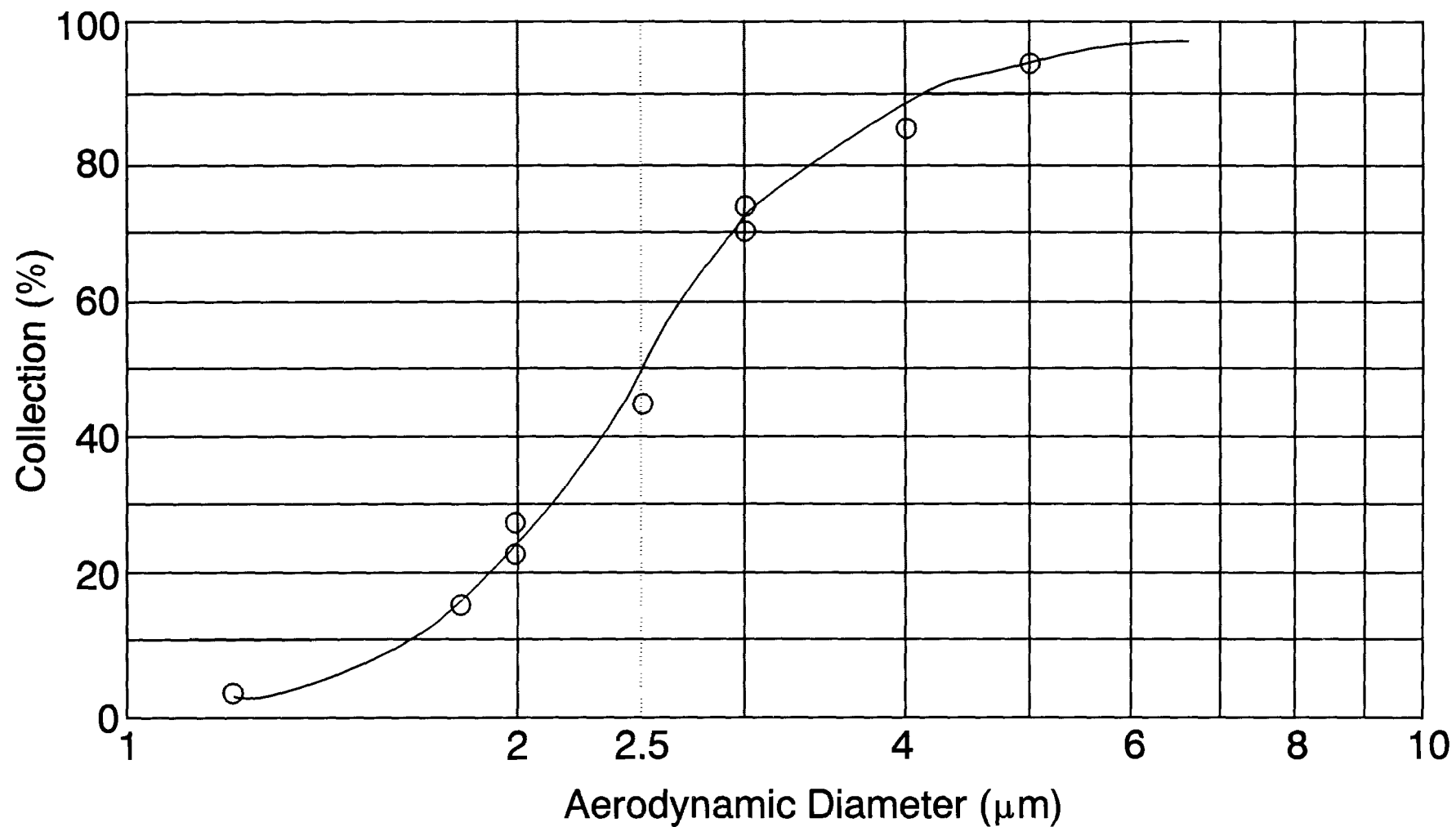


Figure 4-10. Percent collection as a function of aerodynamic diameter.



1 describe several validated aerosol systems for sampling carbonaceous particles that utilize  
2 cyclones with 2.5  $\mu\text{m}$  cutpoints to sample the Fine fraction on either Teflon or quartz  
3 substrates. Spagnolo and Paoletti (1994) describe a dual cyclone ambient aerosol sampler  
4 with a 15  $\mu\text{m}$  inlet (described by Liu and Piu, 1981). This sampler was designed to collect  
5 an “inhalable” 0 to 15  $\mu\text{m}$  fraction, an “extra-thoracic”<sup>7</sup> 0 to 4.0  $\mu\text{m}$  fraction, and a  
6 “respirable” 0 to 2.5  $\mu\text{m}$  fraction. Malm et al. (1994) describe a sampling system with a  
7 PM10 inlet and three parallel channels following a 2.5  $\mu\text{m}$  cutpoint cyclone that was used for  
8 the 40 site IMPROVE network. Over 120,000 fine particle filter substrates of Teflon<sup>®</sup>,  
9 nylon and quartz were collected for chemical analysis over a 6 year period.

#### 11 4.2.3.4 Impactors

12 Impactors have been developed for a wide range of cutpoints and flowrates. In cascade  
13 arrangements (see Section 4.2.7.1.1) with a characterized inlet, impactors provide  
14 distributional information over a range of aerodynamic sizes. Impactors used as components  
15 of inlets or as in-line fractionators, stop and retain the aerosol on a surface (e.g., oil-soaked,  
16 sintered metal or glass) that hopefully provides consistent performance (primarily minimal  
17 bounce) over the entire sampling interval. Recovery and analysis of the deposited particles  
18 in these situations are usually not considerations. Koutrakis et al (1990) described the design  
19 of an 2.1  $\mu\text{m}$  cutpoint impactor for a single stage annular denuder system that exhibited  
20 internal losses of less than 3 %.

21 Marple et al. (1993) noted that the three primary limitations of impactors are particle  
22 bounce, overloading of collection stages and interstage losses. Particles can bounce from a  
23 stage after impaction if the surface forces are not adequate for their retention. Wang and  
24 John (1988) described the effects of surface loading and relative humidity on particle bounce  
25 and growth, and noted that if less than 6% of the impact area was covered by deposited  
26 particles, particle-to-particle collisions (and bounce) could be neglected. They also showed  
27 that ammonium sulfate aerosol growth with increasing humidity resulted in a 25% shift in  
28 cutpoint as the relative humidity increased to 64%. Biswas et al. (1987) showed that,  
29 especially in low pressure zones, the relative humidity and temperature can change rapidly  
30 within a cascade impactor, significantly altering cutpoints and losses. Turner and Hering

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31 <sup>7</sup>The term “extra-thoracic” is most often used to refer to those particles > 10  $\mu\text{m}$ .

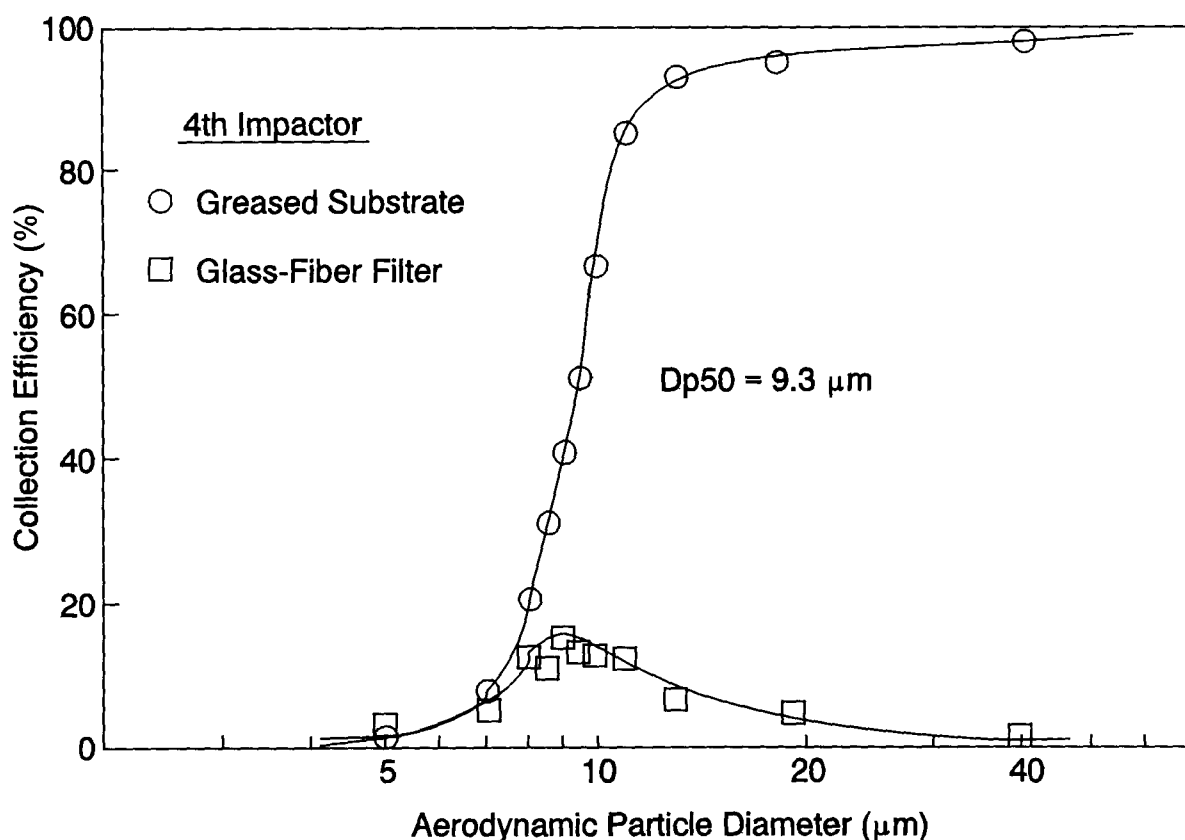
(1987) noted that the stage substrate materials (Mylar<sup>®</sup>, stainless steel and glass) with the same grease (Vaseline<sup>®</sup>) could produce substantially different particle adhesion characteristics. Vanderpool et al. (1987) showed (see Figure 4-11) that using glass fiber filters as impactor surfaces can produce drastically reduced performance as compared to a greased substrate. Markowski (1987) suggested that adding a duplicate (same cutpoint), serial impactor stage can permit reasonable bounce and re-entrainment corrections to be made.

## **4.2.4 Sampling Considerations**

### **4.2.4.1 Siting Criteria**

The selection of an aerosol sampling location is partially guided by siting criteria provided as part of the 1987 PM<sub>10</sub> regulation (U.S. Environmental Protection Agency, 1987c), which provided limited guidance for Pb and PM<sub>10</sub> samplers. The details behind these guidelines for PM<sub>10</sub> are provided by EPA in a guidance document (U.S. Environmental Protection Agency, 1987d), which relates the physical and chemical characteristics of aerosols to the spatial scales (regional, urban, neighborhood, middle and micro) required to define the influences of sources on various populations. Guidance was also provided on the influences of nearby point, line and area sources on sampling location as a general function of particle size. Only limited information was noted to be available on specific influences of local obstructions and topography (e.g., trees, buildings) on the measured aerosol concentrations. The primary focus was establishment of the degree that a sampling location was representative of a specific scale.

The high purchase cost, and occasionally physical size, of aerosol samplers have tended to restrict the number of sampling sites used in air monitoring studies. In an attempt to address the biases resulting from too few aerosol samplers in a field study, a “saturation” sampler approach has been used, utilizing an inexpensive, miniature and battery-powered PM<sub>10</sub> sampler that can be deployed at a large number of sites. Phillips et al. (1994) reported the application of this approach using 15 PM<sub>10</sub> saturation samplers in conjunction with one dichotomous sampler to study the contribution of diesel emissions to the total particulate levels in Philadelphia. Although the mean PM<sub>10</sub> concentrations of the saturation samplers



**Figure 4-11. Performance of glass fiber filters compared to greased substrate.**

was essentially identical to that of the dichotomous sampler, the saturation data showed site-to-site mean differences of as much as  $30 \mu\text{g}/\text{m}^3$ .

#### 4.2.4.2 Averaging Time/Sampling Frequency

The collection frequency for samples to support the EPA  $\text{PM}_{10}$  standard has typically been on an every-6th-day schedule. A statistically-based concern (Shaw et al., 1984) was raised that infrequent collection increases the coefficient of variation about the overall mean concentration value. They observed that the variability of computed Fine mass concentration means increased as the square root of the number of intervals between individual measurements. Symanski and Rappaport (1994), using time series analyses, described the influences of autocorrelation and non-stationary behavior in occupational settings on the concentration distributions constructed from infrequent sampling. They recommended a random sampling design where a sufficient number of locations are sampled repeatedly over

1 an adequate period of time to account for the full range of exposure possibilities. Hornung  
2 and Reed (1990) described a method of estimating non-detectable (or missing) values to  
3 improve the variance about the estimate of the geometric mean, by assuming the  
4 concentration distribution is log-normal.

5 Insufficient sample collections can be remedied by more frequent operation of manual  
6 samplers. The recent  $PM_{10}$  equivalency designations (see section 4.2.5) of two beta gauge  
7 samplers and the TEOM sampler can provide the necessary information, with hourly, rather  
8 than daily, resolution. The initial cost of an automated sampler is typically 2-3 times that of  
9 a manual, single channel  $PM_{10}$  sampler, but can be offset by the savings in operator labor  
10 costs. If the inherent biases described in section 4.2.3.4 for the beta and TEOM samplers  
11 can be accommodated (and they are field reliable), these approaches should prove very useful  
12 in routine regulatory and research monitoring studies. The potential also exists that the  
13 integrating nephelometer may be an acceptable exceedance monitor<sup>8</sup>, using site specific  
14 calibrations relating the measured scattering coefficient,  $b_{sp}$ , to Fine aerosol mass  
15 concentrations (e.g., Larson et al., 1992).

16 Another consideration for setting the sampling interval concerns the setting of start and  
17 stop clock times. Daily 24-h sampling is most often accomplished from midnight-to-  
18 midnight, but occasionally from noon-to-noon to either reduce the number of samplers  
19 required or reduce operator burden. Sampling locations with highly variable diurnal aerosol  
20 concentration patterns (e.g., from night time wood smoke influence or day time traffic dust),  
21 or substantial differences between week days and weekend days may require special  
22 consideration. These influences can be especially significant for sampling periods less than  
23 24 h.

#### 24 25 **4.2.4.3 Collection Substrates**

26 The selection of a filtration substrate for integrated collection of particles must be made  
27 with some knowledge of the expected particle characteristics and a pre-determined analytical  
28 protocol. The expected sampled size distribution places a requirement on the porosity of the  
29 filter media to effectively trap a reasonably high percentage of the particles with a minimum

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30 <sup>8</sup>A Pollutant Standard Index (PSI) monitor used to estimate when a pre-determined exceedance level has been  
31 reached or exceeded, to potentially trigger the operation of an equivalent  $PM_{10}$  gravimetrically-based sampler.

of pressure drop. The most common filter types used in air sampling are fiber and membrane. Fiber filters tend to be less expensive than membrane filters, have low pressure drops, and have high efficiencies for all particle sizes. They are most commonly available in glass fiber, Teflon coated glass fiber and quartz materials. Membrane filters retain the particles on the surface for non-depth analyses (e.g., X-Ray Fluorescence), can have specific porosity's, and are available in a wide variety of materials. Teflon is a popular membrane material because of its inertness, but is 2 to 4 times as expensive as more common materials. Liu et al. (1978) summarize the effective penetration characteristics as a function of particle size and the pressure drops for a wide variety of fiber and membrane filters. Polycarbonate filters with well defined porosity's (e.g., Nuclepore<sup>®</sup>) have been used in "stacked" arrangements as fine particle separators. John et al. (1983) describe using an 8  $\mu\text{m}$  porosity filter in series with a back-up filter to effectively provide a 3.5  $\mu\text{m}$  separation of fine and coarse particles in a small, inexpensive package. Samplers based on this principle were widely used in the early 1980's (Cahill et al., 1990) and their performance under field conditions was shown to be equivalent to later cyclone base  $\text{PM}_{2.5}$  samplers in the IMPROVE network.

The reactivities of filter substrates with the aerosol have been reported extensively. A common problem with glass fiber filters used on high volume samplers is the basic pH of the glass material and its effective conversion of acid gases to particulate sulfates (e.g., Pierson et al., 1976). Appel et al. (1984) also reported similar conversions of nitrogen oxides to particulate nitrates on glass fiber filters. Witz et al. (1990) reported losses of particulate nitrates, chlorides and ammonium (19, 51 and 65 %, respectively) from quartz fiber filters during storage. No significant losses of sulfates were reported from quartz filters. Similarly, Zhang and McMurry (1992) reported the anomalous loss of fine particle nitrates from Teflon filters and noted that predictive loss theories were insufficiently accurate to permit corrections. Lipfert (1994) also observed that nitrate artifacts on glass fiber filters were difficult to quantify on a routine basis. Measurements of particulate nitrate using nylon filters by the IMPROVE protocols show, however, that such effects are minor except in California (Malm et al., 1994). Eatough et al. (1993) found significant losses of particulate organic compounds on quartz filters due to volatilization, such that the ambient concentrations of particulate carbon may be underestimated substantially. Lipfert (1994)

investigated filter artifacts in a field study in New York, and concluded that positive sulfate artifacts inflated  $PM_{10}$  values from glass fiber filters by  $6 \mu g/m^3$ . It was noted that the combination of sulfate and nitrate artifacts on glass fiber filters may inflate TSP concentrations by as much as 10 to  $20 \mu g/m^3$ .

#### 4.2.4.4 Chemical Speciation Sampling

The collection of aerosol samples for chemical speciation analysis adds another dimension to the complexity of the sampling protocol (also see Section 4.3 for additional discussion). The simplest approach utilizes a characterized inlet or separator to define a size fraction, provides an aerosol collection substrate compatible with the analytical technique, and collects an adequate quantity of sample for analysis. This approach is applicable for relatively nonreactive and stable components such as heavy metals. An important consideration is the potential reactivity of the sampling substrate with either the collected aerosols or the gas phase. Appel et al. (1984) predicted the effect of filter alkalinity on the conversion of acid gases to sulfates and nitrates. They provided an upper limit estimate on artifact sulfate formation (added mass) for TSP high volume sampling of  $8-15 \mu g/m^3$  for a 24-h sample.

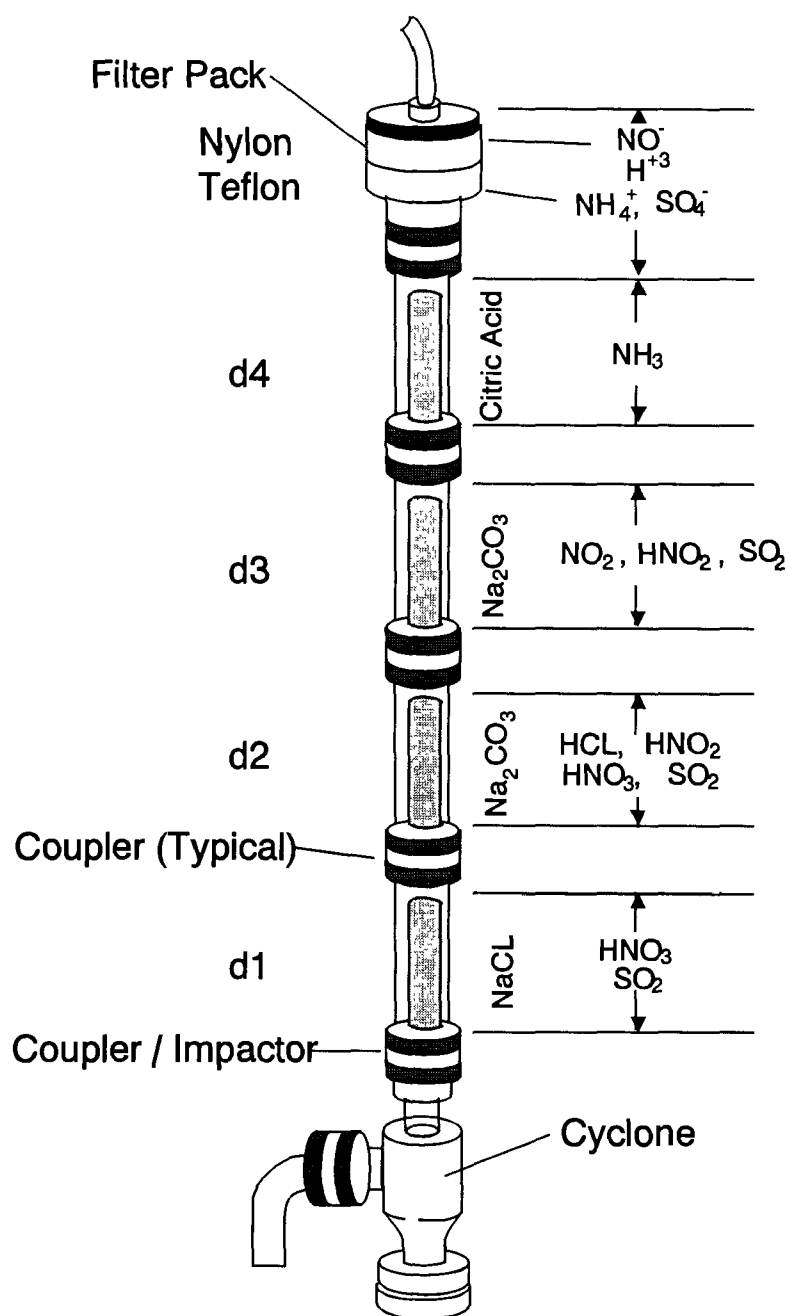
Analyses for semi-volatile organics which are found in both the particle and vapor phases must be collected by adding a vapor trap (e.g., polyurethane foam plug) downstream of the sampling filter. Arey et al. (1987) noted that this arrangement of sequential sampling reservoirs may account for the total mass of organics, but not accurately describe their phase distribution in situ, due to "blow-off" from the filter during sampling. Van Vaeck et al. (1984) measured the volatilization "blow-off" losses of organic species from cascade impactor sampling to be up to 30%, while the loss of total mass was only 10%. McDow and Huntzicker (1990) characterized the face velocity dependence for organic carbon sampling and provided correction models, based on adsorption losses to a backup filter. Turpin et al. (1994) examined organic aerosol sampling artifacts and highlighted the distinction between "organic carbon" and individual organic species. They observed that organic carbon sampled from the atmosphere is unlikely to attain equilibrium between that in the gas phase and that adsorbed on a quartz fiber back-up filter. They also noted that under typical sampling conditions, adsorption is the dominant artifact in the sampling of particulate organic

1 carbon, and longer sampling periods reduce the percentage of collected material that is  
2 adsorbed vapor. It was recommended that collection of aerosols for carbon analyses be  
3 made on a pre-fired quartz filter, with estimates of the adsorption artifact made from a quartz  
4 filter placed behind a Teflon filter in a parallel sampler.

5 For more highly reactive and unstable species, the recognition of the in situ character  
6 of the aerosol in the air must be identified and preserved during all facets of the sampling  
7 process to provide a representative and accurate sample. Durham et al. (1978) described a  
8 denuder to remove sulfur dioxide while sampling for sub-micron aerosols. Spicer and  
9 Schumacher (1979) observed that many artifact reactions may occur if stripping of nitric  
10 acid, sulfuric acid and ammonia is not performed during speciated aerosol sampling. Appel  
11 et al. (1988) described the various loss mechanisms that apply to the aerosol and vapor  
12 phases while sampling for nitric acid. They noted that residence time, surface material  
13 compositions, and conditioning prior to sampling were the predominant variables affecting  
14 transmission efficiency.

15 The determination of strong acidity for atmospheric aerosols (U.S. Environmental  
16 Protection Agency, 1992) describes an "Enhanced" method that recognizes the inter-  
17 relationships between the vapor and aerosol phases for each constituent and the potential  
18 interferences. An inlet cyclone or impactor is used to provide a 2.5  $\mu\text{m}$  cutpoint to exclude  
19 the higher pH aerosols found in the Coarse fraction. As shown in Figure 4-12, denuders are  
20 used in the flowstream which selectively remove gas phase components with minimal,  
21 characterized losses of aerosol. Ye et al. (1991) determined the aerosol losses through an 10  
22 lpm annular denuder system as a function of particle size. They noted that total particle  
23 losses were less than a few percent whether the denuders were coated or uncoated. Forrest  
24 et al. (1982) using parallel annular denuders, found aerosol losses of only 0.2-2.2% for 0.3-  
25 0.6  $\mu\text{m}$  particles, and 4-5% for 1-2  $\mu\text{m}$  particles.

26 Filter packs have been developed, consisting of a sandwich of filters and collection  
27 media of various types in series, to collect aerosols and selectively trap gases and aerosol  
28 volatilization products. Benner et al. (1991) described an annular denuder sampling system  
29 using Teflon and nylon filter packs and annular denuders to quantitatively collect the  
30 distributed ammonium nitrate, nitric acid and ammonia in the vapor and aerosol species.  
31 They observed that volatile nitrates were 71%  $\pm$  27% of the total nitrates during the day and



**Figure 4-12. Schematic diagram of an annular denuder system.**

- 1 55%  $\pm$ 30% at night in arid, southwestern U. S. locations. Masia et al. (1994) described the
- 2 anomalous uptake of ammonia on the nylon filters, which were expected to collect only the
- 3 gas phase nitric acid. Wang and John (1988) reported volatilization losses of ammonium
- 4 nitrate in the Berner impactor of 7% under hot, dry (18% Rh) conditions.



Vossler et al. (1988) reported the results of improvements in an annular denuder system, including Teflon coating of the internal glass surfaces. They found an apparent particle bounce problem with the cyclone inlets (with or without Teflon coating), and proposed adding an additional in-line, greased impactor. John et al. (1988) found that anodized aluminum surfaces absorb nitric acid efficiently and irreversibly. A number of method comparison studies have been reported for systems utilizing annular denuder/filter pack technologies, including Harrison and Kitto (1990), Sickles et al. (1990), and Benner et al. (1991).

#### 4.2.4.5 Data Corrections/Analyses

Aerosol concentration data are reported in units of mass per volume (e.g.,  $\mu\text{g}/\text{m}^3$ ). The current EPA regulations for sampling TSP,  $\text{PM}_{10}$  and Pb require that sampler flowrates be controlled and the sampled volumes be standardized to 760 mm Hg and 25 °C. These requirements may pose problems in the interpretation of concentrations from aerosol samplers. The flowrate through inertial impactors should be maintained at “local” temperatures and pressures to retain the separator’s aerodynamic calibration. Mass flow controllers may significantly affect the separator flow velocity during large diurnal temperature changes, excessively biasing the resulting cutpoint diameter.

Subsequent correction of the sampled aerosol volume to “standard” conditions by mathematically compensating for average meteorological conditions may improperly report the aerosol concentration measurement. If the rationale for aerosol sampling was to mimic respiratory penetration (which occurred at local conditions), a correction after-the-fact may not be appropriate. These corrections are typically small (less than a few percent) except in locations at higher altitudes and those with large diurnal or seasonal temperature changes. The basis for mandating flowrate controller performance for aerosol samplers is sound, but and the subsequent requirements for concentration corrections for temperature and pressure are complex. Although the issue of sampled volume correction for local temperature and pressure is beyond the scope of this document, the scientific bases should be reassessed for aerosol sampling to determine if this requirement is consistent with EPA goals.

The matching of aerosol measurement capabilities with data quality requirements is discussed by Baron and Heitbrink (1993). They note that although aerosol sampler precision

can be determined from collocated measurements, field sampling accuracy is more difficult to define. Generation of mono- or polydisperse calibration aerosols are rarely done in field settings because of the complexity of the calibration process. Typically, only the aerosol sampler flowrate accuracy is determined in the field. Biases between the means from collocated aerosol samplers using different separation techniques, may result from sampler operational errors, or from inadequacies in determining the performance specifications during laboratory testing.

## **4.2.5 Performance Specifications**

### **4.2.5.1 Approaches**

A significant step in the standardization process for aerosol sampling was the EPA definition (U.S. Environmental Protection Agency, 1987a) of the  $PM_{10}$  size fraction, based on the aerodynamic diameter of particles capable of penetrating to the thoracic region of the respiratory system. This definition was followed by implementation of the  $PM_{10}$  provisions of EPA's Ambient Air Monitoring Reference and Equivalent Methods regulation (U.S. Environmental Protection Agency, 1987b). The format of the latter regulation (see section 4.2.5 for specifics) was the adoption of performance specifications for aerosol samplers, based on controlled wind tunnel testing with mono-dispersed aerosols. Controlled laboratory testing is followed by limited field testing, including tests of candidate equivalent methods to demonstrate comparability to designated reference methods. This approach was chosen, rather than the design specification approach taken in 1971 (U.S. Environmental Protection Agency, 1971), which identified the high volume sampler and associated operational procedures as the reference method for Total Suspended Particulates (TSP)<sup>9</sup>. The 1971 regulation had no provisions for the use of alternative or equivalent methods. Subsequent to this design designation, significant problems of the TSP high volume sampler, such as wind speed and direction dependency (McFarland and Rodes, 1979) and off-mode collection (Sides and Saiger, 1976), were reported. These inherent biases complicated the interpretation of TSP concentration data (U.S. Environmental Protection Agency, 1982c) and weakened

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<sup>9</sup>Subsequent identifications in this section: "TSP" for Total Suspended Particulates by high volume sampler, " $PM_{10}$ " for the fraction less than  $10\ \mu m$ , "Fine" (capitalized) for the fraction less than  $2.5\ \mu m$ , and "Coarse" for the fraction between  $2.5$  and  $10\ \mu m$ .

1 correlations with other measures. The problems were estimated to have induced biases of  
2 less than 10% for most situations, but occasionally as high as 30%. The subsequent  
3 development of aerosol testing programs for size selective aerosol samplers (e.g., McFarland  
4 and Ortiz, 1979; Wedding, 1980; John and Wall, 1983; Ranade et al., 1990; Hall et al.,  
5 1992) more rapidly identified weaknesses in existing technologies and facilitated the  
6 development of better methods. No reference standard exists for aerosol concentration  
7 measurements in air. The calibration of aerosol samplers relies primarily on  
8 characterizations under controlled conditions of the sampler sub-systems, including the size  
9 selective inlet, sample conditioning and transmission system, the flow control system, and, if  
10 used, subsequent size separators, sample collection and storage elements, and sensors and  
11 associated electronics. Although the precision of an aerosol sampler is readily obtained by  
12 using replicate, collocated samplers, the accuracy can only be estimated by comparison with  
13 either designated "reference" samplers or with computations of expected aerosol mass  
14 collections. Performance specification limits are used to control the overall aerosol sampling  
15 accuracy. As noted by John (1993) the selection of a comprehensive list of sampling  
16 elements requiring inclusion and the setting of the performance limits for each element is a  
17 difficult task, especially when the range of "real-world" sampling situations is considered.

18 Performance specifications were utilized for the  $PM_{10}$  standard to allow the broadest  
19 spectrum of measurement technologies, hopefully encouraging the development of new and  
20 better methods. A research program was implemented by EPA in parallel with the 1982  
21 Criteria Document to identify the critical specifications and understand the inter-relationships  
22 among the parameters influencing the aerosol sampling process. Studies of the influences of  
23 factors such as wind velocity, particle character, flow rate stability, particle bounce and wall  
24 losses on precision and accuracy substantially advanced the science of large particle  
25 sampling. The performance specification approach was a significant improvement over the  
26 design specification approach used for the TSP high volume sampler, in that it fostered the  
27 development of new information and technologies, and provided for the use of alternative  
28 methods. In retrospect, the primary weakness of the design specification approach for the  
29 TSP reference method was not the process per se, but the technical inadequacy of the  
30 development and testing program that produced the high volume sampler design.

The utilization of a performance specification approach requires that a minimum level of knowledge be available about the measurement process and the associated test procedures. Some significant drawbacks subsequently observed in the performance specification approach for PM<sub>10</sub> included the complexity, expense and scarcity of aerosol wind tunnel test facilities, and the difficulty in defining comprehensive specifications that considered all of the nuances of aerosol sampling. Wind tunnel evaluation and limited field tests do not always identify sampler related problems encountered during extended periods of ambient sampling (e.g., John and Wang, 1991).

#### 4.2.5.2 Critiques

Aerosol sampling research studies since the 1982 Criteria Document have identified a number of factors that influence the precision and accuracy of both wind tunnel sampler performance testing and individual aerosol samplers, demonstrated to meet performance tests. Rodes et al. (1985) and Purdue et al. (1986) showed in field evaluations that PM<sub>10</sub> samplers meeting the EPA performance specifications did provide consistent aerosol concentration measurements within 10%, under a variety of sampling situations, but reported that significant biases were evident. The biases were based on expected collections computed from a knowledge of aerosol inlet penetration by particle size and the size distributions of ambient aerosol mass by particle size. They also noted that sampler precisions (coefficients of variation) were better than  $\pm 10\%$ , with several samplers better than  $\pm 5\%$ .

Mark et al. (1992) reviewed the attributes of wind tunnel testing, and noted that tests using controlled conditions are a necessity to determine whether an aerosol sampler meets a basic cadre of established performance specifications. Hollander (1990) suggested that sampler performance criteria should be evaluated in controlled outdoor tests, given the inability of wind tunnels to accurately mimic the influences of outdoor meteorological conditions on sampling. The current EPA PM<sub>10</sub> performance testing requires field tests to demonstrate sampler precision and flow rate stability, and the comparability of equivalent methods to designated reference methods. The stringency of such tests are highly dependent on the sampling location chosen, local aerosol sources, the existing meteorology and the season.

Kenny and Lidén (1989) noted that the EPA PM<sub>10</sub> sampler performance specifications (U.S. Environmental Protection Agency, 1987b) provided inadequate consideration for defining the uncertainty in each parameter, and suggested that bias mapping approaches be considered. This approach relates the allowable precision of a parameter to the critical values of expected bias that just meet the specifications. Botham et al. (1991) recommended that the wind tunnel test system duplicate the expected field sampling scenarios as closely as possible, including characteristic flow obstructions. They described the wind tunnel testing of personal aerosol samplers mounted on an anthropogenically consistent (e.g., breathing, heated) mannequin. Hoffman et al. (1988) and John et al. (1991) described the adverse influence of internal surface soiling on aerosol collection performance during extended field operation, and noted that the existing EPA PM<sub>10</sub> performance specifications only considered clean samplers.

Significant new innovations in aerosol sensing technologies, that met the PM<sub>10</sub> performance specification and earned designations as equivalent methods (see section 4.2.6) have occurred since the 1982 Criteria Document. These indirect<sup>10</sup> methods include automated beta attenuation monitors (e.g., Merrifield, 1989; Wedding and Weigand, 1993), and the automated Tapered Element Oscillating Microbalance (TEOM) technology (Patashnick and Rupprecht, 1991). These designations added automated sampling capabilities to the previously all-manual list of sampling methods. Recent field tests of both the beta and TEOM methodologies suggest that biases compared to gravimetrically-based samplers may exist that were not identified by the EPA performance test requirements. Arnold et al. (1992) provide data suggesting that the mass concentration data from a Wedding beta gauge averaged 19% lower than a collocated Wedding PM<sub>10</sub> gravimetric sampler. Several researchers, including Hering (1994) and Meyer (1992), have suggested that the TEOM method can exhibit biases (not identified by performance testing) caused by excessive heating (and desiccation) of the sampled aerosol due to operation at an elevated reference temperature (30 or 50 °C) during the measurement process. Devising comprehensive performance specifications and test procedures for aerosol samplers, given the complexities of aerosol mechanics, is a demanding task.

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<sup>10</sup>An alternate technology used instead of direct gravimetric analysis to infer mass concentrations from developed relationships.

1       The size-selective, gravimetrically-based, 24-h manual aerosol concentration  
2 measurement has been the mainstay of compliance sampling for at least two decades.  
3 Although several new sensor technologies have been designated as Equivalent methods for  
4  $PM_{10}$  by EPA, no superior technology has been developed that is a better reference method  
5 than that based on collection of a discrete aerosol sample followed by gravimetric analysis.  
6 Improvements have been made since 1982 in the accuracy and precision of integrated,  
7 manual aerosol sampling. Some of the most significant advances have occurred in aerosol  
8 size separation technologies, improved performance characterization test methods, and  
9 speciation sampling techniques.

10       As discussed by Lippmann (1993), there may be no threshold for health responses  
11 down to the lowest aerosol concentrations. This implies that the precision and lower  
12 detection limit requirements will continue to be important for aerosol measurements across  
13 the concentration spectrum. These factors become even more critical as the size fraction of  
14 interest becomes smaller and fewer total particles are collected. At low concentrations  
15 (especially with small size fractions), normally insignificant factors can become important  
16 contributors to biases. Witz et al. (1990) reported rapid and substantial losses of nitrates,  
17 chlorides and ammonium ion (19, 65 and 51%, respectively) from quartz high volume  
18 sampler filters during storage periods of one week prior to analyses. Transformations can  
19 also occur on glass fiber substrates during sampling, as reported by Sickles and Hodson  
20 (1989) for the rapid conversion of collected nitrites to nitrates in the presence of ozone.  
21 Zhang and McMurry (1992) showed that nearly complete evaporative losses of Fine particle  
22 nitrate can occur during sampling on Teflon filters. Liou et al. (1988), in a study using  
23  $PM_{10}$  samplers, reported 25-34% lower concentration values resulting from losses of glass  
24 fibers from the filter to the filter holder gasket during sampling. Feeney et al. (1984)  
25 reported weight gains in Teflon filters used in contaminated ring cassettes, that posed  
26 significant problems for light aerosol loadings. Grinshpun et al. (1993) suggest that if  
27 unavoidable changes in the aerosol occur during sampling, development of a model that  
28 permits back-calculation of the in situ characteristics is required.

#### 4.2.6 Reference and Equivalent Method Program

Ambient air PM<sub>10</sub> measurements are used (among other purposes) to determine whether defined geographical areas are in attainment or non-attainment with the national ambient air quality standards (NAAQS) for PM<sub>10</sub>. These measurements are obtained by the States in their state and local air monitoring station (SLAMS) networks as required under 40 CFR Part 58. Further, Appendix C of Part 58 requires that the ambient air monitoring methods used in these EPA-required SLAMS networks must be methods that have been designated by the EPA as either reference or equivalent methods.

Monitoring methods for particulate matter (i.e., PM<sub>10</sub>) are designated by the EPA as reference or equivalent methods under the provisions of 40 CFR Part 53, which was amended in 1987 to add specific requirements for PM<sub>10</sub> methods. Part 53 sets forth functional specifications and other requirements that reference and equivalent methods for each criteria pollutant must meet, along with explicit test procedures by which candidate methods or samplers are to be tested against those specifications. General requirements and provisions for reference and equivalent methods are also given in Part 53, as are the requirements for submitting an application to the EPA for a reference or equivalent method determination. The distinction between reference and equivalent methods is a technical one. On one hand, it provides for detailed, explicit specification of a selected measurement technology for reference methods. On the other hand, it allows alternative (including innovative and potentially improved) methodologies for equivalent methods, based only on meeting specified requirements for functional performance and for comparability to the reference method. For purposes of determining attainment or non-attainment with the NAAQS, however, the distinction between reference and equivalent methods is largely, if not entirely, immaterial.

Under the Part 53 requirements, *reference methods* for PM<sub>10</sub> must be shown to use the measurement principle and meet the other specifications set forth in 40 CFR 50, Appendix J. They must also include a PM<sub>10</sub> sampler that meets the requirements specified in Subpart D of 40 CFR 53. Appendix J specifies a measurement principle based on extracting an air sample from the atmosphere with a powered sampler that incorporates inertial separation of the PM<sub>10</sub> size range particles followed by collection of the PM<sub>10</sub> particles on a filter over a 24-h period. The average PM<sub>10</sub> concentration for the sample period is determined by dividing the

1 net weight gain of the filter over the sample period by the total volume of air sampled.  
2 Other specifications are prescribed in Appendix J for flow rate control and measurement,  
3 flow rate measurement device calibration, filter media characteristics and performance, filter  
4 conditioning before and after sampling, filter weighing, sampler operation, and correction of  
5 sample volume to EPA reference temperature and pressure. In addition, sampler  
6 performance requirements in Subpart D of Part 53 include wind tunnel tests for "sampling  
7 effectiveness" (the efficacy of the PM<sub>10</sub> particle size separation capability) at each of three  
8 wind speeds and "50 percent cutpoint" (the accuracy of the primary 10-micron particle size  
9 separation). Field tests for sampling precision and flow rate stability are also specified. In  
10 spite of the instrumental nature of the sampler, this method is basically a manual procedure,  
11 and all designated reference methods for PM<sub>10</sub> are therefore defined as manual methods.

12 *Equivalent methods* for PM<sub>10</sub>, alternatively, need not be based on the measurement  
13 principle specified in Appendix J nor meet the other Appendix J requirements. Instead,  
14 equivalent methods must meet the "sampler" performance specifications set forth in Subpart  
15 D of Part 53 and demonstrate *comparability* to a reference method as required by Subpart C  
16 of Part 53. The provisions of Subpart C specify that a candidate equivalent method must  
17 produce PM<sub>10</sub> measurements that agree with measurements produced by collocated reference  
18 method samplers at each of two field test sites. For this purpose, agreement means a  
19 regression slope of  $1 \pm 0.1$ , a regression intercept of  $0 \pm 5 \mu\text{g}/\text{m}^3$ , and a correlation  $> 0.97$ .  
20 These requirements allow virtually any type of PM<sub>10</sub> measurement technique, and therefore  
21 an equivalent method for PM<sub>10</sub> may be either a manual method or a fully automated  
22 instrumental method (i. e., analyzer).

23 As of this writing, the EPA has designated seven reference methods and three  
24 equivalent methods for PM<sub>10</sub>, as listed in Table 4-1. The reference methods include four  
25 methods featuring high-volume samplers from two manufacturers, with one using a cyclone-  
26 type size separator and the others using an impaction-type separator. The other reference  
27 methods include a low-volume sampler (from a third manufacturer), a low-volume sampler  
28 featuring a secondary size separation at 2.5 microns (dichotomous sampler), and a medium-  
29 volume, non-commercial sampler. The three designated equivalent methods are all  
30 automated PM<sub>10</sub> analyzers and include two operating on the beta-attenuation principle and  
31 one based on a tapered element oscillating microbalance (TEOM™). It should be noted that



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**TABLE 4-1. EPA-DESIGNATED REFERENCE AND EQUIVALENT METHODS FOR PM<sub>10</sub>**

Method No.	Identification	Description	Type	Date
RFPS-1087-062	Wedding & Associates <sup>a</sup> PM <sub>10</sub> Critical Flow High-Volume Sampler.	High-volume (1.13 m <sup>3</sup> /min) sampler with cyclone-type PM <sub>10</sub> inlet; 203 x 254 cm (8 x 10 in) filter.	Manual reference method	10/06/87
RFPS-1287-063	Sierra-Andersen <sup>b</sup> or General Metal Works <sup>c</sup> Model 1200 PM <sub>10</sub> High-Volume Air Sampler System	High-volume (1.13 m <sup>3</sup> /min) sampler with impaction-type PM <sub>10</sub> inlet; 203 x 254 cm (8 x 10 in) filter.	Manual reference method	12/01/87
RFPS-1287-064	Sierra-Andersen <sup>b</sup> or General Metal Works <sup>c</sup> Model 321-B PM <sub>10</sub> High-Volume Air Sampler System	High-volume (1.13 m <sup>3</sup> /min) sampler with impaction-type PM <sub>10</sub> inlet; 203 x 254 cm (8 x 10 in) filter. (No longer available.)	Manual reference method	12/01/87
RFPS-1287-065	Sierra-Andersen <sup>b</sup> or General Metal Works <sup>c</sup> Model 321-C PM <sub>10</sub> High-Volume Air Sampler System	High-volume (1.13 m <sup>3</sup> /min) sampler with impaction-type PM <sub>10</sub> inlet; 203 x 254 cm (8 x 10 in) filter. (No longer available.)	Manual reference method	12/01/87
RFPS-0389-071	Oregon DEQ Medium Volume PM <sub>10</sub> Sampler	Non-commercial medium-volume (110 L/min) sampler with impaction-type inlet and automatic filter change; two 47-mm diameter filters.	Manual reference method	3/24/89
RFPS-0789-073	Sierra-Andersen <sup>b</sup> Models SA241 or SA241M or General Metal Works <sup>c</sup> Models G241 and G241M PM <sub>10</sub> Dichotomous Samplers	Low-volume (16.7 L/min) sampler with impaction-type PM <sub>10</sub> inlet; additional particle size separation at 2.5 micron, collected on two 37-mm diameter filters.	Manual reference method	7/27/89
EQPM-0990-076	Andersen Instruments <sup>b</sup> Model FH62I-N PM <sub>10</sub> Beta Attenuation Monitor	Low-volume (16.7 L/min) PM <sub>10</sub> analyzers using impaction-type PM <sub>10</sub> inlet, 40 mm filter tape, and beta attenuation analysis.	Automated equivalent method	9/18/90
EQPM-1090-079	Rupprecht & Patashnick <sup>d</sup> TEOM Series 1400 and Series 1400a PM-10 Monitors	Low-volume (16.7 L/min) PM <sub>10</sub> analyzers using impaction-type PM <sub>10</sub> inlet, 12.7 mm diameter filter, and tapered element oscillating microbalance analysis.	Automated equivalent method	10/29/90

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**TABLE 4-1 (cont'd). EPA-DESIGNATED REFERENCE AND EQUIVALENT METHODS FOR PM<sub>10</sub>**

Method No.	Identification	Description	Type	Date
EQPM-0391-081	Wedding & Associates <sup>a</sup> PM <sub>10</sub> Beta Gauge Automated Particle Sampler	Low-volume (16.7 L/min) PM <sub>10</sub> analyzer using cyclone-type PM <sub>10</sub> inlet, 32 mm filter tape, and beta attenuation analysis.	Automated equivalent method	3/5/91
RFPS-0694-098	Rupprecht & Patashnick <sup>d</sup> Partisol Model 2000 Air Sampler	Low-volume (16.7 L/min) PM <sub>10</sub> sampler with impactation-type inlet and 47 mm diameter filter.	Manual reference method	7/11/94

4-42

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1 although these latter three automated PM<sub>10</sub> analyzers may be capable of providing continuous  
2 or semi-continuous PM<sub>10</sub> concentration measurements, only 24-h average PM<sub>10</sub>  
3 measurements are recognized as approved under their equivalent method designations.  
4

#### 5 **4.2.7 Determination of Size Distribution**

6 The determination of aerosol size distributions can be a powerful research tool when  
7 studying source contributions and transformation processes. A number of techniques are  
8 available as described by texts such as Willeke and Baron (1993) to make near real-time,  
9 single particle aerosol measurement in addition to cascade impactors.  
10

##### 11 **4.2.7.1 Cascade Impactors**

12 In cascade applications, the aerosol is impacted and trapped onto a series of removable,  
13 coated substrates (e.g., greased foils), including a final total stage collection on a filter for  
14 gravimetric analysis. Marple et al. (1993) list over 30 single stage and cascade impactors  
15 that are either commercially available or still commonly used. The design and calibration of  
16 a miniature eight-stage cascade impactor for personal air sampling in occupational settings is  
17 described by Rubow et al. (1987), operating at 2.0 lpm. Evaluations of the most commonly  
18 used cascade impactor systems have been reported by Vaughan (1989) for the Andersen MK1  
19 and MK2 7-stage cascade impactors, Marple et al. (1991) for the 10-stage Micro-Orifice  
20 Uniform Deposit Impactor (MOUDI), and Wang and John (1988) and Hillamo and  
21 Kauppinen (1991) for the 6-stage Berner, low pressure cascade impactor. The smallest  
22 particle stages of these impactors can have very small diameter jets and/or very low total  
23 pressures to achieve the sub-micron separations. The MOUDI impactor has 2000 holes on  
24 the lowest cutpoint stage. Raabe et al. (1988) describe an 8 stage cascade slit impactor with  
25 slowly rotating impactor drums instead of flat plates. This arrangement, in combination with  
26 a PIXIE analyzer, permitted aerodynamic sizing of elemental components, with temporal  
27 resolution. The skill and care required in the operation of cascade impactors suggests that  
28 they are research rather than routine samplers.

29 The importance of the aerosol calibration of a cascade impactor is illustrated by  
30 Vaughan (1989) in Figure 4-13, which compares the experimental data with the  
31 manufacturer's calibrations and indicates biases as large as 1.0  $\mu\text{m}$ . Marple et al. (1991)

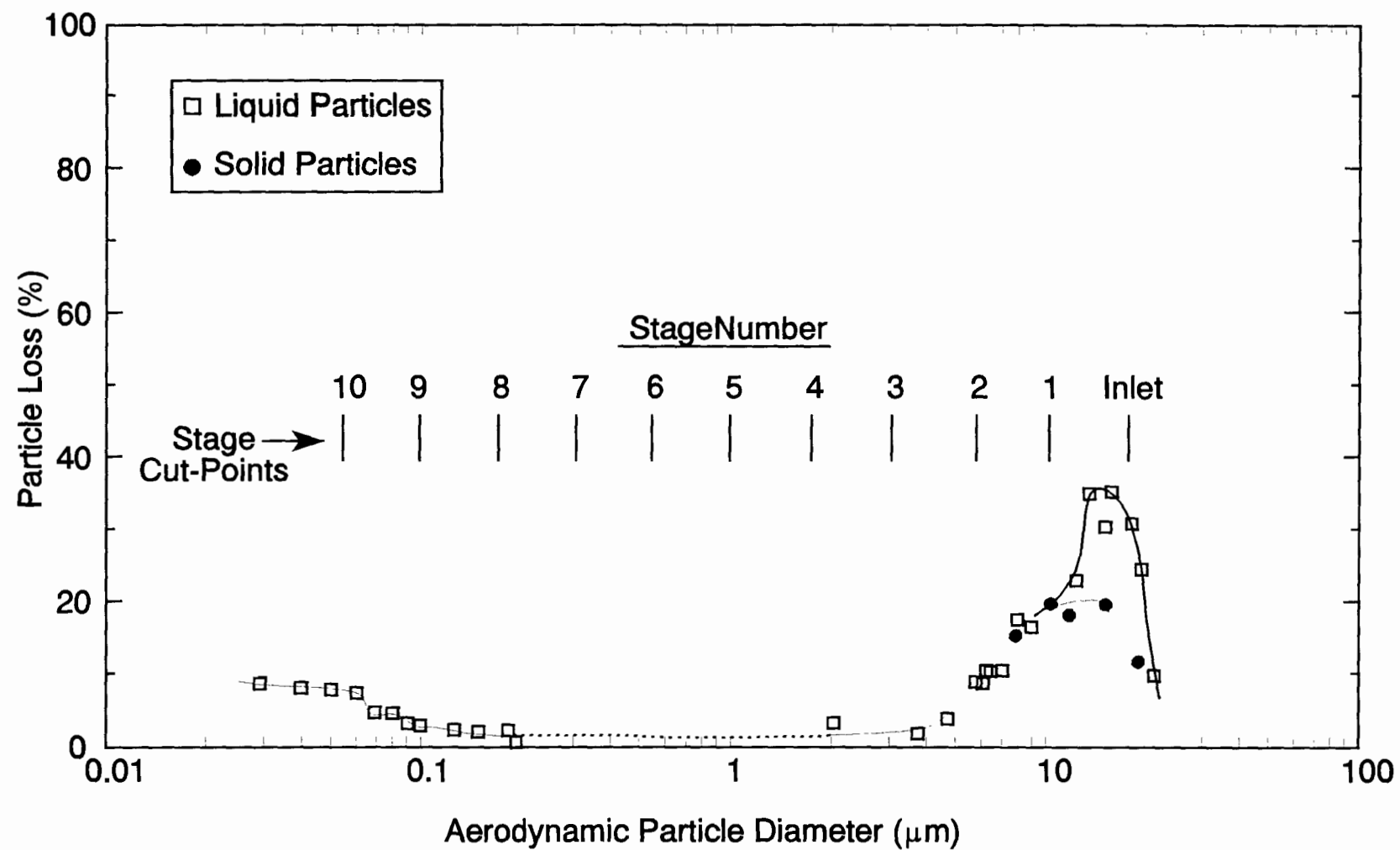


Figure 4-13. Aerosol calibration of a cascade impactor.

provided a similar type of stage calibration for the MOUDI impactor, and included data on the internal particle losses (see Figure 4-9). These loss data showed that an improperly designed inlet to the impactor, combined with the inertial and interception losses of the larger particle sizes, can substantially bias the first stage collections. This was also demonstrated for the inlet to the Andersen impactor by McFarland et al. (1977).

Cascade impactors can be used to construct distributions of mass and speciated constituents as a function of aerodynamic diameter. These distributions can be constructed graphically or using matrix inversion techniques (e.g., Crump and Seinfeld, 1982, Wolfenbarger and Seinfeld, 1990). Marple et al. (1993) notes that impactor stage calibrations which do not demonstrate sharp cutoffs can cause significant between-stage sizing errors if not accommodated. John et al. (1990) measured distributions over the 0.08 to 16  $\mu\text{m}$  range for mass and inorganic ions for several sites in Southern California. They identified the standard Coarse mode, and two separate and previously unreported modes in the 0.1 to 1.0  $\mu\text{m}$  range. This range was referred to by Whitby (1978) as a single "accumulation" mode. John et al. (1990) described a "condensation" mode at  $0.2 \pm 0.1 \mu\text{m}$  containing gas phase reaction products, and a "droplet" mode at  $0.7 \pm 0.2 \mu\text{m}$  which grows from the "condensation" mode by the addition of water and sulfates. Fang et al. (1991) described the effects of flow-induced relative humidity changes on the sizing of acid aerosols in the MOUDI impactor. They noted that it may not be possible to measure size distributions of small (less than about 0.2 to 0.5  $\mu\text{m}$ ) particles with impactors at relative humidities exceeding 80%.

#### **4.2.7.2 Single Particle Samplers**

Aerosol size distribution data are useful in studies of particle transport and transformation processes, source characterization, and particle sizing and collection device performance. In addition to cascade impactors, a number of real time or near real time sizing instruments are available and described in texts such as Willeke and Baron(1993). While cascade impactors provide distributions in terms of aerodynamically sized mass, single particle sampling devices can produce optically sized distributions as a function of particle number (count), with surface area and volume distributions computed during the data reduction, assuming spherical particles. Particle density and shape information as a function

1 of size are required to convert from volume distributions to an estimated mass basis.  
2 Individual particle sizing and counting instruments are generally limited to a particle  
3 detection range of a decade or so, but several devices can overlap to cover the range of  
4 approximately 0.001 to 10  $\mu\text{m}$ . The principle of detection of an instrument restricts the  
5 particle sizes which can be detected. For example, instruments using electrical mobility  
6 analysis are limited to particle sizes less than about 1  $\mu\text{m}$ . Optical methods are typically  
7 used to measure particles larger than about 0.1 to 0.3  $\mu\text{m}$ . Inlet and transport system losses  
8 of coarse particle above about 2  $\mu\text{m}$ , prior to the sensing volume, must be factored into  
9 reported size distributions.

10 The three most commonly used single particle sampler types are aerodynamic particle  
11 sizers, electrical mobility analyzers and optical particle counters (OPC's). Aerodynamic  
12 particle sizers use laser doppler anemometry to measure the velocity of particles in a jet.  
13 The acceleration of the particle is related to the aerodynamic particle diameter. This  
14 technique is typically applied to particles larger than about 0.5  $\mu\text{m}$ . In electrical mobility  
15 analysis, aerosol with a known charge distribution flows through an electric field. The  
16 particles migrate according to their mobility which can be related to size. The original TSI  
17 electrical aerosol analyzer (EAA) performed this separation in an integrated manner over the  
18 total size distribution and detected the particles by unipolar diffusion charging. A more  
19 versatile approach is the differential mobility analyzer, or DMA (Knutson and Whitby, 1975;  
20 Liu et al., 1978) is able examine a narrow slice of the size distribution in an equilibrium  
21 charge state, detected by a condensation nucleus counter (CNC). Differential mobility  
22 analyzers have been employed in pairs (Tandem Differential Mobility Analyzer, or TDMA)  
23 to examine particle characteristics such as  $\text{NH}_3$  and  $\text{H}_2\text{SO}_4$  reaction rates (McMurry et al.,  
24 1983), and the sensitivity of the size distributions of Los Angeles aerosol to relative humidity  
25 (McMurry and Stolzenburg, 1989). The latter research used the first DMA to select particles  
26 of known mobility from the input aerosol, a humidification system to condition the selected  
27 particles, and the second DMA to determine mobility changes. Optical particle counters pass  
28 a jet of aerosol through an optical system. Light scattered from individual particles is  
29 detected and the signal is processed in a multi-channel analyzer. Discrete signals are  
30 counted and sorted by intensity by optical size. An example forward-scattering counter with  
31 an open sensing volume (for use on aircraft), is the Particle Measuring Systems, Inc., FSSP-

300, which can provide high resolution (31 channel) count distributions over the size range of 0.3 to 20  $\mu\text{m}$  (Rader and O'Hern, 1993). Gebhart (1993) described currently available OPC's and their counting efficiencies over a range of diameters.

Single particle samplers have common considerations.

Calibration: They are calibrated with reference aerosol either by the manufacture or by the user. If the properties of the aerosol measured are quite different than the calibration, the indicated size distribution may be quite different than actual distribution. Brockman et al. (1988) demonstrated that the APS calibration can vary significantly with the type of test aerosol, and showed substantial response biases between oleic acid and polystyrene latex spheres above 10  $\mu\text{m}$ . Wang and John (1989) described a procedure to correct the APS response for aerosol particle density. Particle shape can also provide serious sizing errors, and specific calibrations are needed for particles with shape factors significantly different from unity (spherical). Yeh (1993) commented that the calculated geometric standard deviations ( $\sigma_g$ ) determined by the EAA and DMA are generally larger than 1.3, even if the correct value is significantly closer to unity. Woskie et al. (1993) observed, as did Willeke and Degarmo (1988), that optical particle counting devices must be appropriately calibrated using realistic aerosols, especially for low concentration applications. Harrison and Harrison (1982) suggested that the ratio of fine particle mass concentration to optical scattering extinction will be more variable when a significant contribution is made by irregular (shaped) particles - an event likely to occur when the mean mass diameter exceeds 1  $\mu\text{m}$ .

Particle Concentration Effects: Gebhart (1993) noted that the response of single particle counters may be influenced by extremely high particle concentrations. Wake (1989) and Heitbrink et al. (1991) described the coincidence problems of the APS when sampling high total particle concentrations, especially for sizes greater than 1  $\mu\text{m}$ . Baron et al. (1993) reported that the concentration levels giving 1% coincidence in an aerodynamic particle sizer for 0.8, 3 and 10  $\mu\text{m}$  particles, are the relatively low values of 558, 387 and 234 particles/ $\text{cm}^3$ , respectively. Optical particle counters experience coincidence errors (two particles are detected as a single particle) and counter saturation at high particle concentrations. Hinds and Kraske (1986) described the performance of the PMS, Inc. LAS-X and noted a sizing accuracy of  $\pm 2$  channel widths, and coincidence errors of less than

10% for concentrations below 10,000 particles/cm<sup>3</sup>. Clearly, typical particle concentrations found in the atmosphere may produce significant errors if sample dilution is not utilized.

#### 4.2.8 Automated Sampling

Automated methods to provide measures of aerosol concentrations in the air have existed for decades in an attempt to provide temporal definition of suspended particles with a minimum labor expense. Some of the automated samplers described in the 1982 Criteria Document (e.g., British Smoke Shade and AISI tape samplers), were indicator measures of aerosol concentration, using calibrations relating aerosol concentrations to reflected or absorbed light. Tape samplers were used in the U. S. primarily as exceedance (index) monitors.

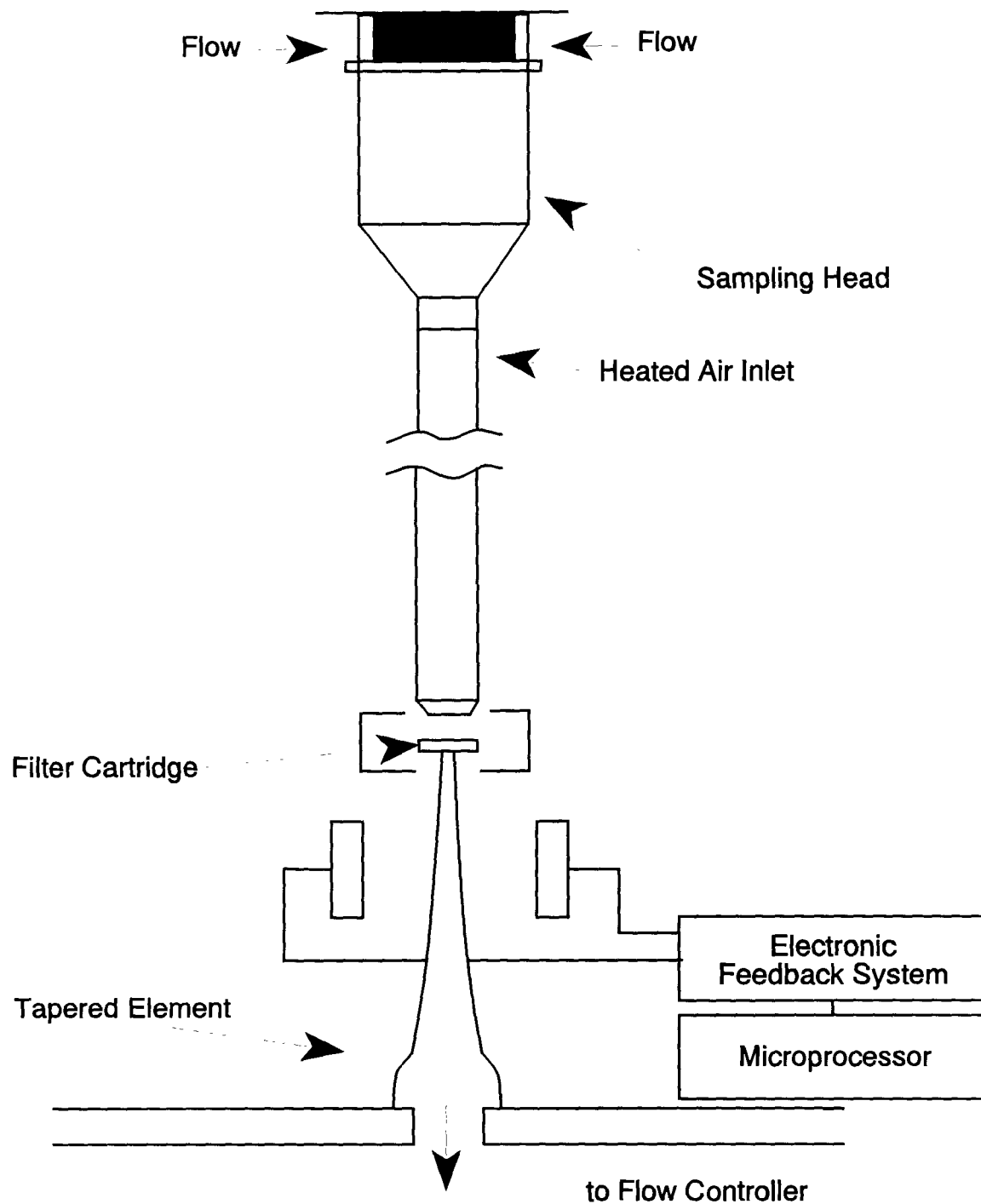
The beta attenuation and integrating nephelometer techniques were described in 1982 primarily as research methods. Refinements to the beta gauge sampling approach and the addition of the Tapered Element Oscillating Microbalance (TEOM) principle have resulted in their designation as equivalent methods for PM<sub>10</sub>.

Presently there are no commercially available, automated high volume (> 1 m<sup>3</sup>/min flowrate) aerosol samplers, excluding the possibility of the timed operation of an array of manual samplers. The physical size of such a sampling system using 8 x 10 inch filters is impractical. The dichotomous sampler is currently the only low volume, gravimetrically-based sampler, commercially available in an automated version.

##### 4.2.8.1 TEOM

The Tapered Element Oscillating Microbalance (R & P, Inc.) sensor was described by Patashnick and Rupprecht (1990), and consists of an oscillating tapered tube with a filter on its free end (see the diagram in Figure 4-14). The change in mass of the filter and collected aerosol produces a shift in the oscillation frequency of the tapered tube that can be directly related to mass. Rupprecht et al. (1992) suggested that the filter can be archived after sampling for subsequent analysis. The sampler inlet has a PM<sub>10</sub> cutpoint and operates at 16.67 lpm. A flow splitter samples a 3 lpm portion of this flow to be filtered. Since the fraction of volatile species (e.g., water, nitrates, organics) in the aerosol is a function of ambient temperature, the TEOM heats the inlet air stream to a constant 50 °C to keep





**Figure 4-14. TEOM**

- 1 moisture in the vapor phase. The mass transducer is also heated to 50 °C to stabilize the
- 2 measurement process. Operation with the flow stream heated to a lower temperature (e.g.,
- 3 30 °C) is possible, but care must be taken to avoid moisture condensation that will confound

1 the measurement. The transducer is also heated to 50 °C to stabilize the mass measurement.  
2 A factory calibration regression is used to electronically correct the computed mass from the  
3 TEOM to that measured by a reference PM<sub>10</sub> sampler.

4 As previously described, several researchers, including Cahill et al. (1994), Hering  
5 (1994) and Meyer et al. (1992) have reported that the modification of the aerosol by the  
6 elevated operating temperature appears to have a significant effect (loss) on mass  
7 concentration. Meyer et al. (1992) collocated a TEOM sampler with an PM<sub>10</sub> SA1200  
8 gravimetric sampler in Mammoth Lakes, CA during a winter heating season (heavy wood  
9 stove usage). The regressions between the TEOM and PM<sub>10</sub> sampler gave strong  
10 correlations ( $r^2 > 0.98$ ), with slopes of 0.55 for operation at 50 °C, and 0.66 for operation  
11 at 30 °C. The negative bias of the TEOM was attributed primarily to losses of semi-volatile  
12 organics from the filter. Cahill et al. (1994) reported that the TEOM showed biases on the  
13 order of 30% low and poor correlations with PM<sub>10</sub> samplers in dry, dusty conditions. The  
14 reasons for this discrepancy were unknown. The field comparison data of Patashnick and  
15 Rupprecht (1990) showed near unity ( $1 \pm 0.06$ ) regression slopes for the TEOM with the  
16 Wedding IP<sub>10</sub> and Sierra-Andersen dichotomous samplers in El Paso, TX and Birmingham,  
17 AL. Since aerosol composition is highly dependent on local sources and meteorology,  
18 volatilization losses could be expected to be site- and season-dependent. More data are  
19 needed to determine the implications of these problems on the ability of the TEOM to be  
20 used in a regulatory setting.

#### 21 22 **4.2.8.2 Beta Gauge**

23 The Andersen FH 62I-N beta attenuation sampler was described by Merrifield (1989)  
24 and uses a 30 mCi Krypton-85 source and detector to determine the attenuation caused by  
25 deposited aerosols on a filter (see diagram in Figure 4-15). To improve the stability over  
26 time, a reference reading is periodically made of a foil with an attenuation similar to that of  
27 the filter and collected aerosol. The Wedding beta attenuation sampler was described by  
28 Wedding and Weigand (1993) and uses a 100 mCi <sup>14</sup>C source. Both samplers have inlets  
29 with a PM<sub>10</sub> cutpoint, with the Andersen sampler operating at 16.67 lpm and the Wedding at  
30 18.9 lpm. The filter material is contained on a roll and advances automatically on a time  
31 sequence, or when a preset aerosol loading is reached. An automatic beta gauge sampler

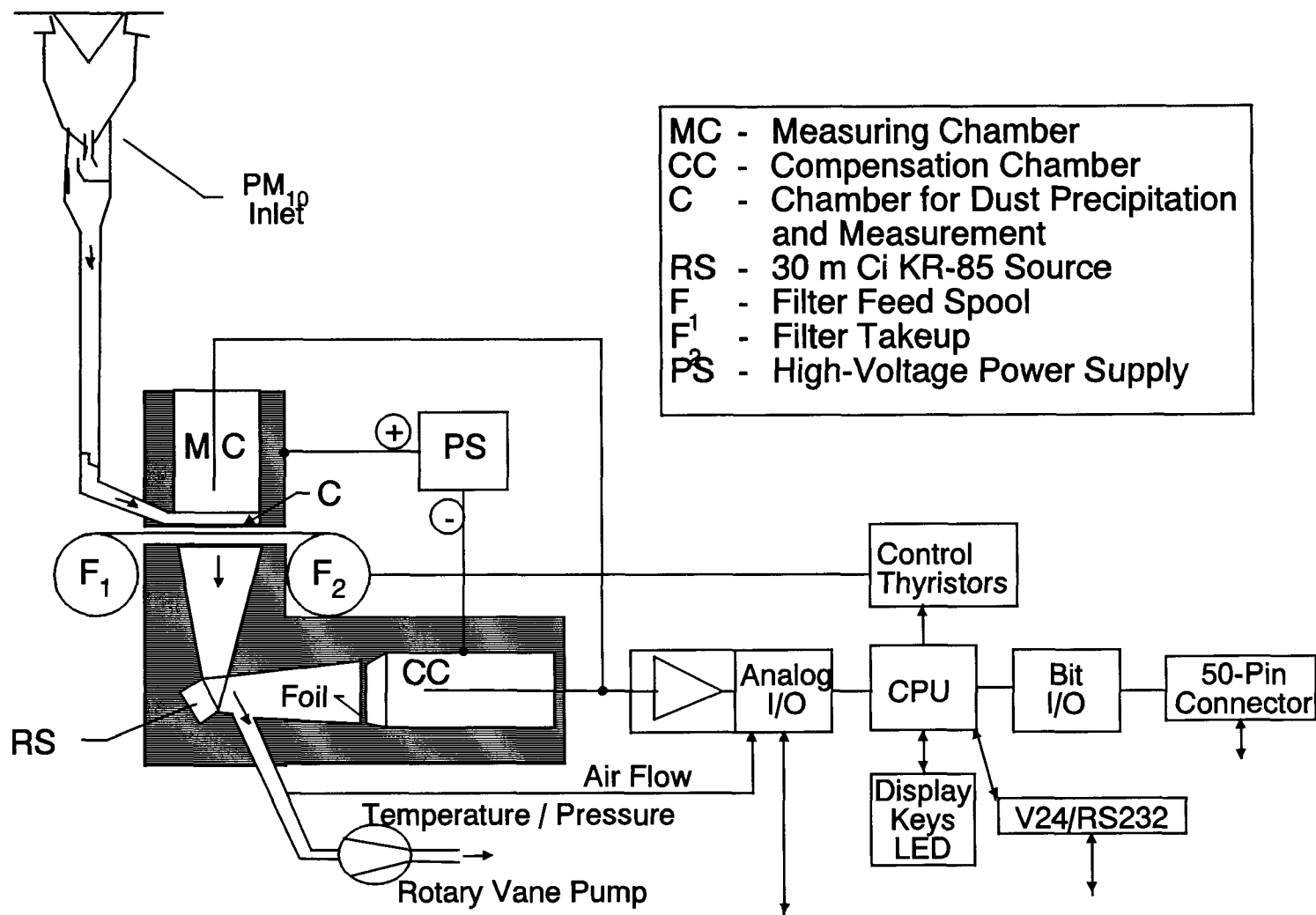


Figure 4-15. Beta gauge.

1 was also described by Spagnolo (1989), using a 15  $\mu\text{m}$  inlet and a  $^{14}\text{C}$  source. The  
2 calibration of a beta gauge is site specific, and a calibration regression must be processed  
3 electronically to provide accurate mass readings. Rupprecht et al. (1992) suggested that the  
4 closer link between deposited mass and frequency shift for the TEOM principle should  
5 provide less site-specific response, compared to the aerosol compositional sensitivity of the  
6 beta gauge technique.

7 Arnold et al. (1992) provided data over a 2 year period in Denver, CO for the mass  
8 concentration regression data from a Wedding beta gauge, showing a range of correlations  
9 ( $r^2$  from 0.72 to 0.86), varying by sampler and season. The authors suggested that  
10 installation of a newer technology beta gauge accounted for the higher correlations, but noted  
11 that unexplained outliers resulted in poorer than expected results. The regression slopes  
12 between the two sampler types showed that the beta gauge averaged 19% lower than a  
13 collocated Wedding  $\text{PM}_{10}$  gravimetric sampler. Field data from Wedding and Weigand  
14 (1993) at two sites (Fort Collins, CO and Cleveland, OH) using the same samplers produced  
15 regressions exhibiting strong correlations ( $r^2 = 0.99$ ) with no apparent outliers and a  
16 composite slope of 1.00. Arnold et al. (1992) operated the  $\text{PM}_{10}$  high volume samplers on  
17 the required every-6th-day schedule and the beta attenuation monitors continuously, and  
18 noted that only 22.5% of the exceedance days, as measured by the beta monitor, were  
19 operational days for the high volume samplers.

#### 21 4.2.8.3 Nephelometer

22 The integrating nephelometer is commonly used as a visibility monitor, measuring the  
23 light scattered by aerosols, integrated over as wide a range of angles as possible. A  
24 schematic diagram of the integrating nephelometer is shown in Figure 4-16 (from Hinds,  
25 1982). The measured scattering coefficient of particles,  $b_{\text{sp}}$ , can be summed with the  
26 absorption coefficient,  $b_{\text{ap}}$ , and the comparable coefficients for the gas phase, to compute the  
27 overall atmospheric extinction coefficient,  $b_{\text{ext}}$ . The atmospheric extinction has been related  
28 to visibility as visual range. The particle scattering coefficient is particle size dependent, as  
29 shown by Charlson et al. (1968) in Figure 4-17, while the absorption coefficient is relatively  
30 independent of size. The field calibration of nephelometers has historically been based on  
31 the refractive index of Freon-12 (and occasionally carbon dioxide), but newer calibration

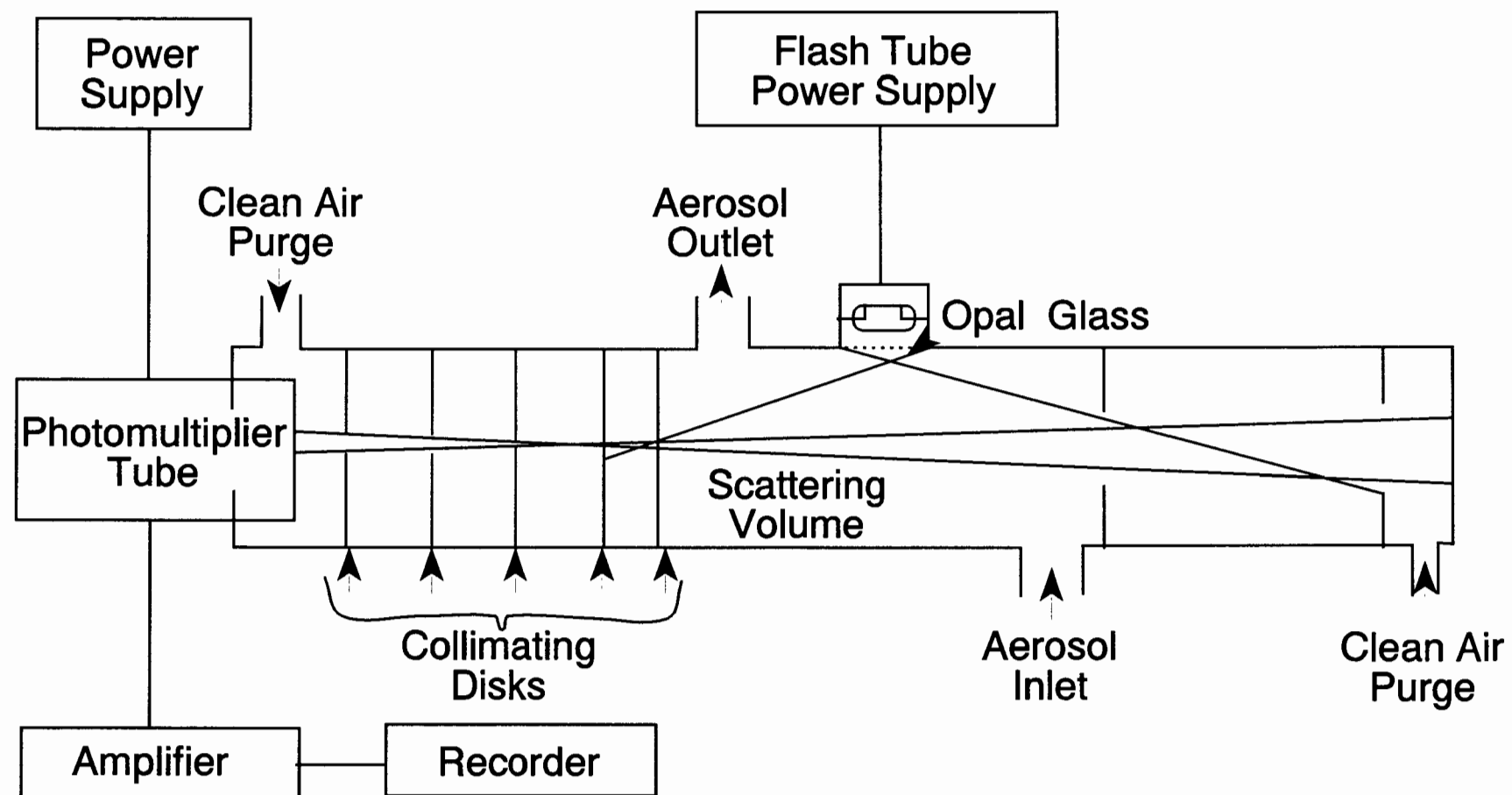


Figure 4-16. Integrating nephelometer.

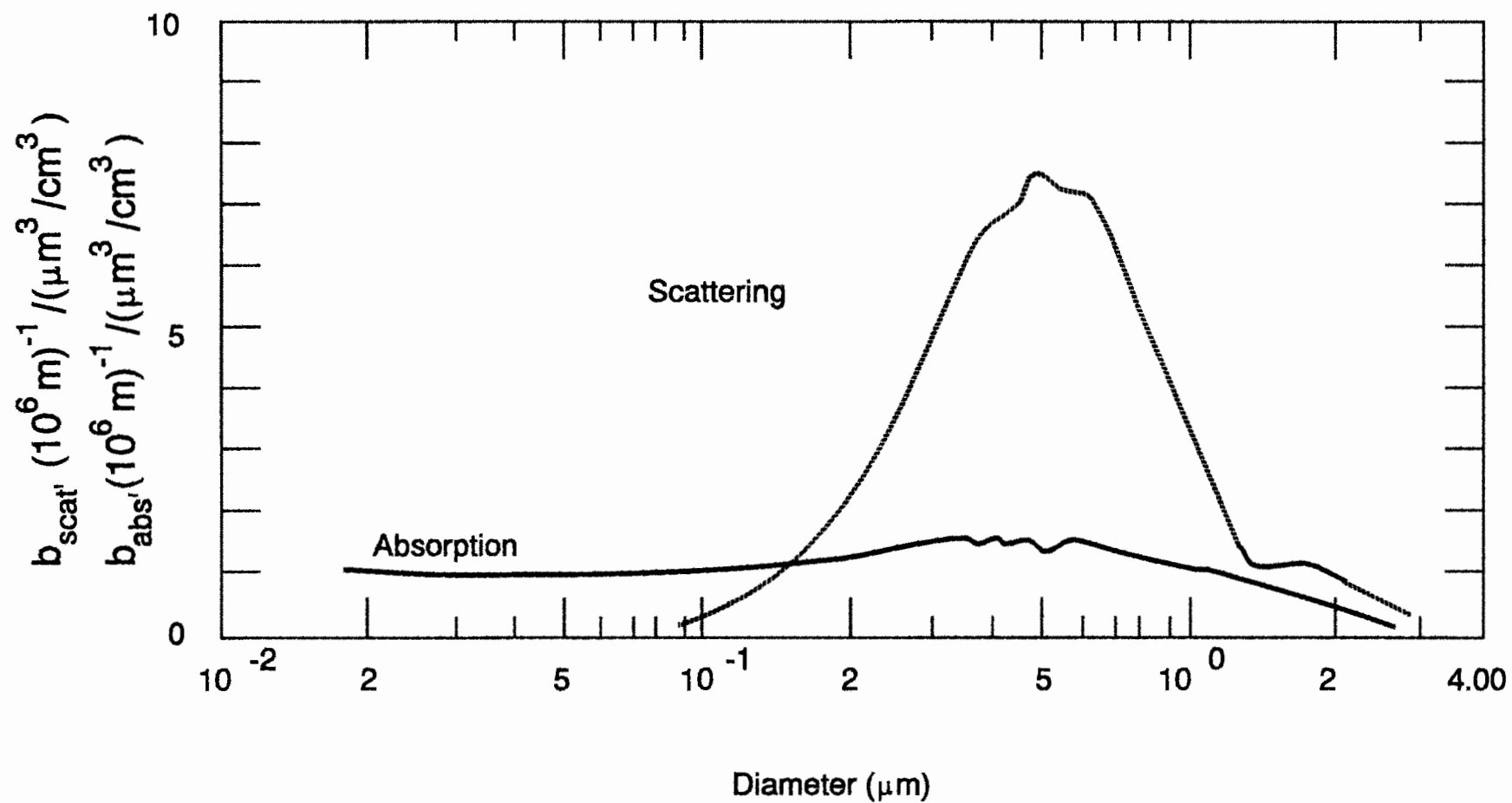


Figure 4-17. Particle-scattering coefficient as a function of particle size.

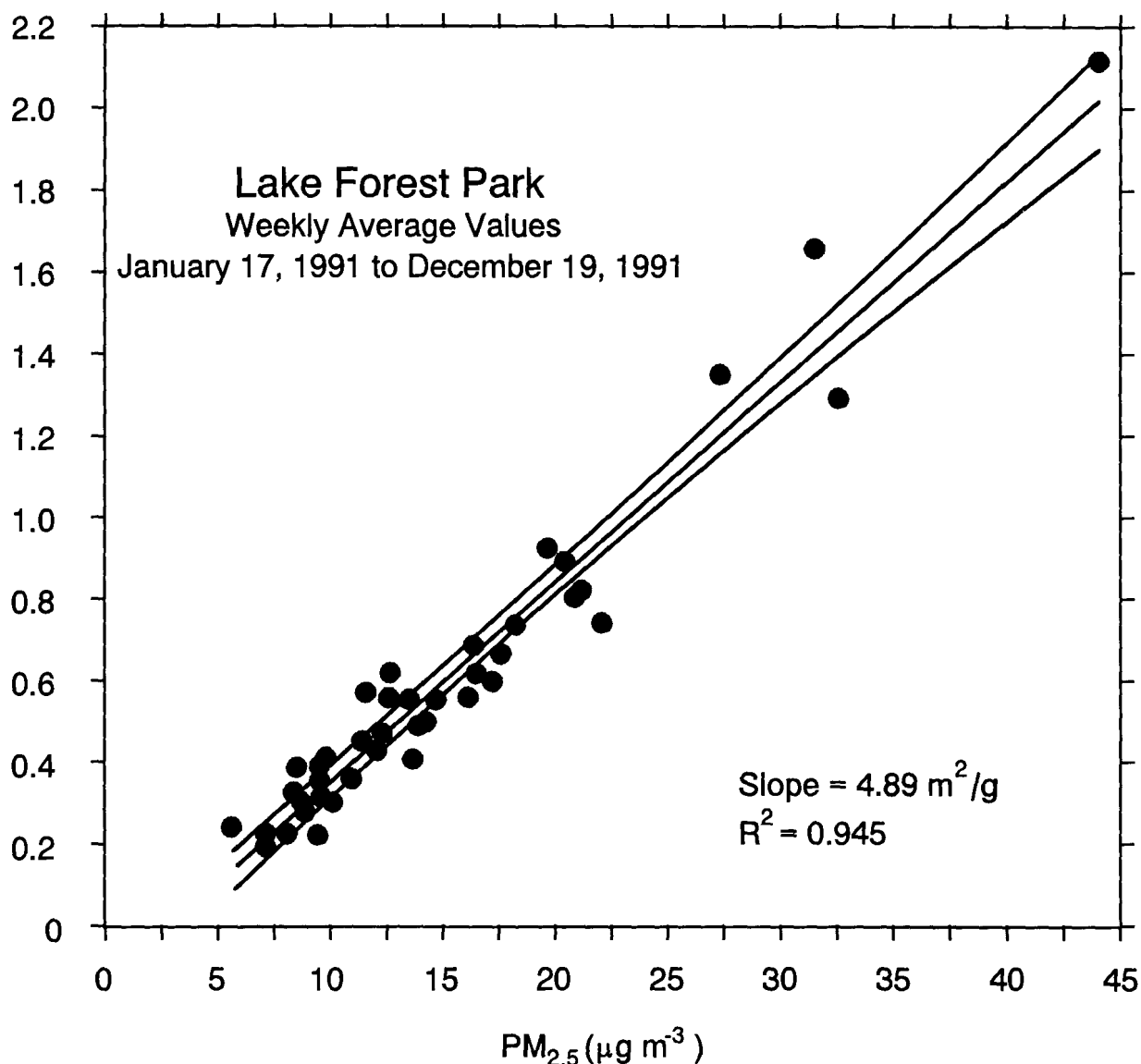
procedures using atomized sugar aerosols have been proposed (Horvath and Kaller, 1994) as more environmentally conscious. Another class of optical instruments which do not resolve the particle size spectrum, measure the laser light scattered from a volume of aerosol containing a number of particles. Gebhart (1993) described devices such as the MIE, Inc.<sup>11</sup>. MINIRAM, often used in portable applications to estimate real-time aerosol concentrations. Woskie et al. (1993) described the calibration and performance of a MINIRAM (using the manufacturer's calibration) against gravimetric borate concentrations, and found significant biases (a regression slope = 4.48).

The relative insensitivity of the nephelometer to particles above  $\sim 2 \mu\text{m}$  provides for poor correlations with  $\text{PM}_{10}$  mass. Larson et al. (1992) showed strong correlations ( $r^2 = 0.945$ ) between  $b_{\text{sp}}$  and Fine fraction mass (see Figure 4-19) for a woodsmoke impacted neighborhood near Seattle, WA, with a slope of  $4.89 \text{ m}^2/\text{g}$ . They noted that this slope fell within the range of values reported by others and was predicted by Mie scattering theory. The slope of the Larson et al. (1992) data could be compared with other site-specific calibrations, such as the data of Waggoner and Weiss (1980), which gave a composite slope of  $3.13 \text{ m}^2/\text{g}$ , characterized by the authors as representative of a "wide range" of sites. Lewis (1981) provided an analysis of the relationships of the features of the ambient size distribution to  $b_{\text{sp}}$ . The inlet air stream to the nephelometers for the latter data was heated from 5 to 15 °C above background. Rood et al. (1987) conducted a controlled comparison of the influence of aerosol properties on  $b_{\text{sp}}$  in Riverside, CA, and reported a regression slope against fine mass (defined as less than  $2.0 \mu\text{m}$ ) of  $2.1 \text{ m}^2/\text{g}$  with an  $r^2$  value of 0.92. In this experiment the relative humidity for  $b_{\text{sp}}$  determinations was controlled to less than 35% and the gravimetric filter substrate was nylon. They attributed the smaller than normal slope reading to possible nitrate evaporation from the filtered aerosol and artifact reactions with the nylon substrate material.

The data scatter in Figure 4-18 (if assumed to be typical of such comparisons) would suggest that fine particle mass concentration estimates from  $b_{\text{sp}}$  values were typically within 5 to  $7 \mu\text{g}/\text{m}^3$  of the gravimetrically determined values. To be useful as a surrogate measure for mass concentration, the site-specific nephelometer calibration should be valid for a wide range of situations, especially during episodes where the concentration levels approach or

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<sup>11</sup>Bedford, MA.



**Figure 4-18. Correlation of  $b_{sp}$  and fine fraction mass.**

1 exceed an action limit. The scattergram of  $b_{sp}$  versus fine particle mass provided by Rood  
 2 et al. (1987), showed much greater variability, with a given  $b_{sp}$  value providing an estimated  
 3 20 to 25  $\mu\text{g}/\text{m}^3$  concentration range. They noted that metastable  $\text{H}_2\text{O}$  contributed 5 to 20%  
 4 of the total particle light scattering coefficient, especially during the late afternoon and early  
 5 evening. The precisions and biases of the dependent and independent variables between  $b_{sp}$   
 6 and Fine mass concentration are not constants, since at least one factor - moisture content of  
 7 the aerosol - affects both measures. The gravimetric sample filters are typically equilibrated  
 8 to a specific relative humidity range (e.g., 40 to 60%) to normalize the tare weighings.



Sloane (1986) and others have noted that light scattering from particles is not solely a function of mass, but very dependent on a summation of the scattering coefficients of each specie. The scattering cross section of a particle is dependent on the water content, and hence the relative humidity in situ.. Pre-heating of the inlet air of the nephelometer normalizes the response to water content, but biases the reading relative to the in situ case. Sloane (1986) also gave the computed and measured scattering coefficients for ammonium sulfate, and noted that chemical interactions can cause a two-fold variation in scattering response to a change in the mass of hygroscopic constituents. It was also observed that the light scattering efficiency of an aerosol such as ammonium acid sulfate is not a constant, but varies with the overall aerosol composition. Eldering et al. (1994) developed and validated a predictive model for  $b_{sp}$  in Southern California. This model used composite size distributions constructed from a TSI, Inc.<sup>12</sup> EAA, a PMS, Inc.<sup>13</sup> LAS-X and a Climet, Inc.<sup>14</sup> multi-channel OPC, and filter-based estimates of refractive indices for ammonium sulfate, ammonium nitrate, organic carbon, elemental carbon and residual aerosol mass concentrations as independent variables. The quality of their comparisons with nephelometer data, suggested that this approach could be used to test models that predict visual range from source emissions. Further research is needed to determine the role of the integrating nephelometer as a predictor of Fine particle mass concentrations.

## 4.2.9 Specialized Sampling

### 4.2.9.1 Personal Exposure Sampling

The application of aerosol measurement technologies to smaller and less obtrusive samplers have resulted in devices used as fixed-location indoor aerosol samplers and personal exposure monitors (PEMs) worn on the body to estimate exposure. The reduction in physical size of personal aerosol sampling systems to reduce participant burden sometimes results in poorer aerosol collection performance as compared to the outdoor counterparts. Wiener and Rodes (1993) noted that personal sampling systems generally have poorer precisions than outdoor aerosol samplers, due to the smaller sampler collections (from lower

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<sup>12</sup>Minneapolis, MN.

<sup>13</sup>Boulder, CO.

<sup>14</sup>Redlands, CA.

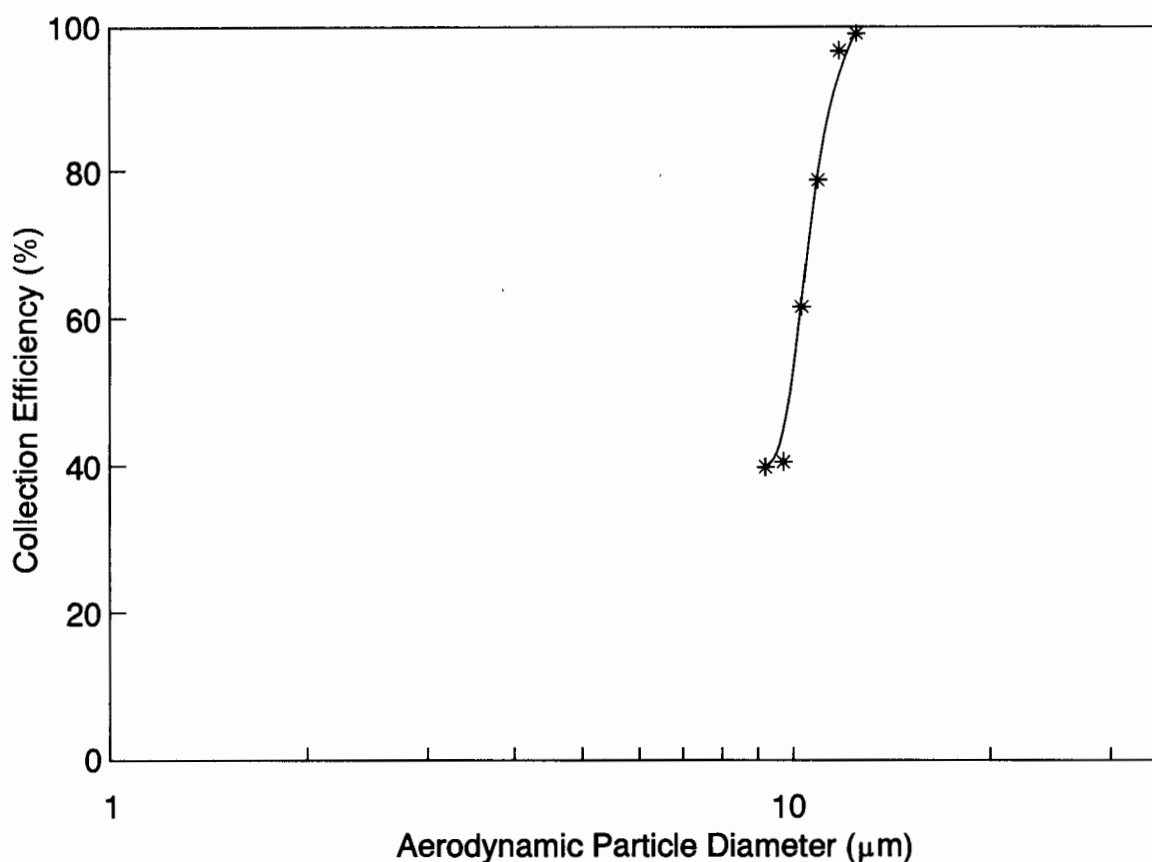
1 flowrates) and poorer flow controllers. Wallace (1994) reported biases for the Particle Total  
2 Exposure Assessment Methodology study averaging a factor of two between personal  
3 exposure measurements and fixed location PM<sub>10</sub> concentrations. He was unable to  
4 completely account for the biases, but attributed portions to proximity to indoor sources, a  
5 difference in inlet cutpoints (11.7 μm vs 10.0 μm) and the collection of aerosols from the  
6 “personal cloud” caused by body dander. Rodes et al. (1991) showed that the ratio of  
7 personal to indoor aerosol measurements for the EPA PTEAM study appeared to be log-  
8 normally distributed with a median value of 1.98 and an unexpectedly high value of 3.7 at  
9 the 90th (“most exposed”) percentile. Ingham and Yan (1994) suggested that the  
10 performance of a personal aerosol sampling inlet in an isolated mode (without mounting on a  
11 representative humanoid bluff body) can result in substantial under-sampling for larger  
12 particles. The relationship between measured aerosol exposure at some external location on  
13 the body and actual uptake through oral and nasal entry is very complex.

14 Buckley et al. (1991) described the collection efficiency of an MSP, Inc.<sup>15</sup> personal  
15 aerosol sampler at 4.0 lpm as shown in Figure 4-19. They evaluated this sampler in a field  
16 comparison study with collocated PM<sub>10</sub> high volume and dichotomous samplers. The  
17 precision for the personal sampler was found to be very good (CV = ±3.2%) with strong  
18 correlations (r<sup>2</sup> = 0.970) with the dichotomous samplers. Lioy et al. (1988) described a  
19 similar comparison for a 10 lpm Air Diagnostics and Engineering, Inc.<sup>16</sup> indoor air  
20 sampler, with a PM<sub>10</sub> inlet characterized by Marple et al. (1987). Correlations against the  
21 PM<sub>10</sub> dichotomous sampler were also described as very strong (r<sup>2</sup> > 0.970), but noted a  
22 substantial bias caused by the loss of fragments from indoor air sampler’s glass fiber filters.  
23 They recommended that exposure studies using samplers that collect small total volumes  
24 should utilize filters with greater integrity, such as Teflon. Colome et al. (1992) describe an  
25 indoor/outdoor sampling study using an impactor [characterized by Marple et al. (1987)] with  
26 a PM<sub>10</sub> cutpoint that had duplicate impactors with the same cutpoint in series. This  
27 sequential arrangement, in combination with a coating of 100 μl of light oil, was used to  
28 minimize particle bounce at 4.0 lpm for 24 h period.

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29 <sup>15</sup>Minneapolis, MN.

30 <sup>16</sup>Naples, ME.



**Figure 4-19. Collection efficiency of the MSP personal aerosol sampler.**

Personal aerosol sampler systems have typically been characterized as burdensome (excessive weight, size, noise). The success of passive detector badges for gaseous contaminants has recently prompted research into passive aerosol samplers. Brown et al. (1994) described a prototype aerosol sampler utilizing electrostatic charge to move the particles to a collection substrate. They noted that preliminary results are encouraging, but the effective sampling rate and size-selectivity of the sampler was dependent on the electrical mobility of the aerosol. This posed calibration problems for real aerosols with a distribution of electrical mobility's. Holländer (1992) described a passive pulsed-corona sampler that has similar collection characteristics as a PM<sub>10</sub> inlet, with only modest wind speed dependence.

The performance characterization of PEMs has been considered for occupational settings by Kenny and Lidén (1989), who reviewed the ACGIH, National Institute for Occupational Safety and Health (NIOSH), and EPA PM<sub>10</sub> aerosol sampler performance programs. They proposed that an international consensus be reached on the basic principles

underlying the experimental protocols for testing personal samplers, as an essential prerequisite to the setting of standards. An ISO working group has made progress in developing such a consensus (Kenny, 1992). As EPA becomes more focused on exposure assessment and personal exposure sampling, it will become even more important for the agency to consider establishing performance specifications for personal aerosol samplers.

Models have become powerful tools in understanding aerosol behavior in the vicinity of personal exposure samplers. This is demonstrated by particle trajectory models that can predict the influences of the geometries and flow field on aerosol capture and losses (e.g., Okazaki and Willeke, 1987, Ingham and Yan, 1994, and Tsai and Vincent, 1993). These models have not only permitted more rapid design changes to accommodate new cutpoints and flowrates, but have added insights as to the influence of air flow obstructions on sampling efficiencies. Vincent and Mark (1982) suggested that there is a critical particle trajectory that determines whether a particle is sampled or rejected by an inlet worn on the body. An extension of this model applicable to personal exposure sampling by Ingham and Yan (1994) suggested that testing the performance of a personal aerosol sampling inlet in an isolated mode (without mounting the inlet on a representative bluff body) can result in under-sampling for larger particles by a factor of two. Validation of this model may explain a portion of the bias reported by Wallace et al. (1994) between personal and indoor sampler measurements.

#### **4.2.9.2 Receptor Model Sampling**

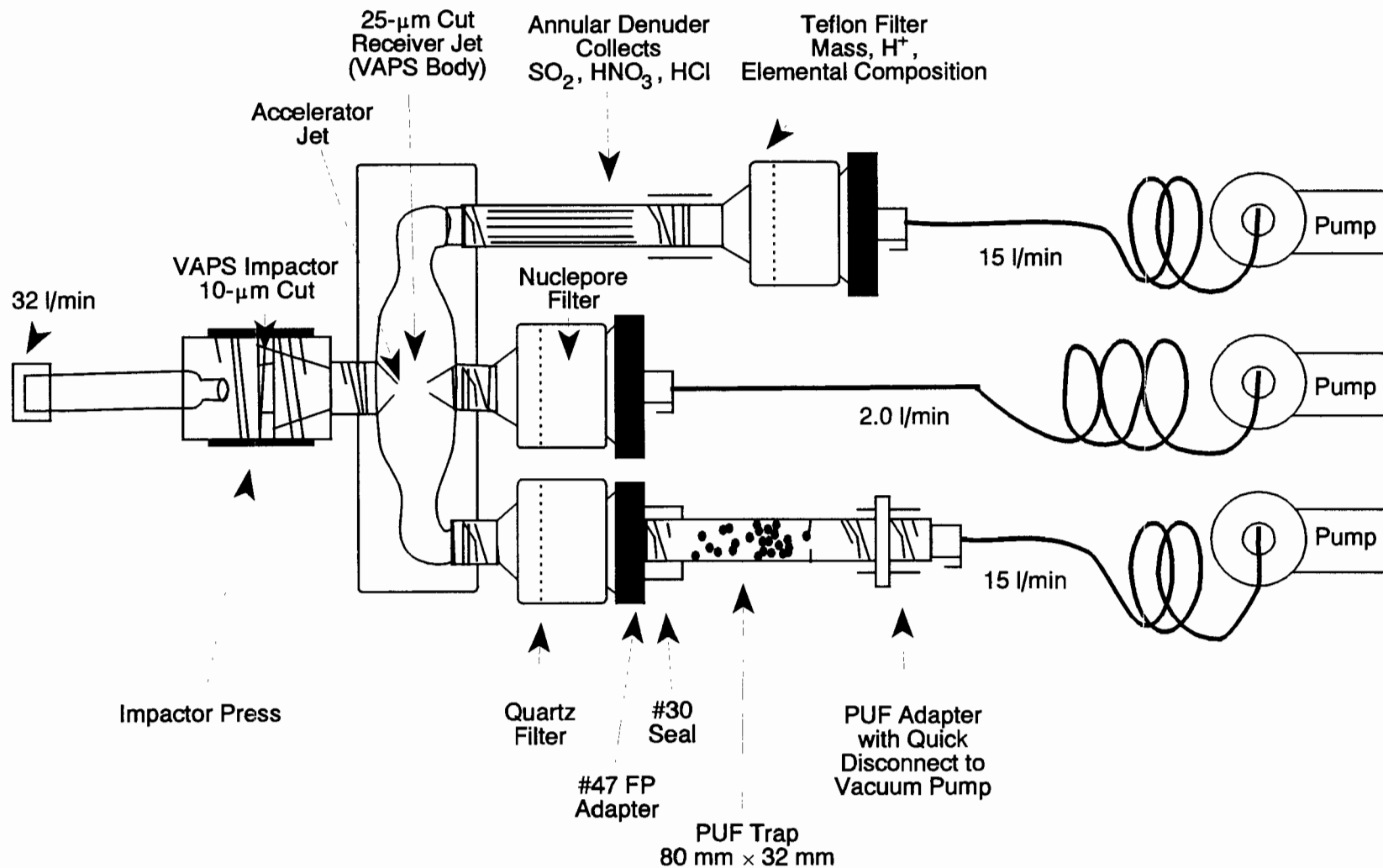
Receptor modeling has become an established tool to relate ambient concentrations of pollutants to major source categories, by apportioning the components in collected ambient aerosol samples using complimentary source “signatures”. Various approaches developed for constructing source/receptor relationships were described by Henry et al. (1984), who also provided a review of modeling fundamentals. They listed the advantages and disadvantages of multivariate models and discussed multi-collinearity problems associated with the presence of two or more sources with nearly identical signatures. Javitz et al. (1988) described the basic Chemical Mass Balance (CMB) approach and showed the influence of the variance in identifying a component in the source signature sample on the projected apportionment. Dzubay et al. (1984) described aerosol source and receptor collection schemes that permitted

the separation of ambient samples into Fine and Coarse fractions for mass, elemental and volatile carbon, and metals analyses. Stevens and Pace (1984) suggested the addition of Scanning Electron Microscopy to permit additional categorization using x-ray diffraction analysis. The most widely used aerosol receptor model is the EPA CMB 7.0 model described by Watson et al. (1990). This paper describes the structure of the model and computer code and the data requirements to evaluate the validity of the estimates. Numerous papers have been published describing the applications of receptor models to the apportionment of the sources of aerosols, with the receptor modeling conference summary by Watson et al. (1989) descriptive of the state-of-the-art.

Stevens et al. (1993) described (see Figure 4-20) a modified dichotomous sampler with a PM<sub>10</sub> inlet, two Fine channels operating at 15 lpm and one Coarse channel operating at 2.0 lpm, designated as the Versatile Air Pollution Sampler (VAPS). The additional Fine fraction channel permitted sampling on a 47 mm Teflon filter for elemental analysis and a 47 mm quartz filter for carbon speciation (elemental and volatile). A Nuclepore filter was used on the Coarse channel for Scanning Electron Microscopy (SEM) evaluation and energy dispersive x-ray diffraction analysis for selected particles.

#### **4.2.9.3 Particle Acidity**

An emphasis was placed on sampling sulfuric acidic aerosols in the 1982 Criteria Document. This was followed by a number of research efforts (e.g., Ferm, 1986; Koutrakis et al., 1988) to identify and study the in situ rate reactions, develop sampling strategies to representatively remove the acid particle from the air, identify the co-existing reactive species (e.g., ammonia, nitric acid aerosol, aerosol sulfates and nitrates), and protect the collected aerosol prior to analysis. A “Standard” and an “Enhanced” method were subsequently described (U.S. Environmental Protection Agency, 1992) for the determination of aerosol acidity using annular denuder technology. The “Standard” method did not account for potential interferences from nitric acid, ammonium nitrate aerosol, or other ammonium salts. The “Enhanced” method added an additional denuder prior to filtration, with nylon and treated glass fiber backup filters to account for these species. These sampling technologies utilized either an inlet impactor or a cyclone with 2.5 μm cutpoints to sample



**Figure 4-20. Modified dichotomous sampler (VAPS).**

the Fine fraction. This technology has recently been extended to other reactive aerosol systems, including semi-volatile organics (e.g., Vossler et al., 1988). Bennett et al. (1994) describe a PM<sub>2.5</sub> cyclone-based, filter pack sampling system designed fine particle network sampling and acidity measurements, as part of the Acid MODES program. The sampler operated at 8.8 lpm, and was designed to selectively remove ammonia, speciate gas and particle phase sulfur compounds, as well as collect gas phase nitric acid. An intercomparison of 18 nitric acid measurement methods was reported by Hering et al. (1988), who noted that measurements differed by as much as a factor of four and biases increased as nitric acid loadings increased. In general the filter pack systems reported the highest acidity measurements, while the denuder-difference techniques reported significantly lower measurements. Benner et al. (1991) in a comparison of the SCENES filter pack sampler with a denuder-based sampler found excellent agreement between sampler types for both nitric acid and total nitrates. They attributed the close agreement to limited positive artifact formations, since the test field site had high nitric acid gas to particulate nitrate ratios. John et al. (1988) noted that internal aluminum sampler surface denude nitric acid, and describe the design of an aluminum denuder for the inlet of a commercially available dichotomous sampler to quantitatively remove nitric acid for extended periods.

Brauer et al. (1989) describe the design of a miniature personal sampler to collect acid aerosols and gases. A significant finding was the lower than expected personal acidity levels, attributed to the "personal cloud" production of ammonia by the body. Personal exposure levels of acid aerosols were reported to be lower than indoor measurements.

#### **4.3 ANALYSIS OF PARTICULATE MATTER**

The interest in the composition of aerosol particles lies in the areas of: (1) explaining and inventorying the observed mass, (2) establishing the effect of aerosols on health and welfare, and (3) attributing ambient aerosols to pollution sources. While any compositional measurement will address one or more of these goals, certain methods excel for specific tasks. In general, no single method can measure all chemical species, and comprehensive aerosol characterization programs use a combination of methods to address complex needs. This allows each method to be optimized for its objective, rather than be compromised to

1 achieve goals unsuitable to the technique. Such programs also greatly aid quality assurance  
2 objectives, since confidence may be placed in the accuracy of a result when it is obtained by  
3 two or more methods on different substrates and independent samplers.

4 In the sections that follow, some of the more commonly used methods that address the  
5 goals state above are described. The sections are designed to be illustrative rather than  
6 exhaustive, since new methods are constantly appearing as old methods are being improved.  
7 These chemical analysis methods for the following section are divided into four categories:  
8 1) mass, 2) elements, 3) water-soluble ions, and 4) organics. Material balance comparing  
9 the sum of the chemical species to the PM mass concentrations show that elements, water  
10 soluble ions, and organic and elemental carbon typically explain 65 to 85% of the measured  
11 mass and are adequate to characterized the chemical composition of measured mass for filter  
12 samples collected in most urban and non-urban areas. Some of these chemical analysis  
13 methods are non-destructive, and these are preferred because they preserve the filter for  
14 other uses. Methods which require destruction of the filter are best performed on a section  
15 of the filter to save a portion of the filter of other analyses or as a quality control check on  
16 the same analysis method. Table 4-2 identifies the elements and chemical compounds  
17 commonly found in air using these methods with typical detection limits.

18 Less common analytical methods, which are applied to a small number of specially-  
19 taken samples, include isotopic abundances (Jackson, 1981; Currie, 1982; Hirose and  
20 Sugimura, 1984); mineral compounds (Davis, 1978, 1980; Schipper et al., 1993); and  
21 function groups (Mylonas et al., 1991; Palen et al., 1992; 1993; Allen et al., 1994). Recent  
22 advances in infrared optics and detectors have resulted in the quantitative determination of  
23 the major functional groups (e.g., sulfate, nitrate, aliphatic carbons, carbonyl carbons,  
24 organonitrates, and alcohols) in the atmospheric aerosol (Allen et al., 1994). The advantages  
25 of functional analysis in source apportionment are that the number of functional groups is  
26 much less than the number of organic compounds to be classified. The cited references  
27 provide information on sampling and analysis methods for these highly-specialized methods.

28 The following section focuses on:

- 29 • Physical analysis of elements and single particle size, shape, and composition,
- 30
- 31 • Wet chemical analysis of anions and cations, and



**TABLE 4.2. INSTRUMENTAL DETECTION LIMITS FOR  
PARTICLES ON FILTERS**

Minimum Detection Limit in ng/m <sup>3a</sup>									
Species	ICP/ AES <sup>b,d</sup>	AA Flame <sup>b,d</sup>	AA Furnace <sup>b</sup>	INAA <sup>b,f</sup>	PIXE <sup>g</sup>	XRF <sup>c</sup>	IC <sup>b</sup>	AC <sup>b</sup>	TOR <sup>b</sup>
Be	0.06	2 <sup>d</sup>	0.05	NA <sup>h</sup>	NA	NA	NA	NA	NA
Na	NA	0.2 <sup>d</sup>	< 0.05	2	60	NA	NA	NA	NA
Mg	0.02	0.3	0.004	300	20	NA	NA	NA	NA
Al	20	30	0.01	24	12	5	NA	NA	NA
Si	3	85	0.1	NA	9	3	NA	NA	NA
P	50	100,000	40	NA	8	3	NA	NA	NA
S	10	NA	NA	6,000	8	2	NA	NA	NA
Cl	NA	NA	NA	5	8	5	NA	NA	NA
K	NA	2 <sup>d</sup>	0.02	24	5	3	NA	NA	NA
Ca	0.04	1 <sup>d</sup>	0.05	94	4	2	NA	NA	NA
Sc	0.06	50	NA	0.001	NA	NA	NA	NA	NA
Ti	0.3	95	NA	65	3	2	NA	NA	NA
V	0.7	52	0.2	0.6	3	1	NA	NA	NA
Cr	2	2	0.01	0.2	2	1	NA	NA	NA
Mn	0.1	1	0.01	0.12	2	0.8	NA	NA	NA
Fe	0.5	4	0.02	4	2	0.7	NA	NA	NA
Co	1	6 <sup>d</sup>	0.02	0.02	NA	0.4	NA	NA	NA
Ni	2	5	0.1	NA	1	0.4	NA	NA	NA
Cu	0.3	4	0.02	30	1	0.5	NA	NA	NA
Zn	1	1	0.001	3	1	0.5	NA	NA	NA
Ga	42	52	NA	0.5	1	0.9	NA	NA	NA
As	50	100	0.2	0.2	1	0.8	NA	NA	NA
Se	25	100	0.5	0.06	1	0.6	NA	NA	NA
Br	NA	NA	NA	0.4	1	0.5	NA	NA	NA
Rb	NA	NA	NA	6	2	0.5	NA	NA	NA
Sr	0.03	4	0.2	18	2	0.5	NA	NA	NA
Y	0.1	300	NA	NA	NA	0.6	NA	NA	NA
Zr	0.6	1000	NA	NA	3	0.8	NA	NA	NA
Mo	5	31	0.02	NA	5	1	NA	NA	NA
Pd	42	10	NA	NA	NA	5	NA	NA	NA

**TABLE 4.2 (cont'd). INSTRUMENTAL DETECTION LIMITS FOR PARTICLES ON FILTERS**

Minimum Detection Limit in ng/m <sup>3a</sup>									
Species	ICP/ AES <sup>b,d</sup>	AA Flame <sup>b,d</sup>	AA Furnace <sup>b</sup>	INAA <sup>b,f</sup>	PIXE <sup>g</sup>	XRF <sup>c</sup>	IC <sup>b</sup>	AC <sup>b</sup>	TOR <sup>b</sup>
Ag	1	4	0.005	0.12	NA	6	NA	NA	NA
Cd	0.4	1	0.003	4	NA	6	NA	NA	NA
In	63	31	NA	0.006	NA	6	NA	NA	NA
Sn	21	31	0.2	NA	NA	8	NA	NA	NA
Sb	31	31	0.2	0.06	NA	9	NA	NA	NA
I	NA	NA	NA	1	NA	NA	NA	NA	NA
Cs	NA	NA	NA	0.03	NA	NA	NA	NA	NA
Ba	0.05	8 <sup>d</sup>	0.04	6	NA	25	NA	NA	NA
La	10	2,000	NA	0.05	NA	30	NA	NA	NA
Au	2.1	21	0.1	NA	NA	2	NA	NA	NA
Hg	26	500	21	NA	NA	1	NA	NA	NA
Tl	42	21	0.1	NA	NA	1	NA	NA	NA
Pb	10	10	0.05	NA	3	1	NA	NA	NA
Ce	52	NA	NA	0.06	NA	NA	NA	NA	NA
Sm	52	2,000	NA	0.01	NA	NA	NA	NA	NA
Eu	0.08	21	NA	0.006	NA	NA	NA	NA	NA
Hf	16	2,000	NA	0.01	NA	NA	NA	NA	NA
Ta	26	2,000	NA	0.02	NA	NA	NA	NA	NA
W	31	1,000	NA	0.2	NA	NA	NA	NA	NA
Th	63	NA	NA	0.01	NA	NA	NA	NA	NA
U	21	25,000	NA	NA	NA	1	NA	NA	NA
Cl <sup>-</sup>	NA	NA	NA	NA	NA	NA	50	NA	NA
NO <sub>3</sub> <sup>-</sup>	NA	NA	NA	NA	NA	NA	50	NA	NA
SO <sub>4</sub> <sup>=</sup>	NA	NA	NA	NA	NA	NA	50	NA	NA
NH <sub>4</sub> <sup>+</sup>	NA	NA	NA	NA	NA	NA	NA	50	NA

**TABLE 4.2 (cont'd). INSTRUMENTAL DETECTION LIMITS FOR PARTICLES ON FILTERS**

Species	Minimum Detection Limit in ng/m <sup>3a</sup>								
	ICP/ AES <sup>b,d</sup>	AA Flame <sup>b,d</sup>	AA Furnace <sup>b</sup>	INAA <sup>b,f</sup>	PIXE <sup>g</sup>	XRF <sup>c</sup>	IC <sup>b</sup>	AC <sup>b</sup>	TOR <sup>b</sup>
OC	NA	NA	NA	NA	NA	NA	NA	NA	100
EC	NA	NA	NA	NA	NA	NA	NA	NA	100

<sup>a</sup>Minimum detection limit is three times the standard deviation of the blank for a filter of 1 mg/cm<sup>2</sup> areal density.

ICP/AES = Inductively Coupled Plasma with Atomic Emission Spectroscopy.

AA = Atomic Absorption Spectrophotometry.

PIXE = Proton Induced X-ray Emissions Spectrometry.

XRF = Non-Dispersive X-ray Fluorescence Spectrometry.

INAA = Instrumental Neutron Activation Analysis.

IC = Ion Chromatography.

AC = Automated Colorimetry.

TOR = Thermal Optical Reflectance.

<sup>b</sup>Concentration is based on the extraction of 1/2 of a 47 mm quartz-fiber filter in 15 ml of deionized-distilled water, with a nominal flow rate of 20 L/min for 24-h samples.

<sup>c</sup>Concentration is based on 13.8 cm<sup>2</sup> deposit area for a 47 mm ringed teflon-membrane filter, with a nominal flow rate of 20 L/min for 24-h samples with 100 sec radiation time.

<sup>d</sup>Harman (1989).

<sup>e</sup>Fernandez (1989).

<sup>f</sup>Olmez (1989).

<sup>g</sup>Eldred (1993).

<sup>h</sup>Not Available.

- Organic analysis of organic compounds and elemental/organic carbon.

### 4.3.1 Mass Measurement Methods

Particulate mass concentration is the most commonly made measurement on aerosol samples. It is used to determine compliance with PM<sub>10</sub> standards and to select certain samples for more detailed, and more expensive, chemical analyses. As noted in Section 2, the beta attenuation and inertial microbalance methods have been incorporated into in situ measurement systems which acquire real-time mass measurements. Gravimetric analysis is used almost exclusively to obtain mass measurements of filters in a laboratory environment. U.S. Environmental Protection Agency (1976) and Watson et al. (1989a) have published detailed procedures for mass analyses associated with 20.32 cm × 25.40 cm fiber filters, but the guidance for other types of filters used for chemical analyses is less well documented.

1 Gravimetry measures the net mass on a filter by weighing the filter before and after  
2 sampling with a balance in a temperature- and relative humidity-controlled environment.  
3 PM<sub>10</sub> reference methods require that filters be equilibrated for 24 h at a constant (within  
4  $\pm 5\%$ ) relative humidity between 20 and 40% and at a constant (within  $\pm 3$  °C) temperature  
5 between 15 and 30 °C. These are intended to minimize the liquid water associated with  
6 soluble compounds and to minimize the loss of volatile species. Nominal values of 30% RH  
7 and 15 to 20 °C best conserve the particle deposits during sample weighing.

8 Balances used to weigh 20.32 cm  $\times$  25.40 cm filters from high volume PM<sub>10</sub> samples  
9 must have a sensitivity of at least 100  $\mu\text{g}$ . Balances used for medium volume PM<sub>10</sub> samples  
10 should have a sensitivity of at least 10  $\mu\text{g}$ , and those used for low-volume PM<sub>10</sub> samples  
11 should have a sensitivity of at least 1  $\mu\text{g}$ . Modifications to the balance chamber are  
12 sometimes needed to accommodate filters of different sizes. All filters, even those from  
13 high-volume PM<sub>10</sub> samplers, should be handled with gloved hands when subsequent chemical  
14 analyses are a possibility.

15 Balance calibrations should be established before and after each weighing session using  
16 Class M and Class S standards, and they should be verified with a standard mass every ten  
17 filters. Approximately one out of ten filters should be re-weighed by a different person at a  
18 later time. These re-weights should be used to calculate the precision of the measurement as  
19 outlined by Watson et al. (1989b).

20 Feeney et al. (1984) examined the gravimetric measurement of lightly loaded membrane  
21 filters and obtained excellent precision and accuracy. The sensitivity of the electrobalance is  
22 about  $\pm 0.001$  mg, though tolerances on re-weights of Teflon-membrane filters are typically  
23  $\pm 0.010$  mg. The main interference in gravimetric analysis of filters results from  
24 electrostatic effects. Engelbrecht et al. (1980) found that residual charge on a filter could  
25 produce an electrostatic interaction between the filter on the pan and the metal casing of the  
26 electrobalance. This charge can be removed by exposing the filter to a radioactive polonium  
27 source before and during sample weighing.

28 Beta attenuation methods have been applied in the laboratory as well as in the field, and  
29 the results are comparable to those of gravimetric measurements. The precision of  
30 beta-gauge measurements has been shown to be  $\pm 5$   $\mu\text{g}/\text{m}^3$  or better for counting intervals of  
31 one minute per sample, which translates into  $\pm 32$   $\mu\text{g}/\text{filter}$  for 37 mm diameter substrates.

This is substantially higher than the  $\pm 6 \mu\text{g}/\text{filter}$  precision determined by gravimetric analysis using an electrobalance (Feeney et al., 1984). Jaklevic et al. (1981) found equivalent accuracy and precision for both techniques as they were used in that study. Courtney et al. (1982) found beta attenuation and gravimetric mass measurements to differ by less than  $\pm 5\%$ . Patashnick and Rupprecht (1991) examine results from TEOM samplers operated alongside filter-based  $\text{PM}_{10}$  samplers and Barnes et al. (1988) and Shimp (1988) report comparisons with beta attenuation field monitors; these comparisons all show good agreement for mass measurements.

### 4.3.2 Physical Analysis

The most common interest in elemental composition derives from concerns about health effects and the utility of these elements to trace the sources of suspended particles. Instrumental neutron activation analysis (INAA), photon-induced x-ray fluorescence (XRF), particle-induced x-ray emission (PIXE), atomic absorption spectrophotometry (AAS), inductively-coupled plasma with atomic emission spectroscopy (ICP/AES), and scanning electron microscopy with x-ray fluorescence (SEM/XRF) have all been applied to elemental measurements of aerosol samples. AAS and ICP/AES are also appropriate for ion measurements when the particles are extracted in deionized-distilled water (DDW). Since air filters contain very small particle deposits ( $20$  to  $100 \mu\text{g}/\text{cm}^2$ ), preference is given to methods that can accommodate small sample sizes. XRF and PIXE leave the sample intact after analysis so that it can be submitted to additional examinations by other methods. Excellent agreement was found for the intercomparison of elements acquired from the XRF and PIXE analyses (Cahill, 1980). The analytical measurement specifications of air filter samples for the different elemental analysis is shown in Table 4.2.

#### 4.3.2.1 X-Ray Fluorescence (XRF) of Trace Elements

In x-ray fluorescence (XRF) (Dzubay and Stevens, 1975; Jaklevic et al., 1977; Torok and Van Grieken, 1994), the filter deposit is irradiated by high energy x-rays that eject inner shell electrons from the atoms of each element in the sample. When a higher energy electron drops into the vacant lower energy orbital, a fluorescent x-ray photon is released. The energy of this photon is unique to each element, and the number of photons is proportional to

the concentration of the element. Concentrations are quantified by comparing photon counts for a sample with those obtained from thin-film standards of known concentration.

Emitted x-rays with energies less than  $\approx 4$  KeV (affecting the elements sodium, magnesium, aluminum, silicon, phosphorus, sulfur, chlorine, and potassium) can be absorbed in the filter, in a thick particle deposit, or even by large particles in which these elements are contained. Very thick filters also scatter much of the excitation radiation or protons, thereby lowering the signal-to-noise ratio. For these reasons, thin membrane filters with deposits in the range of 10 to 50  $\mu\text{g}/\text{cm}^2$  provide the best accuracy and precision for XRF.

XRF methods can be broadly divided into two categories: wavelength dispersive x-ray fluorescence (WDXRF), which utilizes crystal diffraction for observation of fluorescent x-rays, and energy dispersive x-ray fluorescence (EDXRF), which uses a silicon semiconductor detector. The WDXRF method is characterized by high spectral resolution, which minimizes peak overlaps. It requires high power excitation to overcome low sensitivity, resulting in excessive sample heating and potential degradation. Conversely, EDXRF features high sensitivity but less spectral resolution, requiring complex spectral deconvolution procedures.

XRF methods can be further categorized as direct/filtered excitation, where the x-ray beam from the tube is optionally filtered and then focused directly on the sample, or secondary target excitation, where the beam is focused on a target of material selected to produce x-rays of the desired energy. The secondary fluorescent radiation is then used to excite the samples. The direct/filtered approach has the advantage of delivering higher incident radiation flux to the sample for a given x-ray tube power, since about 99% of the incident energy is lost in a secondary fluorescence. However, the secondary fluorescence approach, produces a more nearly monochromatic excitation that reduces unwanted scatter from the filter, thereby yielding better detection limits.

XRF is usually performed on Teflon-membrane filters for sodium, magnesium, aluminum, silicon, phosphorus, sulfur, chlorine, potassium, calcium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, gallium, arsenic, selenium, bromine, rubidium, strontium, yttrium, zirconium, molybdenum, palladium, silver, cadmium, indium, tin, antimony, barium, lanthanum, gold, mercury, thallium, lead, and uranium.

1 A typical XRF system is schematically illustrated in Figure 4-21. The x-ray output  
2 stability should be within  $\pm 0.25\%$  for any 8-h period within a 24-h duration. Typically,  
3 analyses are controlled, spectra are acquired, and elemental concentrations are calculated by  
4 software on a computer that is interfaced to the analyzer.

5 Separate XRF analyses are conducted on each sample to optimize detection limits for  
6 the specified elements. A comparison of the minimum detectable limits of Teflon-membrane  
7 and quartz-fiber filters is listed in Table 4-3. Figure 4-22 shows an example of an XRF  
8 spectrum.

9 Three types of XRF standards are used for calibration, performance testing, and  
10 auditing: 1) vacuum-deposited thin-film elements and compounds (Micromatter); 2) polymer  
11 films (Dzubay et al., 1981); and 3) National Institute of Science and Technology (NIST,  
12 formerly NBS) thin-glass films. The thin film standards cover the largest number of  
13 elements and are used to establish calibration curves, while the polymer film standards are  
14 used to verify the accuracy of the thin film standards. The NIST standards are used to  
15 validate the accuracy of the calibration curves. NIST produces the definitive standard  
16 reference materials, but these are only available for the species of aluminum, silicon,  
17 calcium, iron, cobalt, copper, manganese, and uranium (SRM 1832), and silicon, potassium,  
18 titanium, iron, zinc, and lead (SRM 1833). One or more separate Micromatter thin-film  
19 standards are used to calibrate the system for each element.

20 Sensitivity factors (number of x-ray counts per  $\mu\text{g}/\text{cm}^2$  of the element) are determined  
21 for each excitation condition. These factors are then adjusted for absorption of the incident  
22 and emitted radiation in the thin film. These sensitivity factors are plotted as a function of  
23 atomic number and a smooth curve is fitted to the experimental values. The calibration  
24 sensitivities are then read from these curves for the atomic numbers of each element in each  
25 excitation condition. NIST standards are analyzed on a periodic basis to verify the sensitivity  
26 factors. A multi-layer thin film standard prepared by Micromatter is analyzed with each set  
27 of samples to check the stability of the instrument response. When deviations from specified  
28 values are greater than  $\pm 5\%$ , the system should be re-calibrated.

29 The sensitivity factors are multiplied by the net peak intensities yielded by ambient  
30 samples to obtain the  $\mu\text{g}/\text{cm}^2$  deposit for each element. The net peak intensity is obtained

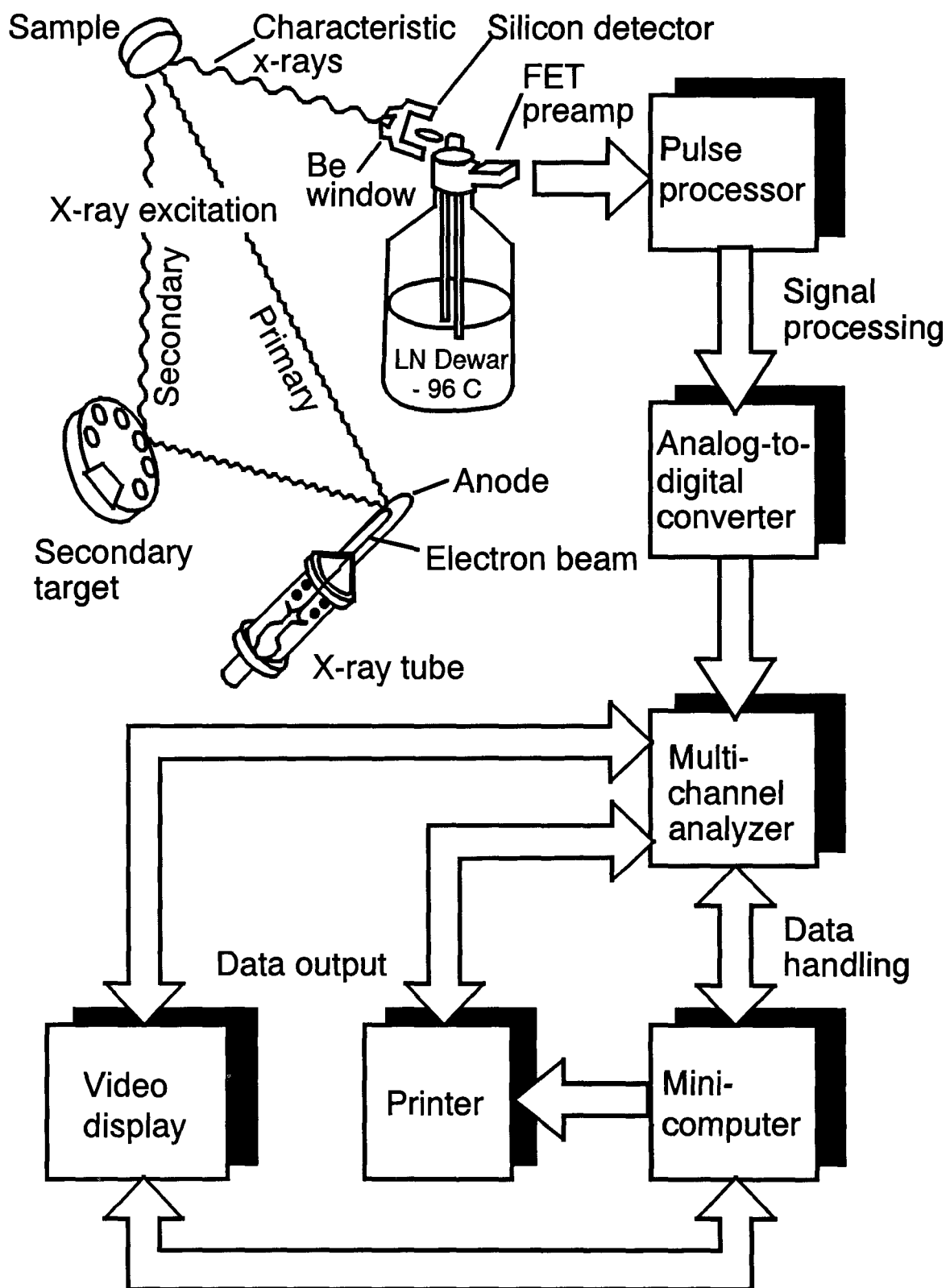


Figure 4-21. Schematic of a Typical X-Ray Fluorescence (XRF) System.



**TABLE 4-3. MINIMUM DETECTABLE LIMITS<sup>a</sup> FOR XRF ANALYSIS  
OF AIR FILTERS**

Element	Condition Number <sup>d</sup>	Quartz-Fiber Filter <sup>b</sup>	Teflon Membrane Filter <sup>c</sup>			
		Protocol QA- A ng/cm <sup>2</sup> <sup>e</sup>	Protocol A ng/cm <sup>2</sup> <sup>d</sup>	Protocol B ng/cm <sup>2</sup>	Protocol C ng/cm <sup>2</sup>	Protocol D ng/cm <sup>2</sup>
Al	5	NA <sup>f</sup>	10	7.2	3.6	2.5
Si	5	NA	6.3	4.4	2.2	1.4
P	5	NA	5.6	4.0	2.0	1.4
S	5	40 <sup>g</sup>	5.0	3.5	1.8	1.2
Cl	4	30	10	7.4	3.7	2.6
K	4	40	6.1	4.3	2.2	1.5
Ca	4	100	4.5	3.2	1.6	1.1
Ti	3	50	2.9	2.1	1.0	0.73
V	3	20	2.5	1.7	0.87	0.62
Cr	3	8	1.9	1.4	0.67	0.48
Mn	3	7	1.6	1.1	0.56	0.40
Fe	3	15	1.5	1.1	0.54	0.38
Co	3	5	0.88	0.62	0.31	0.22
Ni	3	4	0.89	0.63	0.31	0.22
Cu	3	4	1.1	0.76	0.38	0.27
Zn	3	6	1.1	0.76	0.38	0.27
Ga	2	8	1.9	1.4	0.68	0.48
As	2	9	1.6	1.1	0.56	0.39
Se	2	5	1.2	0.86	0.43	0.31
Br	2	5	1.0	0.72	0.36	0.25
Rb	2	5	1.0	0.68	0.34	0.24
Sr	2	8	1.1	0.78	0.39	0.28
Y	2	8	1.3	0.92	0.46	0.33
Zr	2	10	1.7	1.2	0.59	0.42
Mo	4	20	2.7	1.9	0.95	0.67
Pd	1	20	11	7.6	3.8	2.7
Ag	1	20	12	8.6	4.3	3.0
Cd	1	25	12	8.6	4.3	3.0
In	1	30	13	9.5	4.8	3.4

**TABLE 4-3. (cont'd) MINIMUM DETECTABLE LIMITS<sup>a</sup> FOR XRF ANALYSIS OF AIR FILTERS**

Element	Condition Number <sup>d</sup>	Quartz-Fiber Filter <sup>b</sup>	Teflon Membrane Filter <sup>c</sup>			
		Protocol QA-A ng/cm <sup>2</sup> <sup>e</sup>	Protocol A ng/cm <sup>2</sup> <sup>d</sup>	Protocol B ng/cm <sup>2</sup>	Protocol C ng/cm <sup>2</sup>	Protocol D ng/cm <sup>2</sup>
Sn	1	40	17	12	6.2	4.4
Sb	1	50	18	13	6.4	4.5
Ba	1	170	52	37	18	13
La	1	190	62	44	22	16
Au	2	NA	3.1	2.2	1.1	0.77
Hg	2	20	2.6	1.8	0.91	0.65
Tl	2	NA	2.5	1.8	0.88	0.62
Pb	2	14	3.0	2.2	1.1	0.76
U	2	NA	2.3	1.7	0.83	0.59

<sup>a</sup>MDL defined as three times the standard deviation of the blank for a filter of 1 mg/cm<sup>2</sup> areal density.

<sup>b</sup>Analysis times are 100 sec. for Conditions 1 and 4, and 400 sec. for Conditions 2 and 3. Actual MDL's for quartz filters vary from batch to batch due to elemental contamination variability.

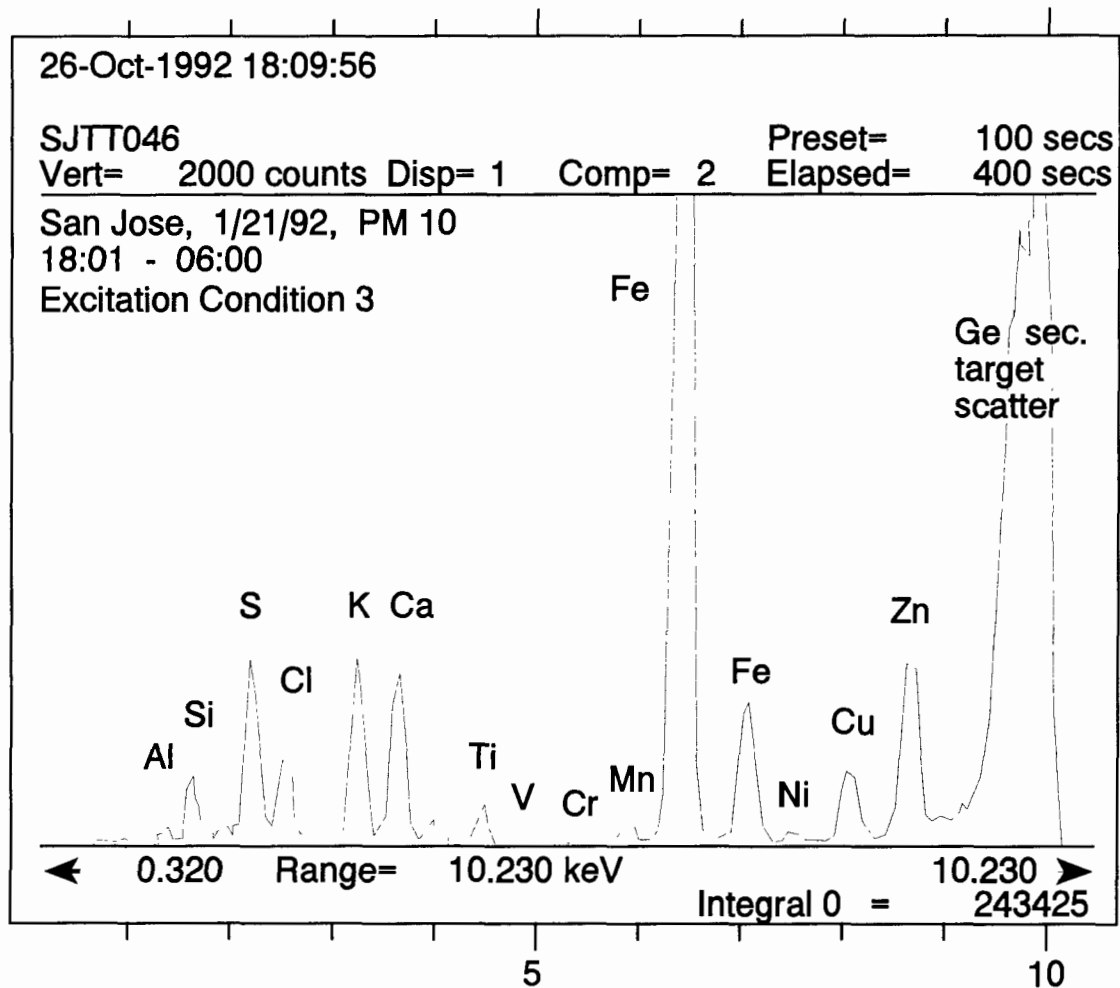
<sup>c</sup>Standard protocol, developed at the Desert Research Institute, University and Community College System of Nevada, Reno, NV, analysis times are 100 sec. for Conditions 1, 4 and 5, and 400 sec. for Conditions 2 and 3 for Protocol A; 200 sec. for Conditions 1, 4 and 5 and 800 sec. for Conditions 2 and 3 for Protocol B; 800 sec. for Conditions 1, 4 and 5 and 3,200 sec. for Conditions 2 and 3 for Protocol C; and 1600 sec. for Conditions 1, 4 and 5 and 6400 sec. for Conditions 2 and 3 for Protocol D.

<sup>d</sup>Condition 1 is direct mode excitation with a primary excitation filter of 0.15 mm thick Mo. Tube voltage is 50 KV and tube current is 0.6 mA. Condition 2 is direct mode excitation with a primary excitation filter of 0.13 mm thick Rh. Tube voltage is 35 KV and tube voltage is 2.0 mA. Condition 3 uses Ge secondary target excitation with the secondary excitation filtered by a Whatman 41 filter. Tube voltage is 30 KV and tube current is 3.3 mA. Condition 4 uses Ti secondary target excitation with the secondary excitation filtered by 3.8  $\mu$ m thick mylar film. Tube voltage is 30 KV and tube current is 3.3 mA. Condition 5 uses direct mode excitation with a primary excitation filter consisting of 3 layers of Whatman 41 filters. Tube voltage is 8 KV and tube current is 0.6 mA. Multi-channel analyzer energy range is 0 to 40 KeV for condition 1, 0 - 20 KeV for condition 2, and 0 to 10 KeV for conditions 3, 4, and 5.

<sup>e</sup>Typical exposed area is 406 cm<sup>2</sup> for standard high-volume filters; 6.4 cm<sup>2</sup> for 37 mm ringed Teflon-membrane filters; and 13.8 cm<sup>2</sup> for 47 mm ringed Teflon-membrane filters.

<sup>f</sup>Information not available.

<sup>g</sup>For condition 4.



**Figure 4-22. Example of an X-Ray Fluorescence (XRF) Spectrum.**

Source: Chow et al. (1990).

by: (1) subtracting background radiation; (2) subtracting spectral interferences; and  
(3) adjusting for x-ray absorption.

The elemental x-ray peaks reside on a background of radiation scattered from the sampling substrate. A model background is formed by averaging spectra obtained from several blank filters of the same type used in ambient sampling. It is important to retain blank filters for this purpose when XRF analysis is anticipated. This model background has the same shape and features of the sample spectra (minus the elemental peaks) if the deposit mass is small relative to the substrate mass (Russ, 1977). This model background is

1 normalized to an excitation radiation scatter peak, or the background areas of the spectrum  
2 that have no elemental peaks, in each sample spectrum to account for the difference in scatter  
3 intensity due to different masses.

4 The number and spacing of the characteristic x-ray lines relative to detector resolution  
5 are such that the peaks from one element can interfere with a peak from another element  
6 (Dzubay, 1986). A variety of methods has been used to subtract these peak overlaps (Arinc  
7 et al., 1977; Parkes et al., 1979; Drane et al., 1983), including least squares fitting to library  
8 spectra, Gaussian and other mathematical functions, and the use of peak overlap coefficients.

9 Peak overlap coefficients are applied to aerosol deposits. The most important of these  
10 overlaps are the K-beta to K-alpha overlaps of elements that increase in atomic number from  
11 potassium to zirconium, the lead L-alpha to arsenic K-alpha interference, and the lead M line  
12 to sulfur K line interference. The ratios of overlap peaks to the primary peak are determined  
13 from the thin film standards for each element for the spectral regions of the remaining  
14 elements. These ratios are multiplied by the net peak intensity of the primary peak and  
15 subtracted from the spectral regions of other elements.

16 The ability of an x-ray to penetrate matter depends on the energy of the x-ray and the  
17 composition and thickness of the material. In general, lower energy x-rays, characteristic of  
18 light elements, are absorbed in matter to a much greater degree than higher energy x-rays.  
19 XRF analysis of air particulate samples has had widest application to samples collected on  
20 membrane-type filters such as Teflon- or polycarbonate-membrane filter substrates. These  
21 membrane filters collect the deposit on their surfaces, which eliminates biases due to  
22 absorption of x-rays by the filter material. These filters also have a low areal density which  
23 minimizes the scatter of incident x-rays, and their inherent trace element content is very low.

24 Quartz-fiber filters used for high-volume aerosol sampling do not exhibit these features.  
25 As noted earlier, blank elemental concentrations in quartz-fiber filters that have not  
26 undergone acceptance testing can be several orders of magnitude higher than the  
27 concentrations in the particulate deposits. The concentrations vary substantially among the  
28 different types of quartz-fiber filters, and even within the same filter type and manufacturing  
29 lot. Blank impurity concentrations and their variabilities decrease the precision of  
30 background subtraction from the XRF spectral data, resulting in higher detection limits.  
31 Impurities observed in various types of glass- and quartz-fiber filters include aluminum,

1 silicon, sulfur, chlorine, potassium, calcium, iron, nickel, copper, zinc, rubidium, strontium,  
2 molybdenum, barium, and lead. Concentrations for aluminum, silicon, phosphorus, sulfur,  
3 and chlorine cannot be determined for quartz-fiber filters because of the large silicon content  
4 of the filters.

5 Quartz-fiber filters also trap particles within the filter matrix, rather than on the  
6 surface. This causes absorption of x-rays within the filter fibers yielding lower  
7 concentrations than would otherwise be measured. The magnitude of this absorption  
8 increases exponentially as the atomic number of the measured element decreases, and varies  
9 from sample to sample. Absorption factors generally are "1.2" or less for iron and heavier  
10 elements, but can be from "2" to "5" for sulfur.

11 Quartz-fiber filters are much thicker than membrane filters resulting in an increased  
12 scattering of x-rays and a consequent increase in background and degradation of detection  
13 limits. The increased x-ray scatter also overloads the x-ray detector which requires samples  
14 to be analyzed at a lowered x-ray intensity. These effects alone can result in degradation of  
15 detection limits by up to a factor of 10 with respect to Teflon-membrane substrates.

16 Larger particles collected during aerosol sampling have sufficient size to cause  
17 absorption of x-rays within the particles. Attenuation factors for fine particles ( $PM_{2.5}$ ,  
18 particles with aerodynamic diameters equal to or less than  $2.5\ \mu m$ ) are generally negligible  
19 (Criss, 1976), even for the lightest elements, but these attenuations can be significant for  
20 coarse fraction particles (particles with aerodynamic diameters from  $2.5$  to  $10\ \mu m$ ).  
21 Correction factors for XRF have been derived using the theory of Dzuby and Nelson (1975)  
22 and should be applied to coarse particle measurements.

23 During XRF analysis, filters are removed from their Petri slides and placed with their  
24 deposit sides down into filter cassettes. These cassettes are loaded into a mechanism that  
25 exposes the filter deposits to x-rays. The sample chamber is evacuated and a computer  
26 program controls the positioning of the samples and the excitation conditions. The vacuum in  
27 the x-ray chamber and the heat induced by the absorption of x-rays can cause certain  
28 materials to volatilize. Therefore, labile species such as nitrate and organic carbon are better  
29 measured on a quartz-fiber filter that samples simultaneously with the Teflon-membrane  
30 filter.

Quality control standards and replicates from previous batches should be analyzed for every 10 to 20 samples. When quality control results differ from specifications by more than  $\pm 5\%$ , or if the replicate concentrations differ from the original values (assuming they are at least 10 times detection limits) by more than  $\pm 10\%$ , the samples should be re-analyzed.

#### **4.3.2.2 Particle Induced X-Ray Emission (PIXE) of Trace Elements**

Particle Induced X-Ray Emission (PIXE) is another form of elemental analysis based on the characteristics of x-rays and the nature of x-ray detection (Cahill et al., 1975; 1987; 1989; 1993; Cahill, 1990). PIXE uses beams of energetic ions, consisting of protons at an energy level of 2 to 5 MeV, to create inner electron shell vacancies. As inner electron shell atomic vacancies are filled by outer electrons, the emitted characteristics of x-rays can be detected by wavelength dispersion, which is scattering from a crystal, or by energy dispersion, which involves direct conversion of x-rays. The development of focusing energetic proton beams (proton microprobes) has expanded the application of PIXE from environmental and biological sciences to geology and material sciences. Figure 4-23 illustrates a typical PIXE setup in a thin target mode (Cahill, 1989). PIXE analysis is often used for impactor samples or small filter substrates, since proton beams can be focused to a small area with no loss of sensitivity (Cahill, 1993).

Very thick filters or thick particle deposits on filter substrates scatter the excitation protons and lower the signal-to-noise ratio for PIXE. X-ray analysis methods, such as PIXE and XRF, require particle size diameter corrections (for low atomic number targets) associated with a spherical particle of a given diameter (typically particles with aerodynamic diameters  $> 2.5 \mu\text{m}$ ), and compositions typical in ambient aerosol studies. These analyses also require correction for sample loadings that reflect the passage of x-rays through a uniform deposit layer. Procedures for instrument calibration, spectrum process, and quality assurance are similar to those documented in Section 4.3.1.2 for XRF.

PIXE analysis can provide one of the widest range of elements in a single analysis, since x-ray results require two or three separate anodes. Attempts to improve sensitivity of PIXE analysis may result in damage to Teflon-membrane filters, however. Recent developments (Malm et al., 1994) using PIXE analysis at moderate sensitivity plus single

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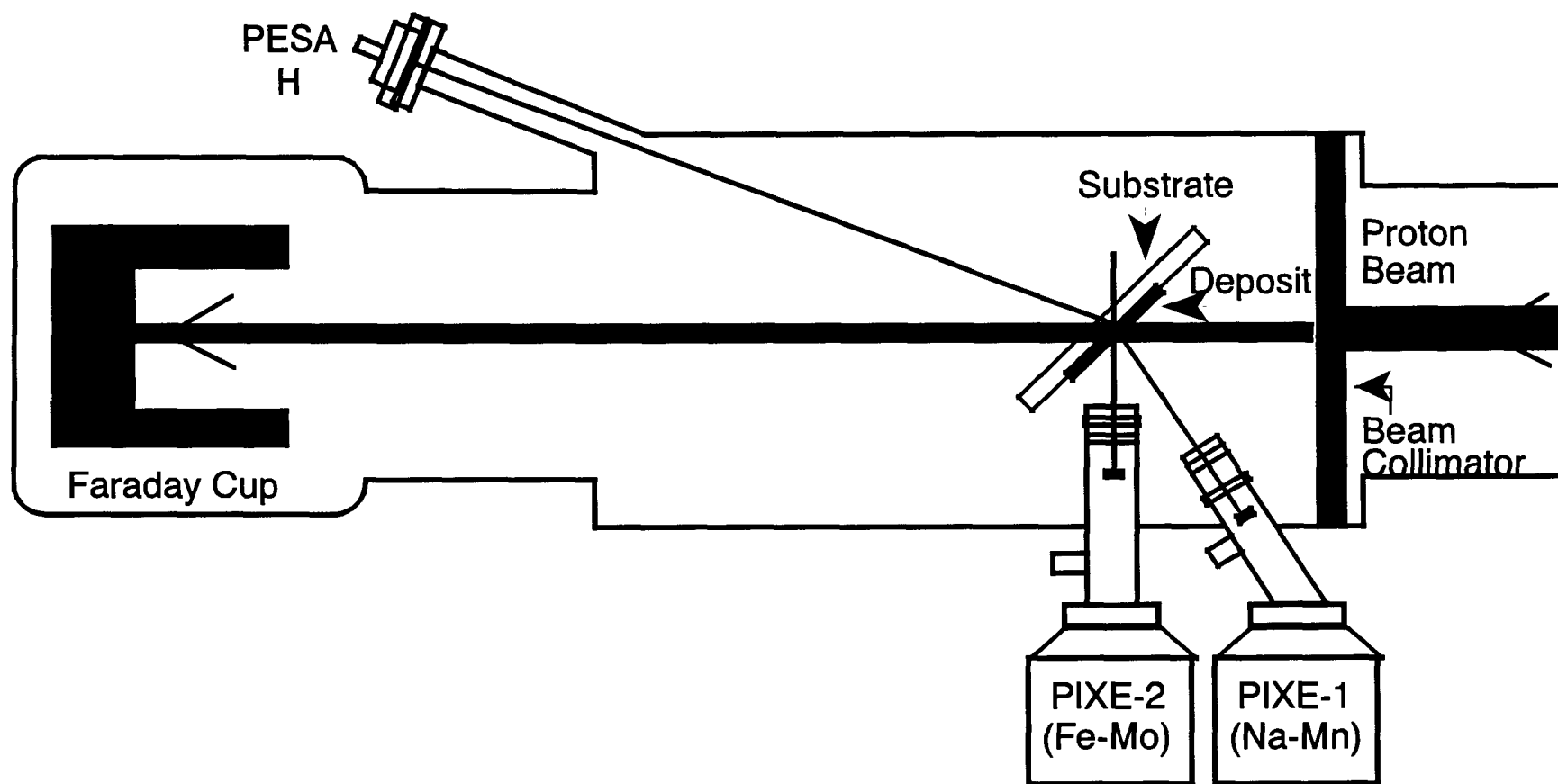


Figure 4-23. Schematic of a PIXE/PESA Analysis System.

anode XRF analysis at high sensitivity for transition/heavy metals have achieved the minimum detectable limits of less than 0.01 ng/m<sup>3</sup>. With the addition of hydrogen analysis (a surrogate for organic matter), almost all gravimetric mass concentrations can be explained (Cahill, 1987).

XRF and PIXE are the most commonly used elemental analysis methods owing to its nondestructive multi-element capabilities, relatively low cost, high detection limits, and preservation of the filter for additional analyses. XRF sometimes needs to be supplemented with INAA when extremely low detection limits are needed, but the high cost of INAA precludes this method from being applied to large numbers of samples. AAS is a good alternative for water-soluble species, especially for low atomic number. ICP/AES analysis is a viable alternative, but it is less desirable because of the sample extraction elements such as sodium and magnesium, but it requires large dilution factors to measure many different elements expense and the destruction of the filter.

#### **4.3.2.3 Instrumental Neutron Activation Analysis of Trace Elements**

Instrumental neutron activation analysis (INAA) (Dams et al., 1970; Zoller and Gordon, 1970; Olmez, 1989; Ondov and Divita, 1990), irradiated the thin membrane filter sample in the core of a nuclear reactor for periods ranging from a few minutes to several hours. Bombardment of the sample with neutrons induces a nuclear reaction of the stable isotopes in the sample. The energies of the gamma rays emitted by the decay of this induced radioactivity are used to identify them, and therefore, their parents. With the use of prepared elemental standards, the amount of parent element in the sample can be determined since the intensity of these gamma rays are proportional to their number.

The gamma-ray spectra of radioactive species are usually collected with a high resolution germanium detector utilizing commercially available amplifiers and multi-channel analyzers. Typical detector efficiencies range from 10 to 40% relative to a 3 × 3 in. sodium iodide detector. Detector system resolution, measured as the full-width at half-maximum for Table 4-4, the 1,332 KeV gamma-ray peak of <sup>60</sup>Co, should be less than 2.3 KeV in order to provide adequate resolution between isotopes of neighboring energies.



**TABLE 4-4. INAA COUNTING SCHEME AND ELEMENTS MEASURED**

Counting Period	Irradiation Time	Cooling Time	Counting Time	Elements Measured
Short-Lived 1	10 min	5 min	5 min	Mg, Al, S, Ca, Ti, V, Cu
Short-Lived 2		20 min	20 min	Na, Mg, Cl, K, Ca, Mn, Zn, Ga, Br, Sr, In, I, Ba
Long-Lived 1	4-6 h	3-4 days	6-8 h	Na, K, Ga, As, Br, Mo, Cd, Sb, La, Nd, Sm, Yb, Lu, W, Au, U
Long-Lived 2		30 days	12-24 h	Sc, Cr, Fe, Co, Zn, Se, Sr, Ag, Sb, Cs, Ba, Ce, Nd, Eu, Gd, Tb, Lu, Hf, Ta, Th

1 In order to obtain a full suite of elemental analysis results (often over 40 elements),  
2 multiple counting periods and irradiations are performed on the same sample (e.g., two  
3 irradiations would produce elements separated into short- and long-lived decay products).  
4 An example of the elements determined from multiple irradiations and counting periods, and  
5 the irradiation, cooling, and counting times used for ambient particulate samples collected on  
6 Teflon-membrane filter material is summarized in Table 4-4 (Divita, 1993). These  
7 irradiations were performed at the 20-MW NIST Research Reactor operated at 15-MW  
8 (neutron flux of  $7.7 \times 10^{13}$  and  $2.7 \times 10^{13}$  neutron/cm<sup>2</sup> × s). Typical gamma-ray spectra  
9 resulting from the counting scheme described in Table 4-4 are shown in Figures 4-24  
10 and 4-25.

11 The power of INAA is that it is not generally subject to interferences like XRF or  
12 PIXE due to a much better ratio of gamma ray peak widths to total spectral width, by a  
13 factor of about 20. INAA does not quantify some of the abundant species in ambient  
14 particulate matter such as silicon, nickel, tin, cadmin, mercury, and lead. While INAA is  
15 technically nondestructive, sample preparation involves folding the samples tightly and  
16 sealing it in plastic, and the irradiation process makes the filter membrane brittle and  
17 radioactive. These factors limit the use of the sample for subsequent analyses by other  
18 methods. The technique also suffers from the fact that a nuclear reactor is usually used as a

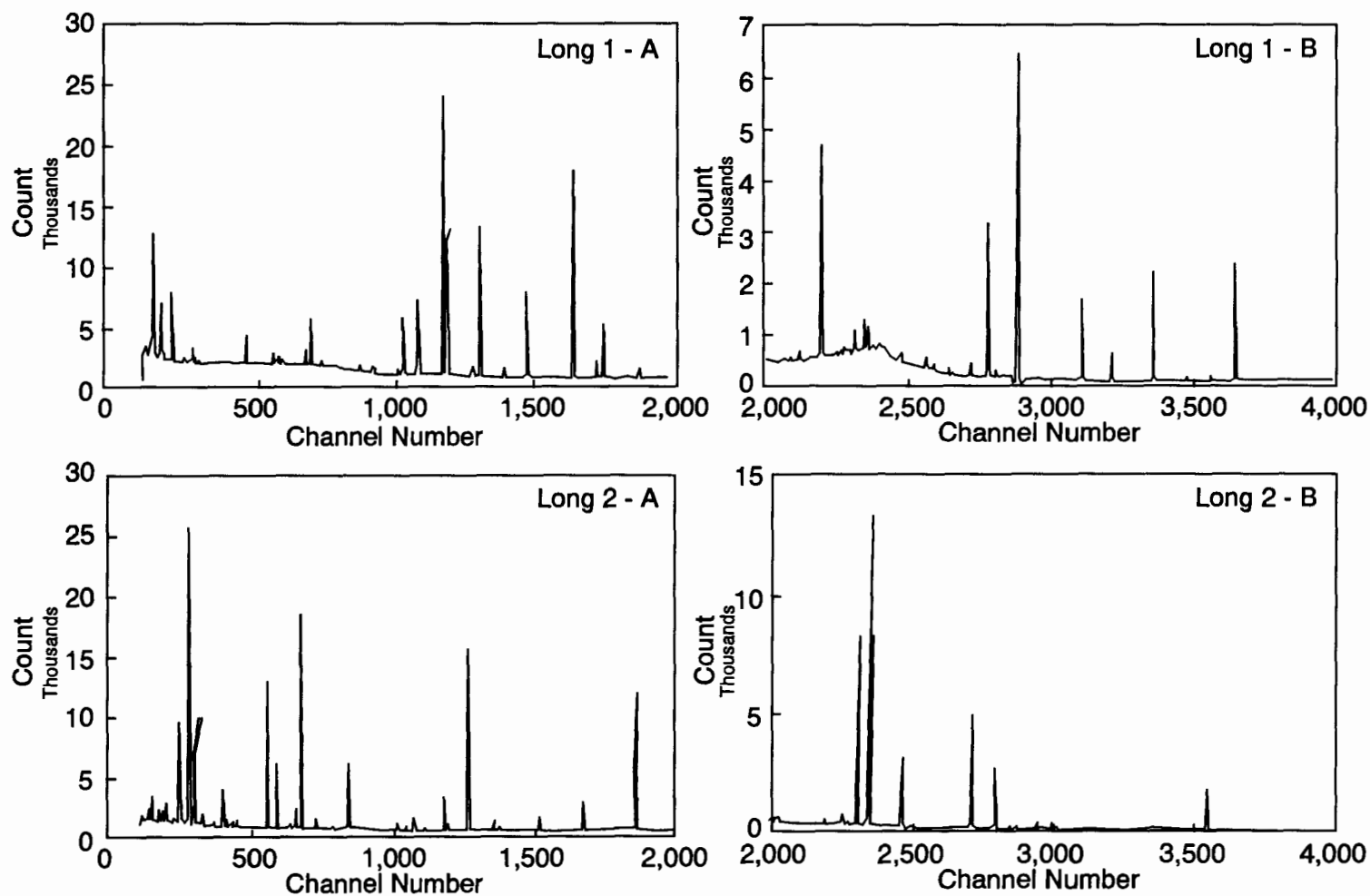


Figure 4-24. Typical Gamma-Ray Spectra Observed for Long Counts.

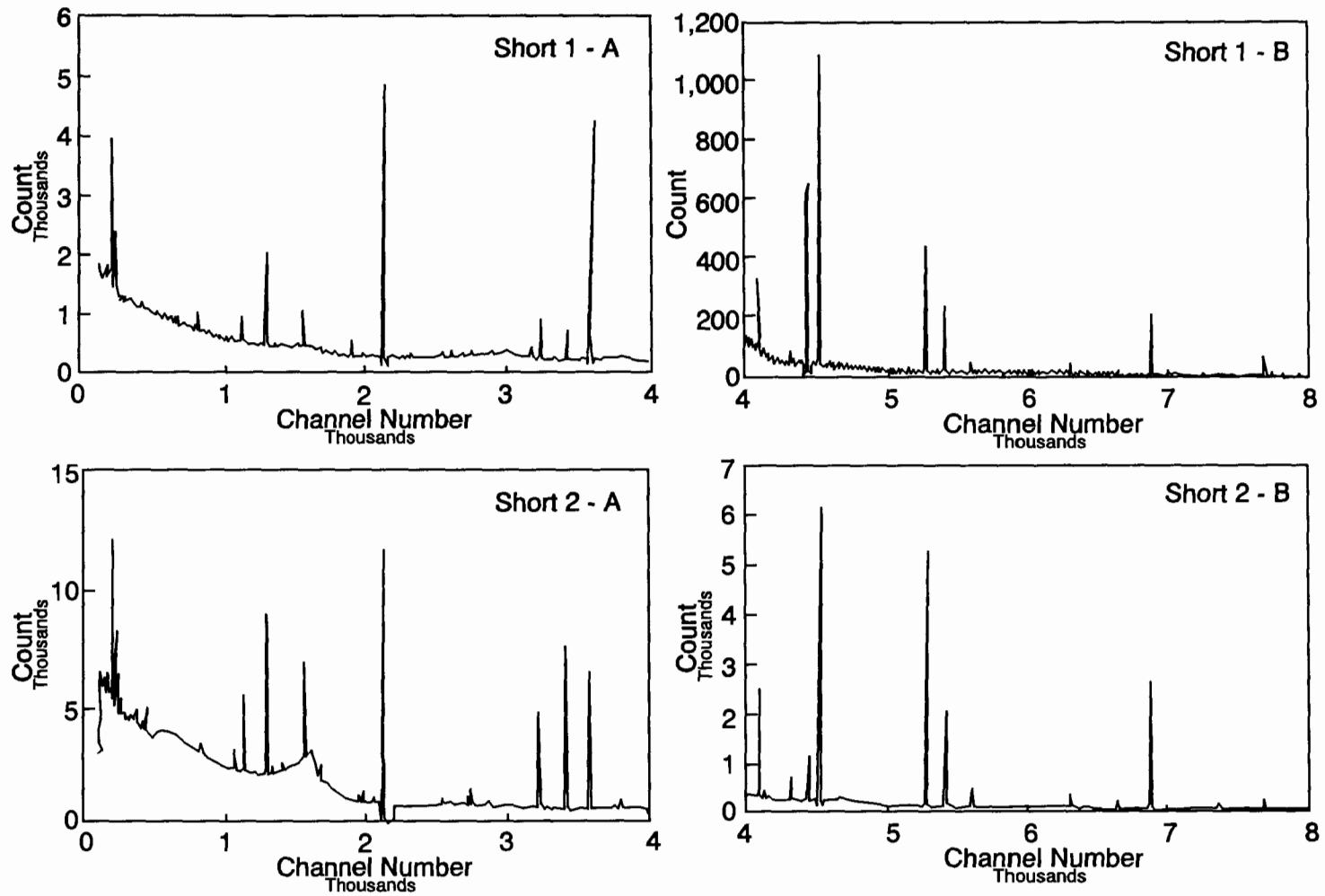


Figure 4-25. Typical Gamma-Ray Spectra Observed for Short Counts.

source of neutrons. However, since the advent of high-resolution gamma-ray detectors, individual samples can be analyzed for numerous elements simultaneously, most at remarkably trace levels without the need for chemical separation. This greatly diminishes the danger of contamination due to excessive sample handling and introduction of chemical reagents used for separation procedures.

#### 4.3.2.4 Microscopy Analysis of Particle Size, Shape, and Composition

Morphological and chemical features of particles can be used to identify the sources and transport mechanism of airborne particles. The chemical analysis of individual particles allows the attribution of specific pollution sources more straightforward while the abundance of a specific group is a representative of the source strength. Both light (optical) and scanning electron microscopy have been applied in environmental studies to examine the single particles (e.g., Casuccio et al., 1983; Bruynseels et al., 1988; Van Borm and Adams, 1988; Javitz and Watson, 1989; Van Borm et al., 1989; Cornille et al., 1990; Hopke and Casuccio, 1991; Hoffer et al., 1991; Cheng et al., 1992; Turpin et al., 1993; 1994; 1995).

Light microscopy has been used for providing particle size information regarding the morphology of microscopic features (Crutcher, 1982). The practical resolution of optical microscopes is limited by the wavelengths associated with light of the visible spectrum. When features of interest occur in micron and submicron size ranges, detailed resolution cannot be obtained. The practical resolution of light microscopy is typically 1 to 2  $\mu\text{m}$  (Meyer-Arendt, 1972).

The use of accelerated electrons in electron microscopy allows for the formation of magnified images and an increased depth of field, and provides the resolution of a few angstroms ( $10^{-4} \mu\text{m}$ ). Electron microscopy has now evolved to include: 1) the transmission electron microscope (TEM); 2) the scanning electron microscope (SEM), and; 3) the scanning transmission electron microscope (STEM) (Hearle et al. 1972; Lee et al., 1979; Scott and Chatfield, 1979; Lee and Fisher, 1980; Lee and Kelly, 1980; Lee et al., 1981; Johnson et al., 1981; McIntyre and Johnson, 1982; Casuccio et al., 1983; Wernisch, 1985, 1986; Kim et al., 1987, 1988; Dzubay and Mamane, 1989; Henderson et al., 1989; Schamber, 1993).

1 The SEM and STEM use accelerated electrons to strike the sample. As the electron  
2 beam strikes the samples, various signals (e.g., secondary, backscattered, and Auger  
3 electrons, characteristic x-rays, photons, and cathodoluminescence) are generated. These  
4 signals can be collected to provide highly detailed information on a point-by-point basis. The  
5 secondary electron signal yields a sample image with three-dimensional perspective, high  
6 depth of field, and illuminated appearance. Back scattered electron images are used to  
7 separate phases containing elements of different atomic number.

8 The information obtained from light and scanning microscopy analyses are usually  
9 considered to be qualitative, due to the limited number of particles counted. To achieve a  
10 quantitative analysis, a sufficient number of particles must be properly sized and identified by  
11 morphology and/or chemistry to represent the entire sample. The selection of filter media,  
12 optimal particle loadings, and sample handling methods are also of importance. In this  
13 manner, the microscopic characteristics can be directly and reliably related to the bulk or  
14 macroscopic properties of the sample (Casuccio et al., 1983).

15 Microscopic analysis requires a high degree of skill and extensive quality assurance to  
16 provide quantitative information. The techniques is complex and expensive when quantitative  
17 analysis is required. The evolution of computer technology has allowed for quantitative  
18 analysis of particle samples of an entire population of features. With advanced pattern  
19 recognition methods, data from individual particle features can be sorted and summarized by  
20 size and composition, permitting improved quantitative source apportionment (Bruynseels  
21 et al., 1988; Hopke and Casuccio, 1991). Casuccio et al. (1983) summarized the pros and  
22 cons of automatic scanning electron microscopy.

23 Recent development of the SEM/XRF allows analysis of elemental compositions and  
24 morphological information on small quantities of material (Bruynseels et al., 1988). Coupled  
25 with statistical data analysis, computer controlled scanning electron microscopy shows great  
26 promise for identifying and quantifying complex pollution sources in the field of receptor  
27 modeling source apportionment (e.g., Griffin and Goldberg, 1979; Janocko et al., 1982;  
28 Johnson et al, 1982; Massart and Kaufman, 1983; Hopke, 1985; Derde et al., 1987, Saucy  
29 et al., 1987; Mamane, 1988a, 1988b; Cheng and Hopke, 1989; Dzuby and Mamane, 1989).

### 4.3.3 Wet Chemical Analysis

Aerosol ions refer to chemical compounds that are soluble in water. The water-soluble portion of suspended particles associates itself with liquid water in the atmosphere when relative humidity increases, thereby changing the light scattering properties of these particles. Different emissions sources may also be distinguished by their soluble and non-soluble fractions. Gaseous precursors can also be converted to their ionic counterparts when they interact with chemicals impregnated on the filter material.

Several simple ions, such as soluble sodium, magnesium, potassium, and calcium are best quantified by atomic absorption spectrometry (AAS) as described above. In practice, AAS has been very useful for measuring water-soluble potassium and sodium, which are important in apportioning sources of vegetative burning and sea salt, respectively. Polyatomic ions such as sulfate, nitrate, ammonium, and phosphate must be quantified by other methods such as ion chromatography (IC) and automated colorimetry (AC). Simple ions, such as chloride, chromium III, and chromium IV, may also be measured by these methods along with the polyatomic ions.

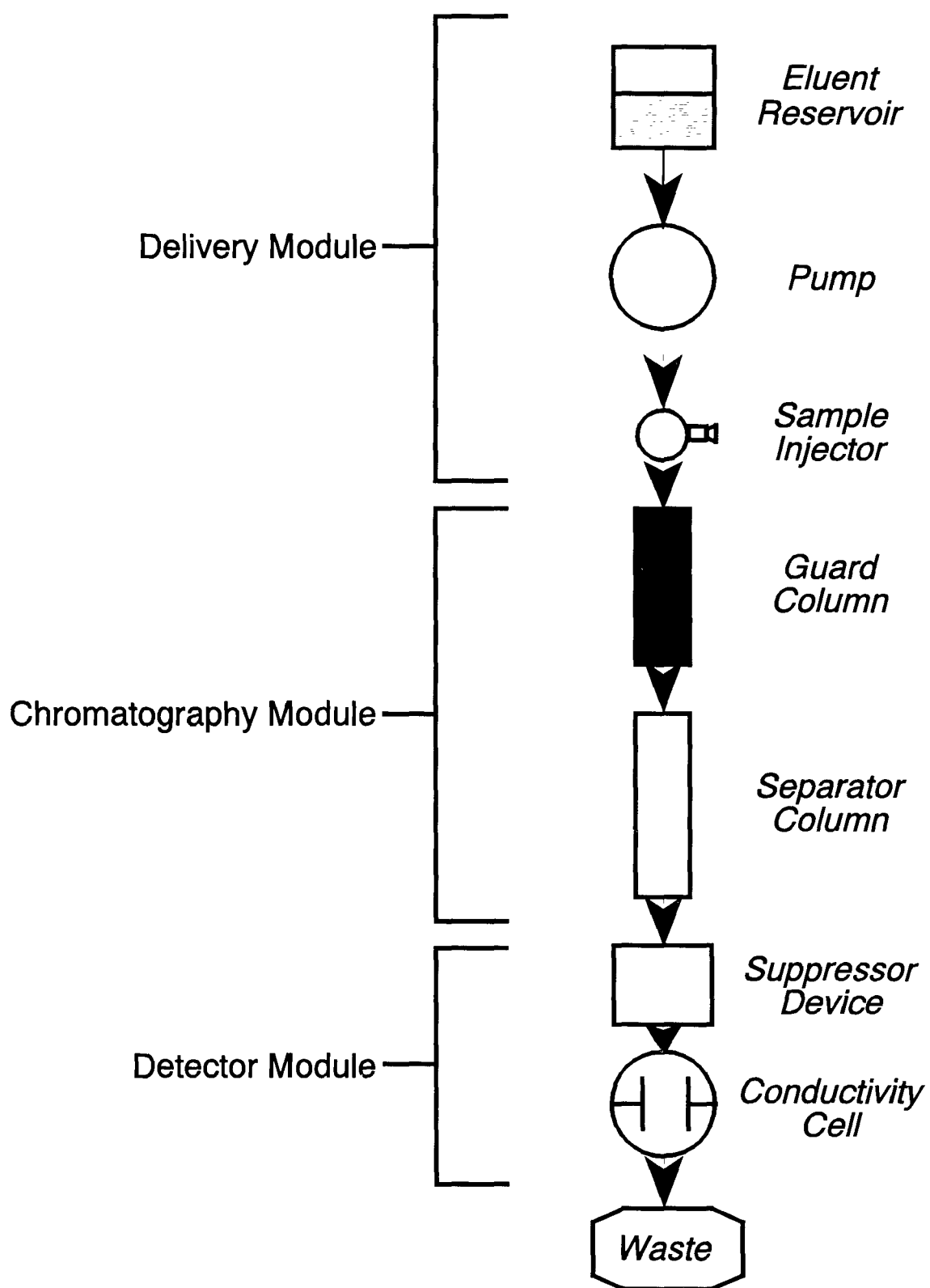
All ion analysis methods require filters to be extracted in DDW and then filtered to remove the insoluble residue. The extraction volume needs to be as small as possible, lest the solution become too dilute to detect the desired constituents. Each square centimeter of filter should be extracted in no more than 2 ml of solvent for typical sampler flow rates of 20 to 30 L/min and sample durations of 24 h. This often results in no more than 20 ml of extract that can be submitted to the different analytical methods, thereby giving preference to those methods which require only a small sample volume. Sufficient sample deposit must be acquired to account for the dilution volume required by each method.

When other analyses are to be performed on the same filter, the filter must first be sectioned using a precision positioning jig attached to a paper cutter. For rectangular filters (typically 20.32 cm by 25.40 cm), a 2.0 cm by 20.32 cm wide strip is cut from the center two-thirds of the filter. Circular filters of 25-, 37-, and 47-mm diameters are usually cut in half for these analyses, so the results need to be multiplied by two to obtain the deposit on the entire filter. Filter materials that can be easily sectioned without damage to the filter or the deposit must be chosen for these analyses.

#### 4.3.3.1 Ion Chromatographic Analysis for Chloride, Nitrate, and Sulfate

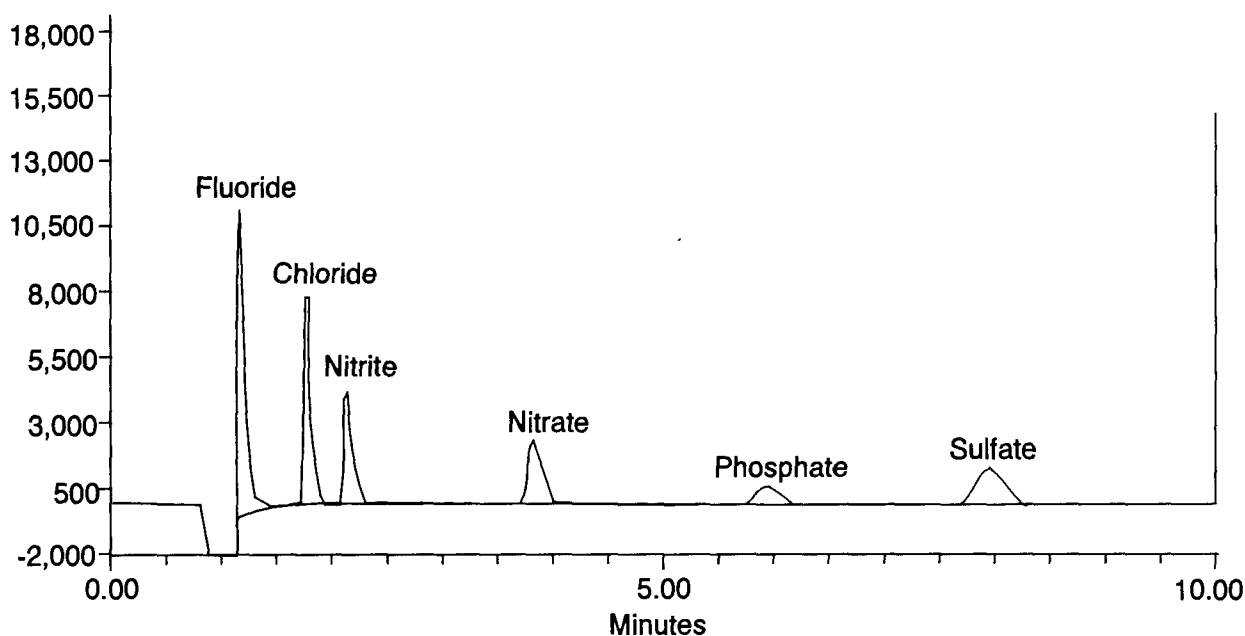
Ion Chromatography (IC) can be used for both anions (fluoride  $[F^-]$ , chloride  $[Cl^-]$ , nitrite  $[NO_2^-]$ , bromide  $[Br^-]$ , nitrate  $[NO_3^-]$ , phosphate  $[PO_4^{3-}]$ , sulfate  $[SO_4^{2-}]$ ) and cations (soluble potassium  $[K^+]$ , ammonium  $[NH_4^+]$ , soluble sodium  $[Na^+]$ ) with separate columns. Applied to aerosol samples, the anions are most commonly analyzed by IC with the cations being analyzed by a combination of atomic absorption spectrophotometry (AAS) and automated colorimetry (AC) (Chow and Watson, 1994). In IC (Small et al., 1975; Mulik et al., 1976, 1977; Butler et al., 1978; Mueller et al., 1978; Rich et al., 1978; Small, 1978), the sample extract passes through an ion-exchange column that separates the ions in time for individual quantification, usually by a electroconductivity detector. Figure 4-26 shows a schematic representation of the IC system. Prior to detection, the column effluent enters a suppressor column where the chemical composition of the eluent is altered, resulting in a lower background conductivity. The ions are identified by their elution/retention times and are quantified by the conductivity peak area or peak height. IC is especially desirable for particle samples because it provides results for several ions with a single analysis and it uses a small portion of the filter extract with low detection limits. Water-soluble chloride ( $Cl^-$ ), nitrate ( $NO_3^-$ ), and sulfate ( $SO_4^{2-}$ ) are the most commonly measured anions in aerosol samples. Figure 4-27 shows an example of an IC anion chromatogram. IC analyses can be automated by interfacing to an automatic sampler that can conduct unattended analysis of as many as 400 samples (Tejada et al., 1978).

In IC, approximately 2 to 3 ml of the filter extract are injected into the IC system. The resulting peaks are integrated and the peak integrals are converted to concentrations using calibration curves derived from standard solutions. For instance, the Dionex system (Sunnyvale, CA) for the analysis of  $Cl^-$ ,  $NO_2^-$ ,  $NO_3^-$ ,  $PO_4^{3-}$ , and  $SO_4^{2-}$  contains a guard column (AG4A column, Cat. No. #37042) and an anion separator column (AS4A column, Cat. No. #37041) with a strong-basic anion-exchange resin, and an anion micro-membrane suppressor column ( $250 \times 6$  mm ID) with a strong-acid ion-exchange resin. The  $4 \times 250$  mm analytical column is composed of 16 micron polystyrene/divinylbenzene substrate agglomerated with anion exchange latex that has been completely aminated. The 0.5% crosslinked latex particles have a diameter of approximately  $0.175 \mu m$  and carry the ion exchange sites. The ion exchange capacity of the  $4 \times 250$  mm analytical column is



**Figure 4-26. Schematic Representation of an Ion Chromatography (IC) System.**





**Figure 4-27. Example of an Ion Chromatogram Showing the Separation of Fluoride, Chloride, Nitrite, Nitrate, Phosphate, and Sulfate Ions.**

20  $\mu\text{eq}/\text{column}$ . The column is stable between pH 0 and 14. The anion eluent consists of sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) and sodium bicarbonate ( $\text{NaHCO}_3$ ) prepared in DDW. The DDW is verified to have a conductivity of less than  $1.8 \times 10^{-5} \text{ ohm}^{-1} \text{ cm}^{-1}$  prior to preparation of the eluent. For quantitative determinations, the IC is operated at a flow rate of 2.0 L/min. The system can also analyze fluoride with an eluent concentration of 1.8 M  $\text{Na}_2\text{CO}_3/1.7 \text{ M NaHCO}_3$ .

The primary standard solution is prepared annually and stored in a refrigerator. It is prepared from the reagent grade sodium salts (e.g., NaF, NaCl,  $\text{NaNO}_2$ , NaBr,  $\text{NaNO}_3$ ,  $\text{Na}_2\text{HPO}_4$ , and  $\text{Na}_2\text{SO}_4$ ). These anhydrous salts are dried in an oven at  $105^\circ \text{C}$  for 1 h and then cooled to room temperature in a dessicator. They are weighed to the nearest 0.10 mg on a routinely calibrated analytical balance under controlled temperature ( $\approx 20^\circ \text{C}$ ) and relative humidity ( $\pm 30\%$ ) conditions. These salts are diluted in precise volumes of DDW. Calibration standards are prepared at least once within each month by diluting the primary standard to concentrations covering the range of concentrations expected in the filter extracts.

1 The normal calibration concentrations prepared are 0.1, 0.2, 0.5, 1.0, and 2.0  $\mu\text{g/ml}$  for  
2 each of the analysis species.

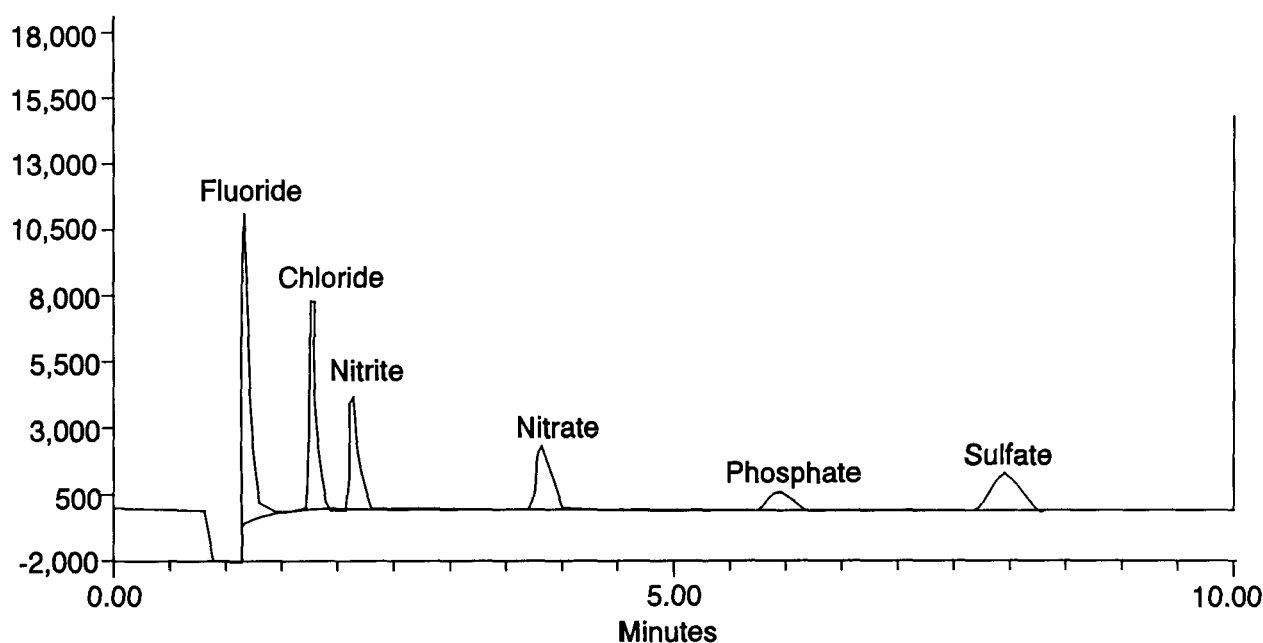
3 Several independent quality assurance (QA) standards should be used to check the  
4 calibration curve. The standards that are traceable to NIST simulated rainwater standards  
5 are: Environmental Resource Associates (ERA, Arvada, CA) custom standards containing  
6 the anions measured at a concentration of 100  $\mu\text{g/ml}$ , ERA Waste Water Nutrient Standard,  
7 ERA Waste Water Mineral Standard, and Alltech individual standards at 200  $\mu\text{g/ml}$ . The  
8 QA standards are diluted in DDW to concentrations that are within the range of the  
9 calibration curve.

10 Calibration curves are performed weekly. Chemical compounds are identified by  
11 matching the retention time of each peak in the unknown sample with the retention times of  
12 peaks in the chromatograms of the standards. The QA standards are analyzed at the  
13 beginning of each sample run to check calibrations. A DDW blank is analyzed after every  
14 20 samples and a calibrations standard is analyzed after every 10 samples. These quality  
15 control (QC) checks verify the baseline and calibration respectively.

#### 17 **4.3.3.2 Automated Colorimetric Analysis for Ammonium, Nitrate, and Sulfate**

18 Automated Colorimetry (AC) applies different colorimetric analyses to small sample  
19 volumes with automatic sample throughput. The most common ions measured are  
20 ammonium, chloride, nitrate, and sulfate (Butler et al., 1978; Mueller et al., 1978; Fung  
21 et al., 1979; Pyen and Fishman, 1979). Since IC provides multi-species analysis for the  
22 anions, ammonium is most commonly measured by AC.

23 The AC system is illustrated schematically in Figure 4-28. The heart of the automated  
24 colorimetric system is a peristaltic pump, which introduces air bubbles into the sample  
25 stream at known intervals. These bubbles separate samples in the continuous stream. Each  
26 sample is mixed with reagents and subjected to appropriate reaction periods before  
27 submission to a colorimeter. The ion being measured usually reacts to form a colored liquid.  
28 The liquid absorbance is related to the amount of the ion in the sample by Beer's Law. This  
29 absorbance is measured by a photomultiplier tube through an interference filter specific to the  
30 species being measured.



**Figure 4-28. Schematic of a Typical Automated Colorimetric (AC) System.**

The standard AC technique can analyze  $\approx 60$  samples per hour per channel, with minimal operator attention and relatively low maintenance and material costs. Several channels can be set up to simultaneously analyze several ions. The methylthymol-blue (MTB) method is applied to analyze sulfate. The reaction of sulfate with MTB-barium complex results in free ligand, which is measured colorimetrically at 460 nm. Nitrate is reduced to nitrite that reacts with sulfanilamide to form a diazo compound. This compound is then reacted to an azo dye for colorimetric determination at 520 nm. Ammonium is measured with the indophenol method. The sample is mixed sequentially with potassium sodium tartrate, sodium phenolate, sodium hypochlorite, sodium hydroxide, and sodium nitroprusside. The reaction results in a blue-colored solution with an absorbance measured at 630 nm.

The system determines carry-over by analysis of a low concentration standard following a high concentration. The percent carry-over is then automatically calculated and can be applied to the samples analyzed during the run.

Formaldehyde has been found to interfere with ammonium measurements when present in an amount exceeding 20% of the ammonium content, and hydrogen sulfide interferes in

1 concentrations exceeding 1 mg/ml. Nitrate and sulfate are also potential interferents when  
2 present at levels exceeding 100 times the ammonium concentration. These levels are rarely  
3 exceeded in ambient samples. The precipitation of hydroxides of heavy metals such as  
4 magnesium and calcium is prevented by the addition of disodium ethylenediamine-tetracetate  
5 (EDTA) to the sample stream (Chow et al., 1980; Chow, 1981). It was learned in the  
6 Sulfate Regional Experiment (SURE) (Mueller et al., 1983) that the auto-sampler should be  
7 enclosed in an atmosphere that is purged of ammonia by bubbling air through a phosphoric  
8 acid solution.

9 The automated colorimetric system requires a periodic standard calibration with the  
10 daily prepared reagents flowing through the system. Lower quantifiable limits of AC for  
11 sulfate and nitrate are an order of magnitude higher than those obtained with IC.

12 Intercomparison studies between AC and IC have been conducted by Butler et al.  
13 (1978); Mueller et al. (1978); Fung et al. (1979); and Pyen and Fishman (1979). Butler  
14 et al. (1978) found excellent agreement between sulfate and nitrate measurements by AC and  
15 IC. The accuracy of both methods is within the experimental errors, with higher blank  
16 values observed for AC techniques. Comparable results were also obtained between the two  
17 methods by Fung et al. (1979). The choice between the two methods for sample analysis is  
18 dictated by sensitivity, scheduling, and cost constraints.

19 Two milliliters of extract in sample vials are placed in an autosampler that is controlled  
20 by a computer. Five standard concentrations (e.g.,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{NaNO}_3$ ) are  
21 prepared from American Chemical Society reagent-grade chemicals following the same  
22 procedure as that for IC standards. Each set of samples consists of two DDW blanks to  
23 establish a baseline, five calibration standards and a blank, then sets of ten samples followed  
24 by analysis of one of the standards and a replicate from a previous batch. The computer  
25 control allows additional analysis of any filter extract to be repeated without the necessity of  
26 loading the extract into more than one vial.

#### 28 **4.3.3.3 Atomic Absorption Spectrophotometric (AAS) and Inductive Coupled Plasma** 29 **Atomic Emission Spectro (ICP/AES) Photometry Analyses for Trace Elements**

30 In AAS (Ranweiler and Moyers, 1974; Fernandez, 1989), the sample is first extracted  
31 in a strong solvent to dissolve the solid material; the filter or a portion thereof is also  
32 dissolved during this process. A few milliliters of this extract are introduced into a flame

1 where the elements are vaporized. Most elements absorb light at certain wavelengths in the  
2 visible spectrum, and a light beam with wavelengths specific to the elements being measured  
3 is directed through the flame to be detected by a monochrometer. The light absorbed by the  
4 flame containing the extract is compared with the absorption from known standards to  
5 quantify the elemental concentrations. AAS requires an individual analysis for each element,  
6 and a large filter or several filters are needed to obtain concentrations for a large number of  
7 the elements specified in Table 4.3.1. AAS is a useful complement to other methods, such  
8 as XRF and PIXE, for species such as beryllium, sodium, and magnesium that are not well-  
9 quantified by XRF and PIXE. Airborne particles are chemically complex and do not  
10 dissolve easily into complete solution, regardless of the strength of the solvent. There is  
11 always a possibility that insoluble residues are left behind and soluble species may  
12 co-precipitate on them or on container walls.

13 In ICP/AES (Fassel and Kniseley, 1974; McQuaker et al., 1979; Lynch et al., 1980;  
14 Harman, 1989), the dissolved sample is introduced into an atmosphere of argon gas seeded  
15 with free electrons induced by high voltage from a surrounding Tesla coil. The high  
16 temperatures in the induced plasma raise valence electrons above their normally stable states.  
17 When these electrons return to their stable states, a photon of light is emitted which is unique  
18 to the element which was excited. This light is detected at specified wavelengths to identify  
19 the elements in the sample. ICP/AES acquires a large number of elemental concentrations  
20 using small sample volumes with acceptable detection limits for atmospheric samples.  
21 As with AAS, this method requires complete extraction and destruction of the sample.  
22

## 23 **4.3.4 Organic Analysis**

### 24 **4.3.4.1 Analysis of Organic Compounds**

25 Organic compounds comprise a major portion of airborne particles in the atmosphere,  
26 thus contributing to visibility degradation, and affecting the properties of clouds into which  
27 these particles are scavenged. Specific groups of organic compounds (e.g., polycyclic  
28 aromatic hydrocarbons, PAHs) have also been implicated in human health effects. However,  
29 due to the very complex composition of the organic fraction of atmospheric aerosols, the  
30 detailed composition and atmospheric distributions of organic aerosol constituents are still not  
31 well understood.

1 Sampling techniques for atmospheric particulate matter have been extensively  
2 investigated, resulting in the development of collection methods for ambient aerosol particles  
3 in a wide range of particle sizes. Particles are most frequently collected on glass or quartz-  
4 fiber filters that have been specially treated to achieve low "carbon blanks". Ambient  
5 organic particulate matter has also been collected on a variety of particle sizing devices, such  
6 as low pressure impactors and Micro Orifice Uniform Deposit Impactors("MOUDI"). Very  
7 recently, diffusion based samplers have been used as well (i.e., Eatough et al., 1994; Tang  
8 et al., 1994). However, the task of sampling organic compounds in airborne particles is  
9 complicated by the fact that many of these compounds have equilibrium vapor pressures  
10 (gaseous concentrations) that are considerably larger than their normal ambient  
11 concentrations. This implies a temperature- and concentration-dependent distribution of such  
12 organics between particulate and vapor phases. It also suggests that artifacts may occur due  
13 to volatilization during the sampling process (Coutant et al., 1988). Such volatilization  
14 would cause the under-estimation of the particle-phase concentrations of organics.  
15 Conversely, the adsorption of gaseous substances on deposited particles, or on the filter  
16 material itself, a process driven by the lowered vapor pressure over the sorbed material,  
17 would lead to over-estimation of the particle-phase fraction (Bidleman et al., 1986; Ligocki  
18 and Pankow, 1989; McDow and Huntzicker, 1990). In addition, several studies have  
19 suggested that chemical degradation of some organics may occur during the sampling  
20 procedure (Lindskog et al., 1985; Arey et al., 1988; Parmar and Grosjean, 1990).

21 The partitioning of semi-volatile organic compounds (SOC) between vapor and particle  
22 phases has received much attention recently (Ligocki and Pankow, 1989; Cotham and  
23 Bidleman, 1992; Lane et al., 1992; Kaupp and Umlauf, 1992; Pankow, 1992; Turpin et al.,  
24 1993). Most estimates of partition have relied on high-volume (hi-vol) sampling, using a  
25 filter to collect particles followed by a solid adsorbent trap to collect the gaseous portion of  
26 SOC (e.g., Kaupp and Umlauf, 1992, Foreman and Bidleman, 1990). It has been shown  
27 recently (Kaupp and Umlauf, 1992) that this approach, although not absolutely free from  
28 sorption and desorption artifacts, produces reliable results. The maximum differences  
29 observed between hi-vol filter-solid adsorbent sampling and impactor sampling (the latter  
30 believed to be less susceptible to these sampling artifacts) did not exceed a factor of two.

1        There is good theoretical and experimental evidence that use of a diffusion denuder  
2        technique significantly improves measurements of vapor-particle phase partitioning (Coutant  
3        et al., 1988, 1989, 1992; Lane et al., 1988). However, at the present state of their  
4        technological development, the reliability of denuders for investigation of atmospheric  
5        partitioning of non-polar SOC needs to be improved, as suggested by contradictions in  
6        published field data (e.g., Kaupp and Umlauf, 1992). A new, improved sampler has recently  
7        been introduced (Gundel et al., 1992) which uses a proprietary XAD-4-coated tube for vapor  
8        collection, followed by filter collection of organic aerosol particles and a sorbent bed to  
9        quantitatively retain desorbed (volatilized) organic vapors. Preliminary results from the use  
10       of this device look very promising for direct measurements of the phase distribution of semi-  
11       volatile organic aerosol constituents. Another promising application of denuder technology  
12       has been their use to remove ozone from an air sampling stream before it reaches the filter,  
13       reducing the potential for artifact formation on the captured particulate material during the  
14       sampling period (Williams and Grosjean, 1990).

15       Since the organic fraction of airborne particulate matter is typically a complex mixture  
16       of hundreds to thousands of compounds distributed over many organic functional groups, its  
17       chemical analysis is an extremely difficult task (Appel et al., 1977; Simoneit, 1984; Flessel  
18       et al., 1991; Hildemann et al., 1991; Li and Kamens, 1993; Rogge et al., 1993a, 1993b,  
19       1993c). Analyses of organics generally begin with solvent extraction of the particulate  
20       sample. A variety of solvents and extraction techniques have been used in the past. One  
21       common method is sequential extraction with increasingly polar solvents, which typically  
22       separates the organic material into nonpolar, moderately polar, and polar fractions (Daisey  
23       et al., 1982, 1987). This step is usually followed by further fractionation using open-column  
24       liquid chromatography and/or high-performance liquid chromatography (HPLC) in order to  
25       obtain several less complicated fractions (e.g., Schuetzle and Lewtas, 1986; Atkinson et al.,  
26       1988). These fractions can then be analyzed further with high resolution capillary-column  
27       gas chromatography (GC), combined with mass spectrometry (GC/MS), Fourier transform  
28       infrared (GC/FTIR/MS) or other selective detectors.

29       Much of the recent work on the identification of nonpolar and semi-polar organics in  
30       airborne samples has used bioassay-directed chemical analysis (Schuetzle and Lewtas, 1986),  
31       and has focused on identification of fractions and compounds that are most likely to be of

1 significance to human health. In particular, PAHs and their nitro-derivatives (nitroarenes)  
2 attracted considerable attention due to their mutagenic and, in some cases, carcinogenic  
3 properties. More than 100 PAHs have been identified in the PM<sub>2.5</sub> fraction of ambient  
4 particulate matter (Lee et al., 1981). While most of the nitroarenes found in ambient  
5 particles are also present in primary combustion-generated emissions, some are formed from  
6 their parent PAH in the atmospheric nitration reactions (e.g., Arey et al., 1986; Zielinska  
7 et al., 1989, Ramdahl et al., 1986).

8 Little work has been done to date to chemically characterize the polar fraction in detail,  
9 even though polar material accounts for up to half the mass and mutagenicity of soluble  
10 ambient particulate organic matter (Atherholt et al., 1985; Gundel et al., 1994). Until  
11 recently the polar fraction has remained analytically intractable, since very polar and labile  
12 species interact with conventional fractionation column packing materials and cannot be  
13 recovered quantitatively. Recently very polar particulate organic matter has been  
14 successfully fractionated using cyanopropyl-bonded silica (Gundel et al., 1994), with good  
15 recovery of mass and mutagenicity (Kado et al., 1991). However, ambient particulate polar  
16 organic material cannot be analyzed with conventional GC/MS because of GC column losses  
17 resulting from adsorption, thermal decomposition, and chemical interactions. New analytical  
18 techniques, such as HPLC/MS and MS/MS, need to be applied if the chemical constituents  
19 of polar particulate organic matter are to be identified and quantified.

20 Most of the recent work on the identification of particulate organic matter has focused  
21 on mutagenic and carcinogenic compounds that are of significance to human health.  
22 Relatively little work has been done to characterize individual compounds or classes of  
23 compounds that are specific to certain sources of organic aerosol. In urban and rural  
24 atmospheres, as well as in the remote troposphere, organic composition corresponding to  
25 fingerprints of plant waxes, resin residues, and long-chain hydrocarbons from petroleum  
26 residues have been found (e.g., Gagosian et al., 1981; Simoneit, 1984; Mazurek et al., 1987,  
27 1989, 1991; Simoneit et al., 1991; Rogge et al., 1994). However, a variety of smaller,  
28 multi-functional compounds characteristic of gas-to-particle conversion have also been  
29 observed (e.g., Finlayson-Pitts and Pitts, 1986). These compounds tend to be present in the  
30 polar fraction of ambient organic aerosol particles, having been formed from atmospheric



chemical reactions of less polar precursors. Little is currently known about the chemical composition of this polar fraction due to the serious analytical difficulties mentioned above.

#### 4.3.4.2 Analysis of Organic and Elemental Carbon

Three classes of carbon are commonly measured in aerosol samples collected on quartz-fiber filters: 1) organic, volatilized, or non-light absorbing carbon; 2) elemental or light-absorbing carbon; and 3) carbonate carbon. Carbonate carbon (i.e.,  $K_2CO_3$ ,  $Na_2CO_3$ ,  $MgCO_3$ ,  $CaCO_3$ ) can be determined on a separate filter section by measurement of the carbon dioxide ( $CO_2$ ) evolved upon acidification (Johnson et al., 1981). Though progress has been made in the quantification of specific organic chemical compounds in suspended particles (e.g., Rogge et al., 1991), sampling and analysis methods have not yet evolved for use in practical monitoring situations.

Many methods have been applied to the separation of organic and elemental carbon in ambient and source particulate samples (McCarthy and Moore, 1952; Mueller et al., 1971; Lin et al., 1973; Patterson, 1973; Gordon, 1974; Grosjean, 1975; Smith et al., 1975; Appel et al., 1976, 1979; Kukreja and Bove, 1976; Merz, 1978; Rosen et al., 1978; Dod et al., 1979; Johnson and Huntzicker, 1979; Macias et al., 1979; Malissa, 1979; Weiss et al., 1979; Cadle et al., 1980a, 1980b; Heisler et al., 1980a, 1980b; Johnson et al., 1980, 1981; Pimenta and Wood, 1980; Daisey et al., 1981; Mueller et al., 1981; Novakov, 1981, 1982; Cadle and Groblicki, 1982; Gerber, 1982; Heintzenberg, 1982; Huntzicker et al., 1982; Muhlbaier and Williams, 1982; Rosen et al., 1982; Tanner et al., 1982; Stevens et al., 1982; Wolff et al., 1982; Japar et al., 1984). Comparisons among the results of the majority of these methods show that they yield comparable quantities of total carbon in aerosol samples, but the distinctions between organic and elemental carbon are quite different (Countess, 1990; Hering et al., 1990).

The definitions of organic and elemental carbon are operational and reflect the method and purpose of measurement. Elemental carbon is sometimes termed "soot", "graphitic carbon," or "black carbon." For studying visibility reduction, light-absorbing carbon is a more useful concept than elemental carbon. For source apportionment by receptor models, several consistent but distinct fractions of carbon in both source and receptor samples are desired, regardless of their light-absorbing or chemical properties. Differences in ratios of

1 the carbon concentrations in these fractions form part of the source profile that distinguishes  
2 the contribution of one source from the contributions of other sources.

3 Light-absorbing carbon is not entirely constituted by graphitic carbon, since there are  
4 many organic materials that absorb light (e.g., tar, motor oil, asphalt, coffee). Even the  
5 "graphitic" black carbon in the atmosphere has only a poorly developed graphitic structure  
6 with abundant surface chemical groups. "Elemental carbon" is a poor but common  
7 description of what is measured. For example, a substance of three-bond carbon molecules  
8 (e.g., pencil lead) is black and completely absorbs light, but four-bond carbon in a diamond  
9 is completely transparent and absorbs very little light. Both are pure, elemental carbon.

10 Chow et al. (1993) document several variations of the thermal (T), thermal/optical  
11 reflectance (TOR), thermal/optical transmission (TOT), and thermal manganese oxidation  
12 (TMO) methods for organic and elemental carbon. The TOR and TMO methods have been  
13 most commonly applied in aerosol studies in the United States.

14 The TOR method of carbon analysis developed by Huntzicker et al. (1982) has been  
15 adapted by several laboratories for the quantification of organic and elemental carbon on  
16 quartz-fiber filter deposits. While the principle used by these laboratories is identical to that  
17 of Huntzicker et al. (1982), the details differ with respect to calibration standards, analysis  
18 time, temperature ramping, and volatilization/combustion temperatures. In the TOR method  
19 (Chow et al., 1993), a filter is submitted to volatilization at temperatures ranging from  
20 ambient to 550°C in a pure helium atmosphere, then to combustion at temperatures between  
21 550 to 800°C in a 2% oxygen and 98% helium atmosphere with several temperature ramping  
22 steps. The carbon that evolves at each temperature is converted to methane and quantified  
23 with a flame ionization detector. The reflectance from the deposit side of the filter punch is  
24 monitored throughout the analysis. This reflectance usually decreases during volatilization in  
25 the helium atmosphere owing to the pyrolysis of organic material. When oxygen is added,  
26 the reflectance increases as the light-absorbing carbon is combusted and removed. Organic  
27 carbon is defined as that which evolves prior to re-attainment of the original reflectance, and  
28 elemental carbon is defined as that which evolves after the original reflectance has been re-  
29 attained. By this definition, "organic carbon" is actually organic carbon that does not absorb  
30 light at the wavelength (632.8 nm) used, and "elemental carbon" is light-absorbing carbon  
31 (Chow et al., 1993). The TOT method applies the same thermal/optical carbon analysis

1 method except that transmission instead of reflectance of the filter punch is measured.

2 Thermal methods apply no optical correction and define elemental carbon as that which  
3 evolves after the oxidizing atmosphere is introduced.

4 The TMO method (Mueller et al., 1982; Fung, 1990) uses manganese dioxide ( $\text{MnO}_2$ ),  
5 present and in contact with the sample throughout the analysis, as the oxidizing agent, and  
6 temperature is relied upon to distinguish between organic and elemental carbon. Carbon  
7 evolving at  $525^\circ\text{C}$  is classified as organic carbon, and carbon evolving at  $850^\circ\text{C}$  is classified  
8 as elemental carbon.

9 Carbon analysis methods require a uniform filter deposit because only a small portion  
10 of each filter is submitted to chemical analysis. The blank filter should be white for light  
11 reflection methods, and at least partially transparent for light transmission methods. The  
12 filter must also withstand very high temperatures without melting during combustion.

13 Since all organic matter contains hydrogen as the most common elemental species,  
14 analysis of hydrogen by proton elastic scattering analysis (PESA) has been developed by  
15 Cahill (1987). A correction must be made for hydrogen in sulfates and nitrates, but since the  
16 analysis is done in a vacuum, water is largely absent. The method has excellent sensitivity  
17 which is approximately 20 times better than combustion techniques. This method requires  
18 knowledge of the chemical state of sulfates, nevertheless, reasonable agreement was found as  
19 compared to the combustion techniques.

#### 21 4.3.5 Quality Assurance

22 The use of multiple methods and parallel samplers achieves both optimum performance  
23 and quality assurance. While this has been a part of major research studies since the 1970's,  
24 its extension to routine monitoring of aerosols was most extensively introduced in the  
25 SCENES and IMPROVE visibility programs (Eldred, 1989). The concept was labeled,  
26 "Integral Redundancy," and was recently adopted by the United Nation's Global Atmospheric  
27 Watch Program.

28 The internal consistency checks applied to the IMPROVE network are listed as follows:

- 29 1) Mass (gravimetric) is compared to the sum of all elements on the Teflon-membrane  
30 filter of Channel A (PIXE, PESA, XRF analysis; Internally XRF and PIXE are  
31 compared for elements around iron). This was pioneered in the SCENES program  
32 and is now the standard practice for many aerosol studies.

- 1           2) Sulfate, by ion chromatography on Channel B's nylon filter, after an acidic vapor  
2           denuder, is compared to sulfur (X3) from Channel A's Teflon-membrane filter by  
3           PIXE. Agreement is excellent, except for summer.  
4  
5           3) Organic matter, by combustion on Channel C's quartz-fiber filter stack, is  
6           compared to organic matter via PESA analysis of hydrogen on Channel A's Teflon-  
7           membrane filter. This is an exceptionally severe test due to the nature of organics.  
8           These comparisons are made for every IMPROVE analysis, yielding about 25,000  
9           comparisons to date (Malm et al., 1994).

10           These types of data validation checks should be carried out in every PM measurement  
11           program to ensure the accuracy, precision, and validity of the chemical analysis data.

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## 5. SOURCES AND EMISSIONS OF SUSPENDED PARTICLES

### 5.1 INTRODUCTION

Excessive particulate concentrations in the atmosphere result from pollutant emissions, meteorological transport of those emissions between source and receptor, and chemical and physical changes during the transport period. Importantly, both primary and secondary particles contribute to ambient PM mass concentrations.

Primary particles are those which are directly emitted by sources, and these particles often undergo few changes between source and receptor. Atmospheric concentrations of primary particles are, on average, proportional to the quantities that are emitted. Primary particles are emitted in several size ranges, the most common being less than 1  $\mu\text{m}$  in aerodynamic diameter from combustion sources and larger than 1  $\mu\text{m}$  in aerodynamic diameter from dust sources. Particles larger than 10  $\mu\text{m}$  in aerodynamic diameter usually deposit to the surface within a few hours after being emitted and do not have a large effect on urban or regional scales. These larger particles may make significant contributions at receptors located within a few kilometers of the emissions source, however. Coarse particles with aerodynamic diameters between 2 and 10  $\mu\text{m}$  may make significant contributions at distances exceeding 10 km from their emissions sources, while particles with aerodynamic diameters  $< 2 \mu\text{m}$  may affect receptors that are more than 100 km distant from emissions sources.

Secondary particles are those that form in the atmosphere from gases that are directly emitted by sources. Sulfur dioxide, ammonia, and oxides of nitrogen are the precursors for sulfuric acid, ammonium bisulfate, ammonium sulfate, and ammonium nitrate particles (Seinfeld, 1986). Several volatile organic compounds (VOC) may also change into particles; the majority of these transformations result from intense photochemical reactions that also create high ozone levels (Grosjean and Seinfeld, 1989). Secondary particles usually form over several hours or days, attain aerodynamic diameters between 0.1 and 1  $\mu\text{m}$ , owing to the complex chemical processes that form them, secondary particle concentrations are not necessarily proportional to the quantities that are emitted, and may affect receptors more than

1 1,000 km distant from the sources of precursor gas emissions. Several of these particles,  
2 notably those containing ammonium nitrate, are volatile and transfer mass between the gas  
3 and particle phase to maintain a chemical equilibrium.

4 Ambient concentrations of secondary aerosol are not necessarily proportional to primary  
5 emissions quantities since the rate at which they form may be limited by factors other than  
6 concentrations of the precursor gases. For example, secondary ammonium nitrate is not a  
7 stable compound; its equilibrium with gaseous ammonia and nitric acid is influenced strongly  
8 by temperature and relative humidity (Watson et al., 1994b). Fugitive dust is predominantly  
9 a primary pollutant, but it does play a role in secondary particle formation. Some  
10 components of dust, such as ammonium nitrate fertilizer, may volatilize into ammonia and  
11 nitric acid gases, thereby contributing to secondary aerosol. Alkaline particles, such as  
12 calcium carbonate, may react with nitric and hydrochloric acid gases while on the ground, in  
13 the atmosphere, or on filter samples to form coarse-mode particle nitrates and chlorides.  
14 Ammonium sulfate fertilizer components and minerals such as gypsum (calcium sulfate) may  
15 be mistaken for secondary sulfates when  $PM_{10}$  filters are chemically analyzed.

16 Due to the complex and varying composition of suspended particles, it is necessary to  
17 consider sulfur dioxide, oxides of nitrogen, ammonia, VOCs, and primary particle emissions  
18 as potential sources of suspended particles in ambient air. Major sources of these emissions  
19 are classified into categories of: (1) major point sources; (2) mobile sources; and (3) area  
20 sources (U.S. Environmental Protection Agency, 1993).

21 Major point sources are ducted emissions that are subject to permit. Emissions of a  
22 single pollutant usually must exceed 25 tons/year to qualify for this category, though some  
23 jurisdictions track individual thresholds at lower levels. This category includes stack  
24 emissions from most industrial facilities in the United States such as steel mills, smelters,  
25 cement plants, electric utilities, refineries, and incinerators. Non-ducted emissions from  
26 these industries, such as VOCs from leaking valves and primary particles from materials  
27 handling are termed "fugitive emissions".

28 Mobile sources include on-road and off-road motor vehicles, trains, aircraft, and ships,  
29 with the majority of emissions resulting from on-road vehicles in most areas. Area sources  
30 include many small stationary emitters that, in their aggregate, can be significant contributors  
31 to suspended particles. These include residential wood and coal combustion, prescribed

1 burning, space heating, cooking, paved and unpaved roads, construction and demolition,  
2 agricultural operations, and wind erosion.

3 Point, mobile, and area source emissions are anthropogenic. Natural sources of  
4 suspended particles such as sea salt, volcanic emissions, wild fires, and aeolian dust from  
5 undisturbed surfaces can also contribute to ambient PM concentrations in certain situations.  
6 One of the major challenges to air quality sciences is to distinguish among contributions from  
7 these different sources when suspended particle concentrations are high.

8 This chapter is organized to present first a concise summary of key information on PM  
9 emissions derived from the previous criteria review in the 1980's and then to provide a more  
10 extensive discussion of newer information appearing in recent years.

11 The main objectives of the ensuing discussion this section are:

- 12 • To identify the sources that are major contributors to suspended particle  
13 concentrations in the United States.
- 14 • To describe the particle sizes and chemical properties of source emissions.
- 15 • To evaluate the limitations and uncertainties of emissions rate estimates and  
16 source contributions for suspended particles and their gaseous precursors.
- 17 •
- 18
- 19

## 21 **5.2 SUMMARY OF 1982 CRITERIA DOCUMENT EMISSIONS** 22 **REVIEW**

23 The U.S. Environmental Protection Agency (EPA) (1982) examined 109 open-literature  
24 references related to particulate emissions published between 1951 and 1981. This  
25 comprehensive review discussed the sources of emissions data and their accuracy, global  
26 particulate emissions from natural sources, U.S. particulate and sulfur dioxide emissions  
27 from manmade sources, and the size and chemical composition of emitted particles. The  
28 major findings of this review were the following:

- 29 • Particulate emissions rates are very uncertain. Two independent EPA estimates  
30 yielded 6.4 (U.S. Environmental Protection Agency, 1980a) and 3.9 (U.S.  
31 Environmental Protection Agency, 1980b) million metric tons per year for the same  
32 industrial process emissions of primary particles in 1977. Particle emissions  
33 estimates from mobile sources were believed to have even greater uncertainty.  
34  
35

- Global particulate emissions include 100 to 500 million metric tons/year (Robinson and Robbins, 1971; Vandegrift et al., 1971) from aeolian dust, 900 million metric tons/year from sea spray (Robinson and Robbins, 1971), and 0.75 to 3.75 million tons/year from volcanoes (Robinson and Robbins, 1971; Granat et al., 1976). Much of these emissions are small particles that do not attain great elevation above ground level and deposit close to their emissions points. Significant fractions of volcanic emissions, however, are injected high into the atmosphere and can have long atmospheric residence times. Primary particle emissions from U.S. wildfires were estimated to be 0.5 to 4.5 million metric tons/year, with most of these emissions being small particles that do not deposit close to the emissions point (Robinson and Robbins, 1971; Yamate, 1973).
- Naturally-emitted volatile organic compounds that might be secondary particulate precursors were estimated at 200 million metric tons/year for the world and 20 million metric tons/year for the United States (Went, 1960). Global emissions of reduced sulfur compounds were estimated at 37 to 91 million metric tons per year (Robinson and Robbins, 1971; Granat et al., 1976).
- Manmade particle emissions in the United States during 1978 included 10.5 million metric tons/year from stationary point sources, 3.3 million metric tons/year from non-ducted industrial processes, 110 to 370 tons/year from non-industrial fugitive dust, and 1.3 million metric tons/year from mobile sources. Stationary point sources, primarily electric utilities, accounted for 26.2 million tons/ year of sulfur dioxide emissions, with the remaining 0.8 million tons/year emitted by mobile sources.
- Primary particle emissions from stationary fuel combustion, industrial processes, solid waste disposal, mobile sources, and burning in the United States decreased from 24.8 million metric tons per year in 1940 to 12.5 million metric tons/year in 1978. All categories decreased except emissions from transportation, which nearly tripled from 0.5 to 1.3 million metric tons/year over this period. Sulfur dioxide emissions increased from 19.5 to 27.0 million metric tons/year between 1940 and 1978, with the major increase in stationary fuel combustion.
- Coal combustion was the major U.S. industrial emitter, with 3,090 out of 10,460 metric tons/year total for primary particles and 17,890 out of 26,180 metric tons per year total for sulfur dioxide during 1978. More than 80% of coal combustion emissions derived from electricity generation.
- Emissions estimates differed substantially among different parts of the United States, especially between the eastern and western regions. The midwest contained more than 70% of particle and sulfur dioxide emissions from industrial sources.
- Fugitive dust source emissions were found primarily in particles sizes larger than 2.5  $\mu\text{m}$ . Seventy to 100% of the primary particle emissions from coal and oil combustion and other ducted industrial emissions were smaller than 2.5  $\mu\text{m}$  in aerodynamic diameter.

- Aluminum, silicon, calcium, potassium, and titanium were found to be abundant in many geologically-related emissions. Several sources of primary particles showed enrichments with respect to crustal abundances for certain elements: (1) copper, lead, and arsenic in smelter emissions; (2) selenium and arsenic in coal combustion emissions; (3) iron and manganese in steel mill emissions; (4) calcium and sulfate in cement emissions; and (5) vanadium and nickel in residual oil combustion emissions.

The U.S. EPA (1982) emphasized emissions from industrial sources, and especially primary particles emitted by these sources. Sulfur dioxide was the only precursor of secondary aerosol that was considered. Emission rates were quantified in terms of Total Suspended Particulate (TSP), i.e., particles with aerodynamic diameters  $< \sim 50 \mu\text{m}$ , since  $\text{PM}_{10}$  had not yet been defined as the size fraction relevant to public health. Measured chemical compositions included many elements and sulfate, but did not include nitrate, ammonium, and carbon.

At the time, this emphasis was appropriate owing to the then available information and to the lack of sufficient emissions controls on many of these sources. Since that time, many ducted emissions have been controlled, yet air quality standards are still exceeded in many areas. Non-sulfate secondary aerosol is a major component of suspended particles in many areas. The particle sizes relevant to health effects are now believed to be much smaller than  $50 \mu\text{m}$ , and possibly substantially smaller than the  $\text{PM}_{10}$  fraction which is currently subject to NAAQS regulation. Much new information has been published since 1982 that enhances and expands upon the conclusions about source contributions to suspended particles.

### 5.3 SOURCE CONTRIBUTIONS TO SUSPENDED PARTICLES

Much of the current knowledge related to source contributions derives from evaluations used in development of control strategies for non-attainment areas where  $\text{PM}_{10}$  concentrations exceed  $50 \mu\text{g}/\text{m}^3$  for an annual arithmetic average and/or  $150 \mu\text{g}/\text{m}^3$  for a 24-h average. Seventy-five areas have been designated in non-attainment. The 1990 Clean Air Act Amendments and several years of ambient  $\text{PM}_{10}$  monitoring resulted in designation of 75 U.S. areas as "moderate" non-attainment areas for  $\text{PM}_{10}$  (Federal Register, 1991; 1994), 5 areas as "serious" non-attainment (Federal Register, 1993), and the remaining areas as unclassifiable. Each state containing non-attainment areas must develop and submit State

1 Implementation Plans (SIPs) that specify the means for reducing  $PM_{10}$  concentrations below  
2 the standards. Extensive efforts were expended in many areas to apportion excessive  $PM_{10}$   
3 concentrations to their sources.

4 The U.S. EPA (1987) recommends the application of both source and receptor models  
5 to quantify the major contributors to excess  $PM_{10}$  concentrations, and linear rollback of  
6 emissions to estimate the effects of alternative emission controls (Pace and Watson, 1987;  
7 U.S. Environmental Protection Agency, 1987). Source models use emissions inventories and  
8 meteorological measurements to predict the  $PM_{10}$  concentrations measured at receptors.  
9 Receptor models use the chemical composition of source emissions and receptor  
10 concentrations to infer the source contributions that constitute the measured  $PM_{10}$  mass.  
11 Source models are most useful when sources have been identified and emissions rates are  
12 known. In many non-attainment areas, however, the majority of emissions emanate from  
13 mobile and area sources that have highly sporadic and often unknown emissions at different  
14 locations and different times. Several non-attainment areas in the mountainous western  
15 United States experience highly variable meteorology induced by complex terrain, and most  
16 dispersion models are not applicable. In these situations, receptor-oriented source  
17 apportionment models were found to be the most appropriate methods to identify sources  
18 and quantify their contributions to measured  $PM_{10}$ .

19 Source contributions to average  $PM_{10}$  for several areas where the Chemical Mass  
20 Balance (CMB) receptor model (Watson et al., 1990; 1991) was applied are shown in  
21 Table 5-1. The values in Table 5-1 are not entirely comparable in an absolute sense, since  
22 published source apportionment studies usually report averages for different sample selections  
23 (often biased toward high  $PM_{10}$  levels) and different seasons. The sampling sites represent a  
24 variety of different source characteristics within different regions of Arizona, California,  
25 Colorado, Idaho, Illinois, Nevada and Ohio. Several of these are background sites,  
26 specifically Estrella Park, Gunnery Range, Pinnacle Peak, and Corona de Tucson, AZ,  
27 Anacapa Island, CA, San Nicolas Island, CA, Vandenberg Air Force Base, CA, and Verdi,  
28 NV. Definitions of source categories also vary from study to study. In spite of these  
29 differences, several features can be observed from the values in this table.

30 Fugitive dust (geological material) from roads, agriculture and erosion is a major  
31 contributor to  $PM_{10}$  at nearly all sampling sites, often contributing up to, but not generally

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TABLE 5-1. RECEPTOR MODEL SOURCE CONTRIBUTIONS TO PM<sub>10</sub>.

Sampling Site	$\mu\text{g}/\text{m}^3$										Measured PM <sub>10</sub> Concentration
	Primary Geological	Primary Construction	Primary* Motor Vehicle Exhaust	Primary Vegetative Burning	Secondary Ammonium Sulfate	Secondary Ammonium Nitrate	Misc. Source 1	Misc. Source 2	Misc. Source 3	Misc. Source 4	
Central Phoenix, AZ (Chow et al., 1991)	33.0	0.0	25.0	2.3	0.2	2.8	0.0	0.0	0.0	0.0	64.0
Corona de Tucson, AZ (Chow et al., 1992a)	17.0	0.0	1.6	0.0	1.9	0.0	0.0	0.0	0.0	0.0	19.1
Craycroft, AZ (Chow et al., 1992a)	13.0	0.0	8.3	0.0	0.7	0.6	1.2 <sup>a</sup>	0.0	0.0	0.0	23.4
Downtown Tucson, AZ (Chow et al., 1992a)	26.0	5.1	14.0	0.0	1.0	0.2	1.3 <sup>a</sup>	0.0	0.0	0.0	48.0
Hayden 1, AZ (Garfield) (Ryan et al., 1988)	5.0	2.0 <sup>b</sup>	0.0	0.0	4.0	0.0	74.0 <sup>c</sup>	5.0 <sup>d</sup>	1.0 <sup>e</sup>	0.0	105.0
Hayden 2, AZ (Jail) (Ryan et al., 1988)	21.0	4.0 <sup>b</sup>	0.0	0.0	4.0	0.0	28.0 <sup>c</sup>	0.0	1.0 <sup>e</sup>	0.0	59.0
Orange Grove, AZ (Chow et al., 1992a)	20.0	0.0	15.0	0.0	0.4	0.4	0.0	0.0	0.0	0.0	34.2
Phoenix, AZ (Estrella Park) (Chow et al., 1991)	37.0	0.0	10.0	0.9	1.6	0.0	0.0	0.0	0.0	0.0	55.0
Phoenix, AZ (Gunnery Rg.) (Chow et al., 1991)	20.0	0.0	5.5	0.0	1.0	0.0	0.0	0.0	0.0	0.0	27.0
Phoenix, AZ (Pinnacle Pk.) (Chow et al., 1991)	7.0	0.0	2.9	1.0	0.9	0.0	0.0	0.0	0.0	0.0	12.0
Rillito, AZ (Thanukos et al., 1992)	42.7	13.8 <sup>b</sup>	1.2 <sup>f</sup>	0.0	0.0	0.0	11.6 <sup>g</sup>	0.0	0.0	0.0	79.5
Scottsdale, AZ (Chow et al., 1991)	25.0	0.0	19.0	7.4	0.6	3.6	0.0	0.0	0.0	0.0	55.0
West Phoenix, AZ (Chow et al., 1991)	30.0	0.0	25.0	10.0	0.4	3.1	0.0	0.0	0.0	0.0	69.0
Anacapa Island, CA (Chow et al., 1994b)	2.2	0.0	4.9	0.0	3.4	1.0	9.6 <sup>h</sup>	0.0	0.0	0.0	26.0
Anaheim, CA (Gray et al., 1988)	21.2	0.0	4.1 <sup>i</sup>	0.0	7.0	9.8	0.4 <sup>j</sup>	1.4 <sup>h</sup>	8.2 <sup>k</sup>	0.0	52.1
Anaheim, CA (Summer) (Watson et al., 1994a)	11.4	0.0	8.5	0.0	9.0	2.9	0.0 <sup>j</sup>	6.5 <sup>h</sup>	0.0	0.0	51.3
Anaheim, CA (Fall) (Watson et al., 1994a)	13.2	0.0	37.2	0.0	3.7	38.5	0.0 <sup>j</sup>	3.1 <sup>h</sup>	0.0	0.0	104.0
Azusa, CA (Summer) (Watson et al., 1994a)	34.9	0.0	15.9	0.0	11.4	6.1	0.0 <sup>j</sup>	5.7 <sup>h</sup>	0.0	0.0	92.1
Bakersfield, CA (Magliano, 1988)	27.4	3.0	5.5	9.6 <sup>j</sup>	5.6	0.0	0.5 <sup>j</sup>	0.0	0.0	0.0	67.6
Bakersfield, CA (Chow et al., 1992b)	42.9	1.6	7.7	6.5	5.5	12.7	1.0 <sup>m</sup>	1.5 <sup>n</sup>	0.6 <sup>k</sup>	0.0	79.6
Burbank, CA (Gray et al., 1988)	21.3	0.0	6.1 <sup>i</sup>	0.0	7.2	10.2	0.1 <sup>j</sup>	0.9 <sup>h</sup>	9.8 <sup>k</sup>	0.0	56.6
Burbank, CA (Summer) (Watson et al., 1994a)	14.0	0.0	17.0	0.0	12.4	6.5	0.0 <sup>j</sup>	5.7 <sup>h</sup>	0.0	0.0	72.3
Burbank, CA (Fall) (Watson et al., 1994a)	11.0	0.0	39.1	0.0	3.1	25.1	0.0 <sup>j</sup>	1.9 <sup>h</sup>	0.0	0.0	94.8
Chula Vista 1, CA (Bayside) (Cooper et al., 1988)	6.7	0.0	0.8	0.0	7.5	0.0	0.4 <sup>j</sup>	2.7 <sup>h</sup>	2.0 <sup>k</sup>	0.0	28.8
Chula Vista 2, CA (Del Ray) (Cooper et al., 1988)	8.2	0.3	1.5	0.0	8.9	0.0	0.6 <sup>j</sup>	1.8 <sup>h</sup>	0.0	0.0	31.1
Chula Vista 3, CA (Cooper et al., 1988)	9.7	0.3	1.4	0.0	8.2	0.0	0.6 <sup>j</sup>	1.7 <sup>h</sup>	0.0	0.0	29.6
Claremont, CA (Summer) (Watson et al., 1994a)	19.4	0.0	14.4	0.0	9.5	6.3	0.0 <sup>j</sup>	4.7 <sup>h</sup>	0.0	0.0	70.0
Crows Landing, CA (Chow et al., 1992b)	32.2	0.0	2.2	3.4	2.8	6.5	0.5 <sup>m</sup>	1.5 <sup>n</sup>	1.2 <sup>k</sup>	0.0	52.5



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TABLE 5-1 (cont'd). RECEPTOR MODEL SOURCE CONTRIBUTIONS TO PM<sub>10</sub>.

Sampling Site	$\mu\text{g}/\text{m}^3$										Measured PM <sub>10</sub> Concentration
	Primary Geological	Primary Construction	Primary Motor Vehicle Exhaust	Primary Vegetative Burning	Secondary Ammonium Sulfate	Secondary Ammonium Nitrate	Misc. Source 1	Misc. Source 2	Misc. Source 3	Misc. Source 4	
Downtown Los Angeles, CA (Gray et al., 1988)	23.8	0.0	6.4 <sup>i</sup>	0.0	7.6	11.2	0.0	1.3 <sup>h</sup>	7.9 <sup>k</sup>	0.0	60.2
Downtown Los Angeles, CA (Summer) (Watson et al., 1994a)	12.7	0.0	16.2	0.0	13.0	4.4	0.0 <sup>j</sup>	6.5 <sup>h</sup>	0.0	0.0	67.6
Downtown Los Angeles, CA (Fall) (Watson et al., 1994a)	9.4	0.0	41.1	0.0	3.9	27.5	0.0 <sup>j</sup>	1.8 <sup>h</sup>	0.0	0.0	98.6
Fellows, CA (Chow et al., 1992b)	29.0	1.4	2.1	3.4	5.1	7.5	7.0 <sup>m</sup>	1.4 <sup>n</sup>	1.4 <sup>k</sup>	0.0	54.6
Fresno, CA (Magliano, 1988)	17.1	0.7	4.0	9.2 <sup>i</sup>	1.8	0.0	0.1 <sup>j</sup>	0.0	0.0	0.0	48.1
Fresno, CA (Chow et al., 1992b)	31.8	0.0	6.8	5.1	3.6	10.4	0.3 <sup>m</sup>	1.0 <sup>n</sup>	0.1 <sup>k</sup>	0.0	71.5
Hawthorne, CA (Summer) (Watson et al., 1994a)	7.5	0.0	5.6	0.0	15.0	0.6	0.0 <sup>j</sup>	7.0 <sup>h</sup>	0.0	0.0	45.9
Hawthorne, CA (Fall) (Watson et al., 1994a)	8.9	0.0	35.1	0.0	5.1	20.4	0.0 <sup>j</sup>	3.7 <sup>h</sup>	0.0	0.0	85.1
Indio, CA (Kim et al., 1992)	33.0	3.0	4.4	7.1	3.6	4.1	0.2 <sup>j</sup>	1.0 <sup>h</sup>	0.0	0.0	58.0
Kern Wildlife Refuge, CA (Chow et al., 1992b)	15.1	2.0	2.2	4.0	3.3	1.5	0.5 <sup>m</sup>	1.5 <sup>n</sup>	0.7 <sup>k</sup>	0.0	47.8
Lennox, CA (Gray et al., 1988)	16.0	0.1	4.6 <sup>i</sup>	0.0	7.6	7.9	0.2 <sup>j</sup>	3.1 <sup>h</sup>	7.6 <sup>k</sup>	0.0	46.9
Long Beach, CA (Gray et al., 1988)	20.7	0.0	5.1 <sup>i</sup>	0.0	8.0	9.2	0.1 <sup>j</sup>	2.0 <sup>h</sup>	6.4 <sup>k</sup>	0.0	51.9
Long Beach, CA (Summer) (Watson et al., 1994a)	11.1	0.0	6.3	0.0	10.9	0.8	0.1 <sup>j</sup>	2.2 <sup>h</sup>	0.0	0.0	46.1
Long Beach, CA (Fall) (Watson et al., 1994a)	11.3	0.0	42.8	0.0	3.8	23.2	0.0 <sup>j</sup>	2.7 <sup>h</sup>	0.0	0.0	96.1
Magnolia, CA (Chow et al., 1992c)	31.7	0.0	11.2	0.0	4.9	19.7	0.3 <sup>j</sup>	1.2 <sup>h</sup>	1.2 <sup>o</sup>	0.0	66.0
Palm Springs, CA (Kim et al., 1992)	16.4	1.4	2.3	5.1	3.7	4.2	0.1 <sup>j</sup>	0.5 <sup>h</sup>	0.0	0.0	35.1
Riverside, CA (Chow et al., 1992c)	32.6	0.0	7.0	0.0	4.8	21.4	0.3 <sup>j</sup>	1.3 <sup>h</sup>	1.1 <sup>o</sup>	0.0	64.0
Rubidoux, CA (Gray et al., 1988)	43.1	4.0 <sup>j</sup>	5.6 <sup>i</sup>	0.0	6.4	21.3	0.3 <sup>j</sup>	1.0 <sup>h</sup>	5.9 <sup>k</sup>	0.0	87.4
Rubidoux, CA (Summer) (Watson et al., 1994a)	34.9	4.5	17.3	0.0	9.5	27.4	0.0 <sup>j</sup>	5.1 <sup>h</sup>	0.0	0.0	114.8
Rubidoux, CA (Fall) (Watson et al., 1994a)	19.2	16.1	30.3	0.0	2.1	31.6	0.0 <sup>j</sup>	1.1 <sup>h</sup>	0.0	0.0	112.0
Rubidoux, CA (Chow et al., 1992c)	48.0	0.0	10.2	0.0	5.3	21.7	0.4 <sup>j</sup>	1.5 <sup>h</sup>	5.7 <sup>o</sup>	0.0	87.0
San Jose, CA (4th St.) (Chow et al., 1994a)	13.1	0.0	9.2	31.3	2.3	13.3	0.9 <sup>h</sup>	0.0	0.0	0.0	68.4
San Jose, CA (San Carlos St.) (Chow et al., 1994a)	11.8	0.0	8.9	31.3	2.1	12.8	0.7 <sup>h</sup>	0.0	0.0	0.0	64.9
San Nicolas Island, CA (Summer) (Watson et al., 1994a)	1.6	0.0	0.9	0.0	3.7	0.5	0.0 <sup>j</sup>	4.3 <sup>h</sup>	0.0	0.0	17.4
Santa Barbara, CA (Chow et al., 1994b)	9.5	0.0	14.7	0.0	3.2	1.0	6.4 <sup>h</sup>	0.0	0.0	0.0	34.0
Santa Barbara, CA (GTC) (Chow et al., 1994b)	3.2	0.0	5.1	0.0	2.8	0.5	6.3 <sup>h</sup>	0.0	0.0	0.0	20.5
Santa Maria, CA (Chow et al., 1994b)	7.4	0.0	7.6	0.0	3.1	1.4	5.7 <sup>h</sup>	0.0	0.0	0.0	27.0

TABLE 5-1 (cont'd). RECEPTOR MODEL SOURCE CONTRIBUTIONS TO PM<sub>10</sub>.

Sampling Site	$\mu\text{g}/\text{m}^3$										Measured PM <sub>10</sub> Concentration
	Primary Geological	Primary Construction	Primary Motor Vehicle Exhaust	Primary Vegetative Burning	Secondary Ammonium Sulfate	Secondary Ammonium Nitrate	Misc. Source 1	Misc. Source 2	Misc. Source 3	Misc. Source 4	
Santa Ynez, CA (Chow et al., 1994b)	4.6	0.0	6.8	0.0	2.2	0.6	4.0 <sup>h</sup>	0.0	0.0	0.0	19.0
Stockton, CA (Chow et al., 1992b)	34.4	0.5	5.2	4.8	3.1	7.0	0.7 <sup>m</sup>	1.8 <sup>n</sup>	0.0 <sup>k</sup>	0.0	62.4
Upland, CA (Gray et al., 1988)	25.4	0.4 <sup>i</sup>	4.1 <sup>i</sup>	0.0	6.4	14.5	0.6 <sup>j</sup>	0.6 <sup>h</sup>	7.8 <sup>k</sup>	0.0	58.0
Vandenberg AFB, CA (Watt Road) (Chow et al., 1994b)	4.5	0.0	3.2	0.0	1.9	1.0	9.3 <sup>h</sup>	0.0	0.0	0.0	20.6
Telluride 1, CO (Central) (Dresser and Baird, 1988)	32.0	0.0	0.0	98.7	0.0	0.0	61.3 <sup>p</sup>	0.0	0.0	0.0	208.0
Telluride 2, CO (Society Turn) (Dresser and Baird, 1988)	12.1	0.0	0.0	7.3	0.0	0.0	7.3 <sup>p</sup>	0.0	0.0	0.0	27.0
Pocatello, ID (Houck et al., 1992)	8.3	7.5 <sup>q</sup>	0.1	0.0	0.0	0.0	0.0	0.0	84.1 <sup>r</sup>	0.0	100.0
S. Chicago, IL (Hopke et al., 1988)	27.2	2.4	2.8	0.0	15.4 <sup>s</sup>	0.0	15.1 <sup>t</sup>	2.2 <sup>u</sup>	0.0	0.0	80.1
S.E. Chicago, IL (Vermette et al., 1992)	14.7 <sup>v</sup>	0.0	0.9 <sup>f</sup>	0.0	7.7	0.0	0.8 <sup>t</sup>	0.3 <sup>h</sup>	1.1 <sup>w</sup>	7.7 <sup>g</sup>	41.0
Reno, NV (Non-sweeping) (Chow et al., 1990)	9.7	0.0	8.7	0.1	0.6	0.2	0.0	0.0	0.0	0.0	20.4
Reno, NV (Sweeping) (Chow et al., 1990)	11.8	0.0	11.0	1.2	0.8	0.2	0.0	0.0	0.0	0.0	24.9
Reno, NV (Chow et al., 1988)	14.9	0.0	10.0	1.9	1.3	0.6	0.0	0.0	0.0	0.0	30.0
Sparks, NV (Chow et al., 1988)	15.1	0.0	11.6	13.4	2.7	0.9	0.0	0.0	0.2 <sup>k</sup>	0.0	41.0
Verdi, NV (Chow et al., 1988)	7.8	0.0	4.0	1.1	0.9	0.1	0.0	0.0	0.0	0.0	15.0
Follansbee, OH (Skidmore et al., 1992)	10.0	0.0	35.0	0.0	16.0	--	9.3 <sup>t</sup>	0.0	0.0	0.0	66.0
Mingo, OH (Skidmore et al., 1992)	12.0	0.0	14.0	4.1	15.0	--	3.4 <sup>t</sup>	11.0 <sup>x</sup>	0.0	0.0	60.0
Sewage Plant, OH (Skidmore et al., 1992)	22.0	0.0	12.0	0.0	13.0	--	6.6 <sup>t</sup>	8.7 <sup>x</sup>	0.0	0.0	62.0
Steubenville, OH (Skidmore et al., 1992)	8.3	0.0	14.0	0.8	14.0	--	3.8 <sup>t</sup>	5.0 <sup>x</sup>	0.0	0.0	46.0
WTOV Tower, OH (Skidmore et al., 1992)	7.4	0.0	16.0	0.2	15.0	--	3.4 <sup>t</sup>	7.9 <sup>x</sup>	0.0	0.0	49.0

<sup>a</sup>Smelter background aerosol.<sup>b</sup>Cement plant sources, including kiln stacks, gypsum pile, and kiln area.<sup>c</sup>Copper ore.<sup>d</sup>Copper tailings.<sup>e</sup>Copper smelter building.<sup>f</sup>Heavy-duty diesel exhaust emission.<sup>g</sup>Background aerosol.<sup>h</sup>Marine aerosol, road salt, and sea salt plus sodium nitrate.<sup>i</sup>Motor vehicle exhaust from diesel and leaded gasoline.<sup>j</sup>Residual oil combustion.<sup>k</sup>Secondary organic carbon.<sup>l</sup>Biomass burning.<sup>m</sup>Primary crude oil.<sup>n</sup>NaCl + NaNO<sub>3</sub>.<sup>o</sup>Lime.<sup>p</sup>Road sanding material.<sup>q</sup>Asphalt industry.<sup>r</sup>Phosphorus/phosphate industry.<sup>s</sup>Regional sulfate.<sup>t</sup>Steel mills.<sup>u</sup>Refuse incinerator.<sup>v</sup>Local road dust, coal yard road dust, steel haul road dust.<sup>w</sup>Incineration.<sup>x</sup>Unexplained mass.

1 more than 50% of the average  $PM_{10}$  mass concentration. The average fugitive dust source  
2 contribution is highly variable among sampling sites within the same urban areas, as seen by  
3 differences between the Central Phoenix ( $33 \mu\text{g}/\text{m}^3$ ) and Scottsdale ( $25 \mu\text{g}/\text{m}^3$ ) in Arizona.  
4 It is also highly variable between seasons, as evidence by the summer and winter  
5 contributions at Rubidoux, CA. In general, these studies found that fugitive dust was  
6 chemically similar, even though it came from different emitters, so that further  
7 apportionment into sub-categories was not possible. An exception was for road sanding in  
8 Telluride, CO. Road sand often contains salts that allow it to be distinguished from other  
9 fugitive dust sources. It is usually the only exposed fugitive dust source when other sources  
10 are covered by snowpack. Dust from some construction activities and cement plants can also  
11 be separated from other sources due to enrichments in calcium content of these emissions, as  
12 seen in studies at Rubidoux, CA and Rillito, AZ (near cement plants), in Pocatello, ID (near  
13 chemical and fertilizer production plants), and Tucson, AZ (where a nearby community  
14 center was undergoing renovation).

15 Primary motor vehicle exhaust contributions account for up to approximately 40% of  
16 average  $PM_{10}$  at many of the sampling sites. Vehicle exhaust contributions are also variable  
17 at different sites within the same non-attainment area. Vegetative biomass burning, which  
18 includes agricultural fires, wildfires, prescribed burning, and residential wood combustion,  
19 was found to be significant at residential sampling sites such as: Craycroft, Scottsdale, and  
20 West Phoenix, AZ; San Jose, Fresno, Bakersfield, and Stockton, CA; Telluride, CO; Sparks,  
21 NV; and Mingo, OH. The predominance of these contributions during winter months and  
22 the local rather than regional coverage indicates that residential wood combustion was the  
23 major sub-category, even though chemical profiles are too similar to separate residential  
24 combustion from other vegetative burning sources. For example, Chow et al. (1988) show  
25 substantial differences between the residential Sparks, NV and urban-commercial Reno, NV  
26 burning contributions even though these sites are separated by less than 10 km.

27 Sites near documented industrial activity show evidence of that activity, but not  
28 necessarily from primary particles emitted by point sources. Hayden, AZ, for example,  
29 contains a large smelter, but the major smelter contributions appear to arise from fugitive  
30 emissions of or copper tailings rather than stack emissions. Secondary sulfate contributions  
31 at Hayden were low, even though sulfur dioxide emissions from the stack were substantial

1 during the time of the study. Fellows, CA, is in the midst of oilfields facilities that burn  
2 crude oil for tertiary oil extraction. The Follansbee, Mingo, Sewage Plant, Steubenville, and  
3 Tower sites in Ohio are all close to each other in the Ohio River Valley and show evidence  
4 of the widespread steel mill emissions in that area.

5 Marine aerosol is found, as expected, at coastal sites such as Long Beach, San Nicholas  
6 Island, and Anacapa Island, CA, but these contributions are relatively low compared to  
7 contributions from manmade sources.

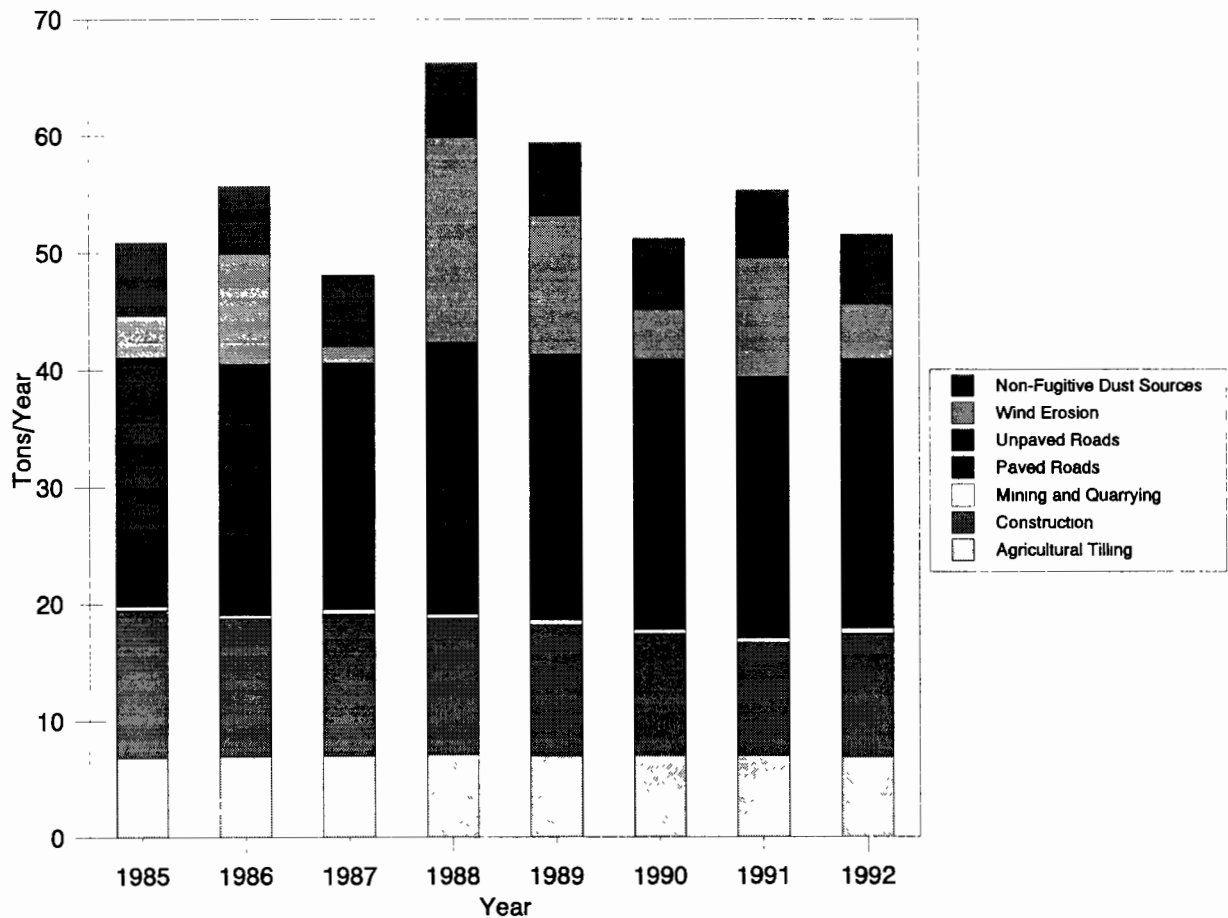
8 Of great importance are the contributions from secondary ammonium sulfate and  
9 ammonium nitrate. These are especially noticeable at sites in California's San Joaquin  
10 Valley (Bakersfield, Crows Landing, Fellow, Fresno, Kern Wildlife, and Stockton), in the  
11 Los Angeles area, and in the Ohio River Valley. Nitrate was not measured at the Ohio sites,  
12 but there was a large portion of unexplained mass in the CMB source apportionments that  
13 could be composed in part by ammonium nitrate.

14 Other aerosol characterization and receptor model source apportionment studies have  
15 been performed for  $PM_{10}$  and  $PM_{2.5}$  that could be added to Table 5-1. The general  
16 conclusions drawn from this table would not change substantially.

## 19 **5.4 NATIONAL EMISSION RATES AND ANNUAL TRENDS**

20 Figure 5-1 (U.S. Environmental Protection Agency, 1993) shows the primary  $PM_{10}$   
21 emissions estimated for the period of 1985 through 1992 using the National Trends data base.  
22  $PM_{10}$  fugitive dust emissions were not estimated prior to 1985. Figure 5-1 shows fugitive  
23 dust from paved and unpaved roads, agricultural operations, construction, and soil erosion to  
24 constitute ~90% of nationwide primary emissions. All of the emissions have remained  
25 relatively constant over the 8-year period except for those from soil erosion.

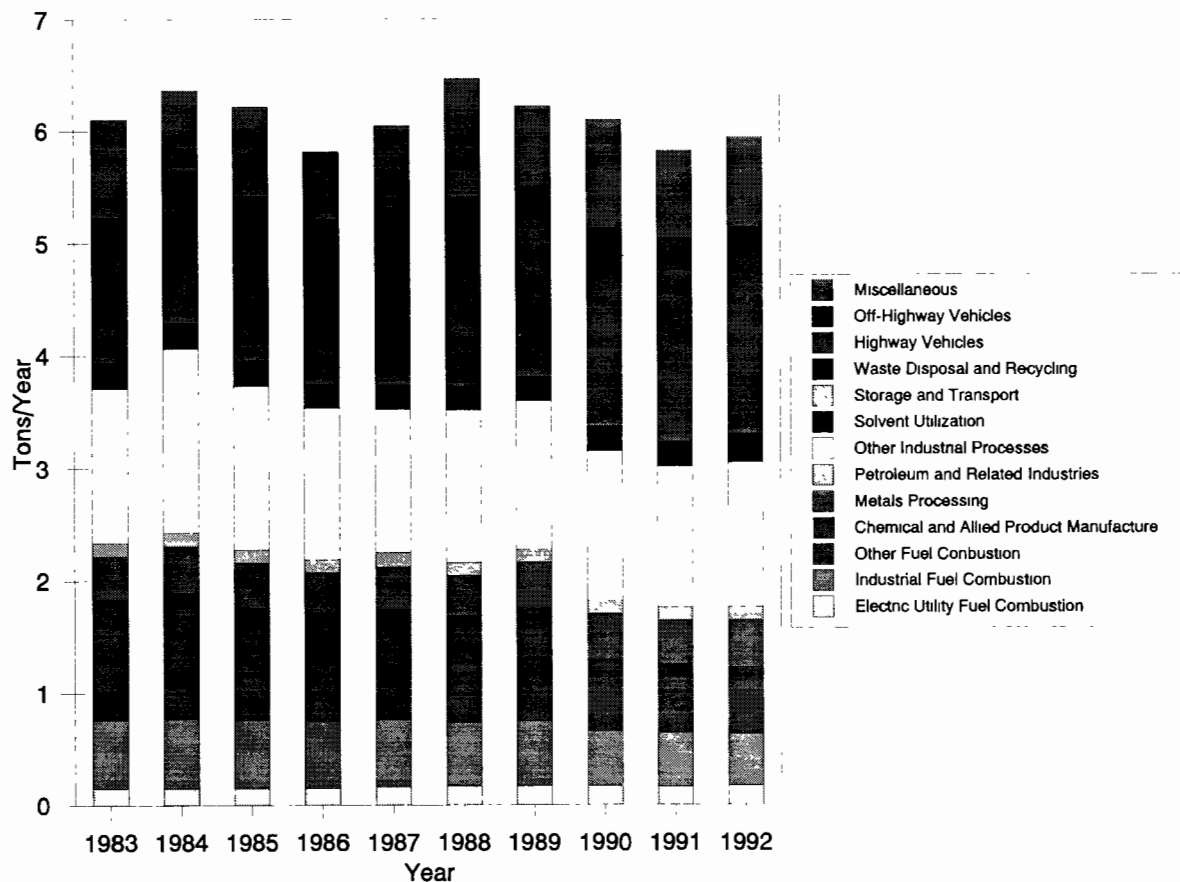
26 A more detailed geographical breakdown of the erosion emissions shows that the  
27 majority of wind erosion occurs in the "dustbowl" region of the United States that includes  
28 the Oklahoma and Texas panhandles (Barnard and Stewart, 1992; Fryrear, 1992). Wind-  
29 induced erosion estimates are also highly influenced by annual precipitation and wind-speed  
30 distributions. Erosion emissions estimates during 1986, 1989, and 1991 were approximately  
31 twice those determined in other years owing to changes in these variables.



**Figure 5-1. Primary PM<sub>10</sub> emissions estimated for 1983 to 1992.**

Figure 5-2 (U.S. Environmental Protection Agency, 1993) expands the non-fugitive dust portion of Figure 5-1 into the indicated sub-categories. PM<sub>10</sub> emissions from these have been extrapolated from early TSP estimates back to 1983. The major non-fugitive dust emitters are other industrial processes (several of which include materials handling which are sources of industrial fugitive PM<sub>10</sub>) and exhaust from highway vehicles. Each of these emitters is only ~2% of the total emissions noted in Table 5-1. Fuel combustion from utilities, industrial, and other sources together contribute between 1 to 2% to total primary particle emissions. Solvent use and petroleum storage and transport are included for comparability to gaseous emissions inventories and have no primary particle emissions.

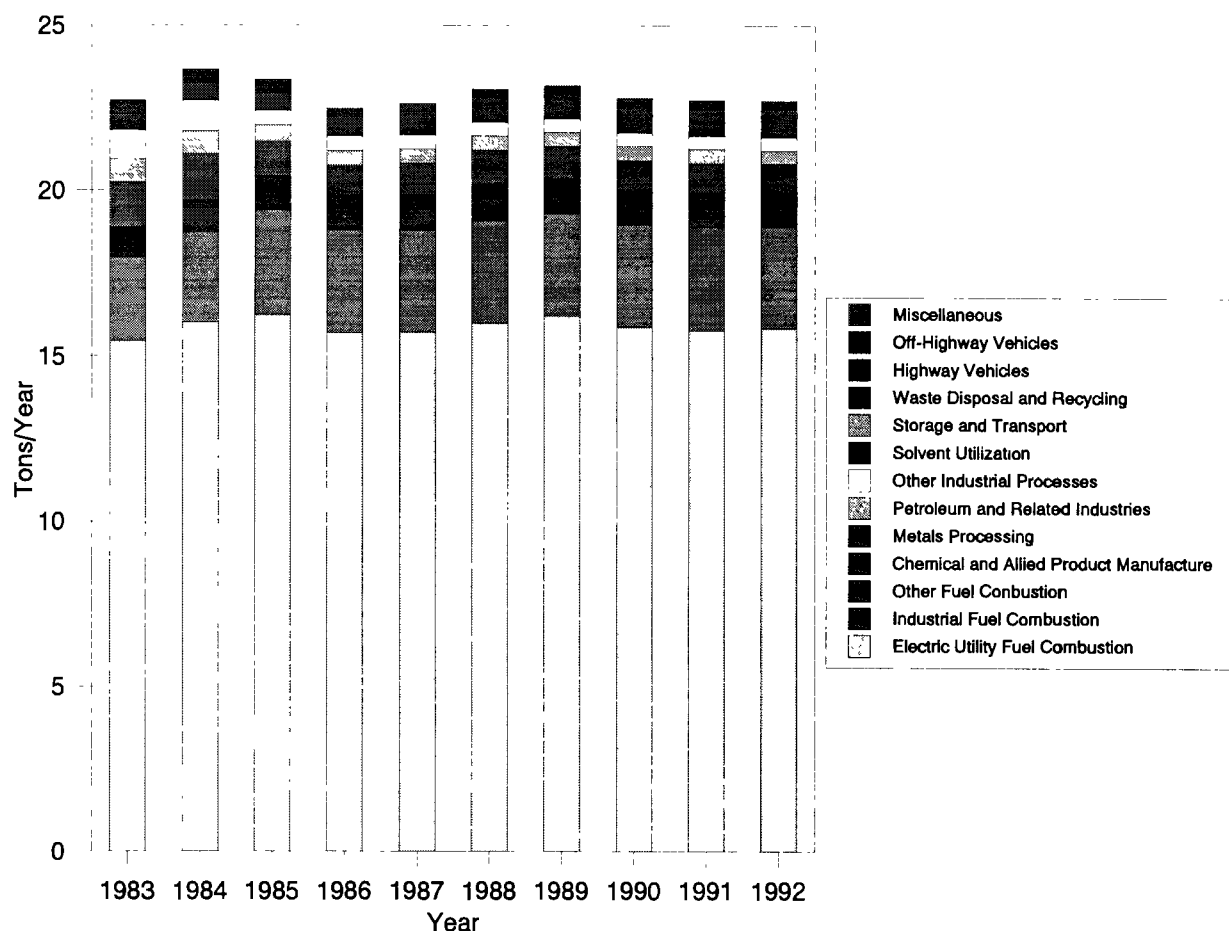
Industrial fuel combustion emissions were reduced by one-third and other fuel combustion emissions were reduced by one half between 1983 and 1992, mostly owing to



**Figure 5-2. Sub-categories of non-fugitive dust emissions, 1983 to 1992.**

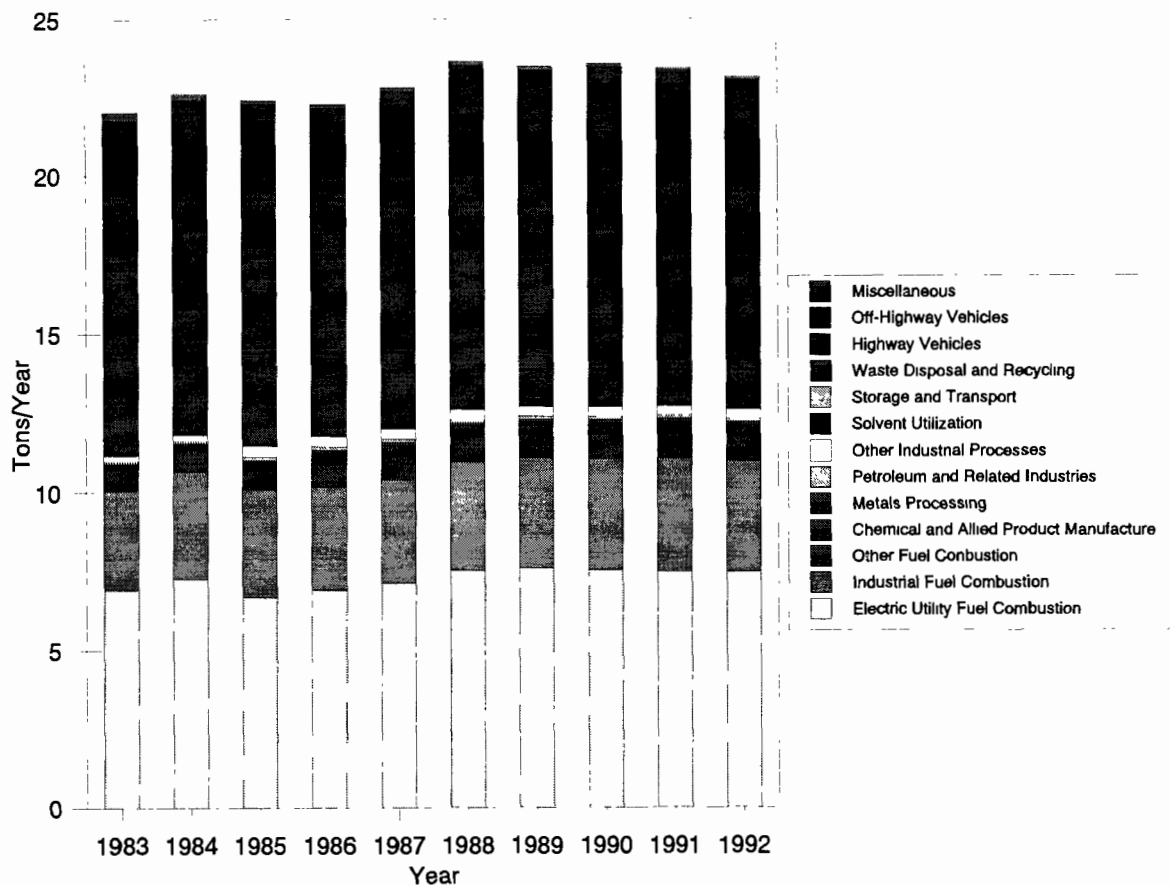
increased use of natural gas and the addition of particle removal devices as part of source permitting. On-highway vehicle emissions increased by 50%, despite lower emissions and better gas mileage in newer vehicles. This is primarily due to large increases in the number of vehicle miles traveled. To the greatest extent possible, U.S. EPA (1993) adjusted previous years emissions to conform to current emissions estimation methods, so the year-to-year changes reflect real changes in emissions rather than changes in the estimation methods.

Figures 5-3 through 5-5 show national emissions for sulfur dioxide, oxides of nitrogen, and VOCs for the 1983 through 1992 period. As found by U.S. EPA (1982), electric utilities account for the largest fraction of sulfur dioxide, nearly 70% of total emissions. These emissions have not changed substantially over the 10 years reported, and when translated into metric tons, they are lower than the 19.4 million short tons/year estimated for



**Figure 5-3. National emissions of sulfur dioxide, 1983 to 1992.**

1 utilities in 1978 by U.S. EPA (1982). This difference may be due to methodological  
 2 changes. Emissions from industrial fuel combustion increased by approximately 20% from  
 3 1983 to 1985, then leveled off at about 3.1 million short tons/year. A similar increase  
 4 between 1983 and 1985 is found for chemical manufacturing, with a leveling off at 0.42  
 5 million short tons/year after 1985. Sulfur dioxide emissions from highway vehicles increased  
 6 by 60% between 1983 and 1992, while off-highway vehicle emissions decreased to a low of  
 7 0.23 million short tons/year in 1986, then slowly increased to 0.27 million short tons per  
 8 year by 1990. Major sulfur dioxide emissions reductions are observed for petroleum  
 9 processing and other industrial processes, with decreases of 40% to 50% over the ten year  
 10 period. In total, however, sulfur dioxide emissions estimates in 1992 are identical to those  
 11 found in 1983 at 22.73 million short tons/year.

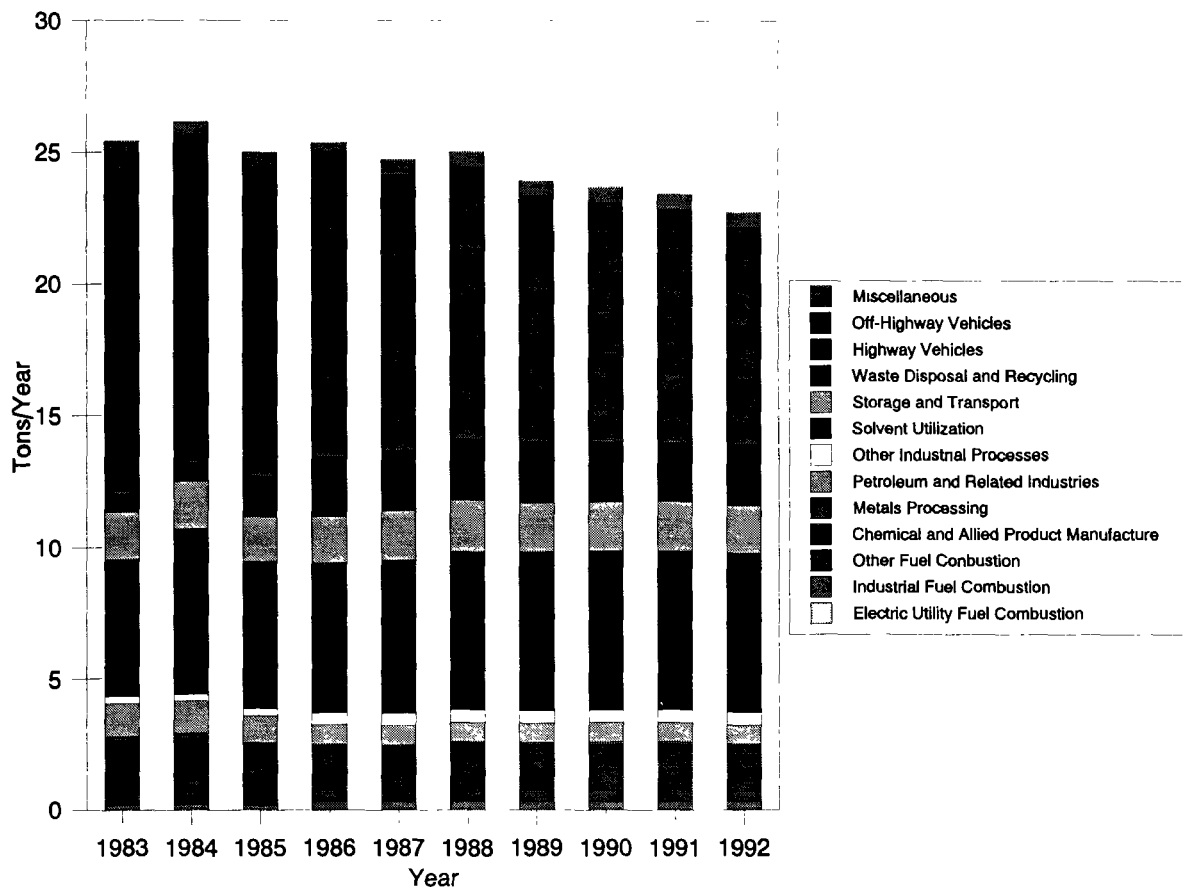


**Figure 5-4. National emissions for oxides of nitrogen, 1983 to 1992.**

Figure 5-4 shows a less than 5% increase in total nitrogen oxides emissions over the ten year period. Utility and motor vehicle emissions are about equal at ~7.5 million short tons/year, and together these account for two-thirds of total emissions. Industrial and other fuel combustion and off-highway vehicles account for nearly all of the remaining third. There is little change in any of the source categories from year to year, with slight reductions for highway vehicles and slight increases for utility, industrial and other fuel combustion, and off-highway vehicles.

Volatile organic compound (VOC) emissions in Figure 5-5 are dominated by highway vehicles and solvent use that account for nearly 60% of total emissions. Off-highway vehicles, petroleum-related industries, chemical manufacturing, and petroleum storage and transport account for most of the remaining amounts. VOC emissions from highway vehicles





**Figure 5-5. National emissions for volatile organic compounds, 1983 to 1992.**

1 were reduced by 40%, in spite of increased vehicle mileage. Most of this is due to the  
 2 presumed effectiveness of emissions controls on newer vehicles. VOC emissions from  
 3 petroleum industries were also reduced substantially, as were those from miscellaneous  
 4 sources. Emissions from other categories increased slightly or remained approximately the  
 5 same. Although U.S. EPA (1993) includes a category for “natural sources,” there are  
 6 entries of zero emissions for all years for the category and it has, therefore, been omitted  
 7 from Figure 5-5.

8 The spatially and temporally averaged emissions rates presented above were compiled  
 9 according to standardized procedures and provide a good starting point for the identification  
 10 of potential contributors to ambient particulate concentrations which exceed the PM NAAQS.

1 These estimates are insufficient, however, to develop effective emissions reductions strategies  
2 for specific standard exceedances that might affect public health.

3 Several potentially important source categories are not included in current inventories.  
4 For example, Hildemann et al. (1991) identify charbroiling and frying of meat in homes and  
5 restaurants as a potential PM source neglected in previous PM<sub>10</sub> inventories. Their studies  
6 show almost all of these emissions to be in the PM<sub>2.5</sub> size fraction. Emissions rates  
7 measured for regular and extra-lean hamburger meat which was charbroiled or fried on a  
8 restaurant-style grill (with commonly used grease traps) were: 40 g/kg for charbroiled  
9 regular meat; 7.1 g/kg for charbroiled extra-lean meat; 1.1 g/kg for fried regular meat; and  
10 1.4 g/kg for fried extra-lean meat. Fugitive dust emitters such as golf course turf  
11 replacement, feedlots and dairies, equestrian events, off-road vehicle competitions, and  
12 parking lot sweeping are not quantified. These emissions may be small on a national basis  
13 but could be important in specific non-attainment areas. Vegetative burning sources are also  
14 omitted, as are potential precursor VOC emissions from biogenic sources. Lamb et al.  
15 (1993) estimate national VOC emissions from a variety of vegetative sources (based on land  
16 use maps) to be  $\approx$  47 million short tons/year. This is twice the emissions from all other  
17 sources combined in Figure 5-5.

18 As noted above, ammonia is a major participant in atmospheric reactions which form  
19 ammonium sulfate and ammonium nitrate, but it is not included in the National Trends  
20 inventory. Only a small fraction of total ammonia emissions are related to activity levels  
21 which are quantified by current emissions inventory methods. Russell and Cass (1986)  
22 attributed 52% of all ammonia emissions in the Los Angeles area to livestock; 23% to dogs,  
23 cats, and humans (allocated by population); 15% to bare soil surfaces; 9% to sewage  
24 treatment; and 5% to fertilizer applications. Less than 4% of ammonia emissions were  
25 attributed to stationary and mobile fuel combustion sources. For 27 European countries,  
26 Buijsman et al. (1987) estimated that 81% of anthropogenic ammonia is emitted by livestock  
27 waste, 17% by fertilizers, and less than 2% by industrial sources.

28 Annual averages do not reflect the seasonality of certain emissions. Residential wood  
29 burning in fireplaces and stoves, for example, is a seasonal practice which usually reaches its  
30 peak during December in response to very cold weather. Cold weather also affects motor

1 vehicle exhaust emissions, both in terms of chemical composition and emission rates (e.g.,  
2 Watson et al., 1990c). Planting, harvesting, and fertilizing and harvesting are also seasonal.

3 Several of the sources in Figures 5-1 through 5-5 are episodic rather than continuous  
4 emitters. This is especially true of prescribed and structural fires and fugitive dust  
5 emissions. For example, Engineering Science (1988) based windblown dust estimates for  
6 Phoenix, AZ, on high wind speeds that occur from 5 to 10 times per year. Although  
7 windblown dust emissions are low on an annual average, they are likely to be quite large  
8 during those few episodes when wind speeds are high.

9 Source categories are not adequately desegregated. This is especially true of the mobile  
10 sources, in which particulate emissions from several vehicle types and emissions points are  
11 combined in emissions models. Construction dust estimates, for example, are based on acres  
12 under construction rather than on the individual processes involved in construction. This  
13 complicates the evaluation of specific control strategies which might target specific vehicles  
14 or processes.

15 As shown in Table 5-1, there is substantial variation in contributions to suspended  
16 particles even for nearby sources. The national averages in Figures 5-1 through 5-5 do not  
17 take into account the regionality and zones of influence of different emissions sources.

18 Finally, the emissions factors applied to activity data are of questionable accuracy. For  
19 example, Engineering Science (1988) took many samples from paved and unpaved roadways  
20 in Phoenix, AZ, and they found silt loadings ranging from 0.02 to 0.75 grains/ft<sup>2</sup>. An  
21 average of these measurements was used to represent the loadings for all paved roads. It is  
22 very likely that the loadings of suspendable dust on paved roads varies over time in ways  
23 which can never be known.

24 Several of these deficiencies may be unimportant, and the source apportionments  
25 provided by receptor modeling allows their importance to be evaluated. Others of these  
26 deficiencies can, and should be, corrected by better emissions modeling methods. It is  
27 revealing, for example, that fugitive dust constitutes 90% of the annual average emissions  
28 inventory, but it seldom averages more than 50% of the contribution to average PM<sub>10</sub>  
29 concentrations as evidenced in Table 5-1. The contributions from primary motor vehicle  
30 exhaust, residential wood combustion, and industrial sources are definitely underestimated by  
31 the relative emissions from these sources in the national emissions inventory. Some of these

deficiencies, such as fugitive dust emissions, are probably intractable and the best that can be done is to estimate the uncertainties in these emissions and to value the data accordingly when decisions are made. These issues are examined in greater detail for major source categories in the next section.

## **5.5 EMISSIONS PROCESSES AND ESTIMATION METHODS**

The national emissions estimates shown in Figures 5-1 through 5-5 must be considered within the context of their estimation methods. Many of these methods are empirically derived, rather than process-related, and they are often extrapolated beyond the original empirical data sets used to derive them. The U.S. EPA (1982) did a credible job of describing estimation methods for industrial and natural sources, but it did not describe estimation methods for emissions from area and mobile sources. Since Table 5-1 shows that fugitive dust and motor vehicle are major contributors to suspended particles in several areas, this ensuing review will focus on methods to estimate such emissions.

### **5.5.1 Fugitive Dust**

Fugitive dust consists of geological material that is suspended into the atmosphere by natural wind and by anthropogenic activities from sources such as paved and unpaved roads, construction and demolition of buildings and roads, storage piles, wind erosion, and agricultural tilling. Though qualitative descriptions of fugitive dust emissions are easy to understand, translating these descriptions into quantitative estimates of emission rates, locations, temporal variability, and contributions to suspended particles measured at receptors has been a scientific and engineering challenge.

The movement of soil, and especially its suspension from the surface of the earth into the atmosphere, has been studied in many branches of science. "Aeolian dust," named for Aeolia, the Greek goddess of the wind, is a major discipline in the fields of geology and archaeology (Pye, 1987). Wind erosion is of great concern to agriculturists and soil scientists. Meteorologists study interactions between the atmosphere and the earth's surface. Air pollution scientists devise methods to estimate contributions from dust suspended by the wind and other mechanisms to particles which might cause adverse health effects. The

published literature on the mechanisms for dust suspension are widely dispersed and not entirely comparable in terms of the properties studied and the units of measure. Much of the work on dust suspension has been done by agriculturists to minimize soil erosion. Erosion estimates include all of the mechanisms which might affect the removal of topsoil from a given area, one of which is suspension into the atmosphere.

Air pollution scientists are only concerned with that portion of eroded soil which is removed by suspension into the atmosphere and transported reasonable distances (typically greater than 100 m, the nominal dimension of significant fugitive dust emissions sources) without deposition to the surface. This suspension depends on: (1) particle size of the erodible material; (2) surface loadings; (3) moisture; (4) surface roughness; (5) wind speed and direction; (6) suspension height; and (7) vehicular ejection mechanisms. The current status of knowledge of each of these characteristics is discussed below.

Very little is known about the respirable size fractions in dust, despite their adverse health potential, long residence times, and high potential for vertical mixing. The most comprehensive information on particle sizes in geological material is contained in soil surveys compiled by the Soil Conservation Service (SCS). These surveys provide detailed boundaries for different soil types on 7.5-minute maps corresponding to U.S. Geological Survey (USGS) maps. The codes are associated with data in a printed summary which accompanies the maps for each survey area.

Particle sizes in soil surveys are indicated by qualitative descriptions in terms of the amount of sand (50 to 2,000  $\mu\text{m}$  geometric diameter), silt (2 to 50  $\mu\text{m}$  geometric diameter), and clay ( $< 2 \mu\text{m}$  geometric diameter). These particle size fractions in the soil survey are estimated by the individuals conducting the survey based on the visual similarity of the observed soils to a sub-set of soil samples which are submitted to particle size analysis in a laboratory. AP-42 emissions factors for fugitive dust often contain silt loading as one of their input variables largely because of the availability of SCS soil survey data for large portions of the United States.

The particle sizing procedure American Society for Testing and Materials, 1990a; 1990b) which is most commonly followed for soil surveys creates a soil/water suspension in which soil aggregates are broken into their component parts prior to sieving. While this disaggregation is useful for agricultural, construction, and other land uses, it is not especially

1 useful for estimating air pollution emissions because it does not accurately estimate the size  
2 of aggregates which are suspended by surface winds. Gillette (1980) applied two methods to  
3 determine the small particle content of soil which might be entrained by winds and cause  
4 pollution problems. The first method (i.e., gentle sieve) consists of drying the soil sample  
5 and sieving it gently with about twenty circular gyrations parallel to the plane of the sieve  
6 (Chepil, 1952). The second method (i.e., hard sieve) consists of up to one-half hour of  
7 vigorous shaking (usually using a shaking machine). The gentle sieve method best represents  
8 the suspension properties of the soil in the state in which it was sampled. The hard sieve  
9 method represents the potential of that soil for resuspension when disaggregating activities  
10 (e.g., vehicle traffic) occur. Gillette's threshold suspension velocity measurements apply to  
11 soil characteristics obtained by the gentle sieve method.

12 The size distribution of dust particles affects the suspension process. A flat bed of  
13 particles with diameters less than 20  $\mu\text{m}$  is very difficult to suspend by wind, as Bagnold  
14 (1937) showed by blowing wind in excess of 100 cm/sec over a bed of fine Portland cement.  
15 In this situation, there is no large cross section for wind to act on. A bed of large particles  
16 with diameters exceeding 1 mm interspersed with fine particles also mitigates suspension.  
17 Particles larger than 0.5 mm cannot be lifted by wind, but they absorb wind energy as they  
18 roll along the surface. They also shelter smaller particles on their lee sides from the effects  
19 of high wind speeds. Gillette and Stockton (1989) sprinkled glass spheres with diameters  
20 ranging from 2.4 to 11.2 mm onto a bed of glass spheres with sizes from 0.107 to 0.575  $\mu\text{m}$   
21 and found major reductions in suspension of the smaller particles. Bagnold (1941) estimated  
22 that 80  $\mu\text{m}$  particles are the most susceptible to suspension by wind, even though their large  
23 masses cause them to settle to the surface very rapidly.

24 The amount of suspendable dust on a surface influences how much might be suspended.  
25 Most surfaces are limited reservoirs, and the suspendable dust is depleted after a short time  
26 period. On exposed land, fine particle which are blown away often expose larger rocks  
27 which then shield the suspendable particles from the wind. When surfaces are continually  
28 disturbed, however, by very intense winds or by vehicular movement, they may become  
29 unlimited reservoirs which emit dust whenever winds exceed threshold suspension velocities.  
30 There are few (< 500 for the entire U.S.) reported data on the surface loadings of silt

( $< 75 \mu\text{m}$ ) and absolutely no data on surface loadings of respirable particle sizes for any surface included in fugitive dust emissions inventories.

Water adheres to individual soil particles, thus increasing their mass and mitigating suspension and transport. It also increases the cohesive forces among individual particles, and these forces often persist after the water has evaporated as evidenced by aggregates and surface crusts. Chepil (1956), Belly (1964), Bisal and Hsieh (1966), and Svasek and Terwindt (1974) show that substantially greater wind forces are needed when soil surface moisture is increased by less than 1% from its dry state.

Soil surveys include plastic limits and moisture limits to the ability of soils to absorb moisture. The "plastic limit" is the moisture content at which a soil changes from a semi-solid to a plastic. The plastic limit is determined by adding water to dry soil sample until it can be rolled into a coherent cylinder. Soil surveys also report liquid limits (the quantity of water required to create a slurry with the consistency of water), the infiltration rate (the movement of water through soil layers), and field moisture capacity.

Kinsey and Cowherd (1992) show how watering might reduce emissions at a construction site. A large pollution control benefit might be derived from initially doubling the area which is watered with lower benefits achieved as more water is applied to the site. Control efficiency is ultimately limited because grading operations are continually exposing dry earth and burying the moistened topsoil. A portion of this moistened soil adheres to the construction vehicles and can be carried out to paved and unpaved roads for subsequent resuspension.

While the moisture capacities and retentions of different geological materials are well documented in the soil surveys, the actual moisture content at a given time or place is not recorded. Thornthwaite (1931) proposed the ratio of precipitation to evaporation as an indicator of the availability of moisture for soils. Thornthwaite's major concern was the agricultural potential of land in different areas. The precipitation-evaporation effectiveness index (P-E index) is 10 times the sum of the monthly precipitation to evaporation ratios. Using precipitation, evaporation, and temperature data taken prior to 1921 at twenty-one U.S. monitoring sites, Thornthwaite (1931) devised an empirical precipitation-evaporation index (P-E index) to classify all North America as wet (P-E index  $> 128$ ), humid ( $64 < \text{P-E index} < 128$ ), sub-humid ( $32 < \text{P-E index} < 64$ ), semi-arid ( $16 < \text{P-E index}$

1 < 32), or arid (P-E index < 16). Much of the western United States is in the arid and  
2 semi-arid categories, while much of the eastern United States is in the humid category. The  
3 P-E index is cited for several AP-42 emission factors to estimate the moisture content of  
4 different soils.

5 Moisture content of soils will vary throughout the year depending on the frequency and  
6 intensity of precipitation events, irrigation, and relative humidity and temperature of the  
7 surrounding air. Large amounts of rain falling during 1 mo of a year will not be as effective  
8 in stabilizing dust as the same amount of rain interspersed at intervals throughout the year.

9 Moisture also causes dust to adhere to vehicle surfaces so that it can be carried out of  
10 unpaved roads, parking lots, and staging areas. Carryout also occurs when trucks exit  
11 heavily watered construction sites. This dust is deposited on paved roadway surfaces as it  
12 dries, where it is available for suspension far from its point of origin. Fugitive dust  
13 emissions from paved roads are often higher after rainstorms in areas where unpaved  
14 accesses are abundant, even though the rain may have flushed existing dust from many of the  
15 paved streets.

16 Windblown dust is a major contribution from all exposed surfaces. Each surface has a  
17 threshold velocity that depends on the cohesiveness of the particles and the surface  
18 roughness. Surface roughness height is the distance above average ground level at which the  
19 average wind velocity approaches zero. Surface roughness is also a meteorological concept;  
20 it is related to, but not identical to, measured heights of obstructions in an open area. Larger  
21 surface roughness shelters suspendable dust from suspension. Surface roughness depends  
22 both on the height and spacing of roughness elements, but is not well characterized for most  
23 surfaces. Friction velocity is the slope of the logarithm of wind speed versus elevation above  
24 ground level.

25 Dust arises due to suspension of the disturbed surface by wind. Chepil and Woodruff  
26 (1963) and Gillette and Hanson (1989) show that the amount of soil which can be suspended  
27 by wind depends on the particle size distribution, wind velocity at the soil surface, the  
28 roughness of the surface, the relative fractions of erodible (< 2  $\mu\text{m}$  diameter) and non-  
29 erodible (> 2  $\mu\text{m}$  diameter) material, and the cohesion of the soil particles with one another.  
30 Values for each of these variables affect other variables. For example, a higher moisture  
31 content increases cohesion among particles and shifts the size distribution to larger particles.



1 Larger agglomerations of small particles increase surface roughness which decreases wind  
2 speeds at the surface.

3 All of these variables collectively affect threshold friction velocity, which is  
4 experimentally determined by placing a wind tunnel over an example of the affected soil and  
5 measuring the velocity near the surface at which visible soil movement is first observed.  
6 Wind speeds must approach 0 near the earth's surface, and experiments show that wind  
7 speed increases exponentially with height. Both friction velocity and surface roughness are  
8 determined experimentally for different situations by taking measurements at different  
9 elevations. When the actual friction velocity is less than the threshold friction velocity for  
10 soil erosion, no particles are suspended into the atmosphere. Most ambient wind speed  
11 measurements are made at elevations between 5 and 10 m above ground level, and these  
12 must be translated to surface friction velocities to determine suspension. For a given  
13 threshold friction velocity, particulate emissions factors for windblown dust use the fastest  
14 mile wind speed as reported in the National Weather Service (NWS) Local Climatological  
15 Summaries. Gillette (1980) shows that threshold wind speeds vary from 0.19 to 1.82 m/s for  
16 disturbed soils. Even though emissions are initiated at these velocities, the wind force  
17 contains insufficient energy to suspend much of the erodible soil mass. The amount of dust  
18 suspended increases at approximately the cube of the wind speed above the threshold  
19 velocity.

20 Particles suspended into the atmosphere are acted upon by gravity in a downward  
21 direction and by atmospheric resistance in an upward direction. Every particle attains an  
22 equilibrium between these forces at its terminal settling velocity. The settling velocity  
23 increases as the square of the particle diameter or when the particle density increases. For  
24 very small particles ( $< 10 \mu\text{m}$  diameter), vertical air movements caused by turbulence can  
25 counteract the gravitational settling velocity and such particles can remain suspended for long  
26 times. Particle deposition for particles larger than  $\sim 20 \mu\text{m}$  diameter is dominated by the  
27 force of gravity, however. Transport distance depends on the initial elevation of a particle  
28 above ground level, the horizontal wind velocity component in the direction of interest at the  
29 particle elevation, and the gravitational settling velocity. For this reason, large TSP  
30 emissions rates do not give a good impression of contributions to suspended particles that are  
31 very distant from the receptor site. Pye (1987) shows vertical profiles for different sized

1 particles which might be elevated through a 100 m depth during a wind storm. The particles  
2 smaller than 10  $\mu\text{m}$  are nearly uniformly distributed through this depth, while the larger  
3 particles exhibit much higher concentrations closer to the surface.

4 Dust on paved roads, unpaved roads, parking lots, and construction sites is suspended  
5 by natural winds and vehicular movement. Vehicular traffic in these areas adds to  
6 suspension because tire contact with the road lifts particles into the air. Vehicle wakes  
7 create turbulent eddies which act much like natural winds to raise particles. The grinding of  
8 particles by tires against the road surface shifts the size distribution toward smaller particles,  
9 especially those in respirable size fractions.

10 Unpaved roads and other unpaved areas with vehicular activity are unlimited reservoirs  
11 of dust loading when vehicles are moving. These surfaces are always being disturbed, and  
12 wind erosion seldom has an opportunity to increase their surface roughness sufficiently to  
13 evade particle suspension. The U.S. EPA AP-42 emission factor (U.S. Environmental  
14 Protection Agency, 1988) for unpaved road dust emissions contains variables which account  
15 for silt loading, mean vehicle speed, mean vehicle weight, mean number of wheels, and  
16 number of days with detectable precipitation, to determine annual  $\text{PM}_{10}$  dust emissions for  
17 each vehicle-kilometer-traveled. These relationships are derived from imprecise correlations  
18 of variables, however, and a full physical understanding of the vehicle suspension process is  
19 lacking for unpaved roads. Muleski and Stevens (1992) note that more than 90% of the tests  
20 which acquired data for the AP-42 factor were conducted with vehicle speeds slower than  
21 56 km/h (35 mph), and more than 80% was derived from industrial haul roads. AP-42  
22 emission factors may not be applicable to publicly maintained unpaved roads, desert  
23 shortcuts, and agricultural roads which are common in most  $\text{PM}_{10}$  non-attainment areas.

24 Dust on paved roads must be continually replenished, however, and reducing the  
25 deposition of fresh dust onto these surfaces is a viable method for reducing particulate  
26 emissions. Dust loadings on a paved road surface build up by being tracked out from  
27 unpaved areas such as construction sites, unpaved roads, parking lots, and shoulders; by  
28 spills from trucks carrying dirt and other particulate materials; by transport of dirt collected  
29 on vehicle undercarriages; by wear of vehicle components such as tires, brakes, clutches, and  
30 exhaust system components; by wear of the pavement surface; by deposition of suspended  
31 particles from many emissions sources; and by water and wind erosion from adjacent areas.

1       The relative contribution from each of these sources is unknown. Axetell and Zell  
2 (1977) estimated typical deposition of 240 lb/mile of curb/day for particles of all sizes from  
3 the following sources: (1) 42% from mud and dirt carryout; (2) 17% from litter;  
4 (3) 8% from biological debris; (4) 8% from ice control compounds (in areas with cold  
5 winters); (5) 8% from erosion of shoulders and adjacent areas; (6) 7% from motor vehicles;  
6 (7) 4% from atmospheric dustfall; (8) 4% from pavement wear; and (9) less than 1% from  
7 spills. These proportions are highly uncertain because they apply to the TSP size fraction  
8 (rather than to the respirable size fractions) and because these investigators did not consider  
9 all of the sources cited above. Axetell and Zell (1977) cite these fractions without describing  
10 the methodology used to estimate them. No other published quantitative apportionments of  
11 paved road dust loadings to their sources were found.

12       Nicholson et al. (1989) and Mollinger et al. (1993) identify the turbulent wake of  
13 vehicles on roads as a major cause of dust suspension from roads; their research suggests  
14 that vehicle shapes might be altered to reduce emissions potential. Mollinger et al. (1993)  
15 mounted a cylinder, an elliptical cylinder, and a rectangular solid on a pendulum which  
16 swung back and forth over dust-covered test areas. After 20 passes by the cylinder and  
17 elliptical cylinder, 65% and 45% of the dust remained in the test area, respectively. After  
18 20 passes by the rectangular solid traveling at the same velocity, less than 20% of the dust  
19 remained.

20       Other than the information inferred from the chemical composition of road dust and  
21 from multivariate relationships between downwind concentrations and vehicle variables, there  
22 is no detailed physical understanding of the effects of tire contact with particles and their  
23 suspension into the atmosphere. This knowledge is essential to understanding how these  
24 particles are suspended and how far they are transported.

25       There are obvious discrepancies between the proportion of fugitive dust in primary  
26 emissions and geological contributions to  $PM_{10}$  calculated by receptor models. To some  
27 extent, this is due to contributions from secondary aerosols, which are not included in the  
28 primary  $PM_{10}$  emission estimates. Even when secondary aerosol is subtracted, however,  
29 other sources such as vegetative burning and wood combustion make larger relative  
30 contributions to ambient concentrations than is indicated by the emissions inventories.

1 Fugitive dust estimates are especially affected by the general limitations of emissions  
2 inventories described above. Annual and spatial averages do not reflect the seasonality of  
3 certain emissions. Planting and harvesting are seasonal, as are high winds which might cause  
4 erosion. Paved road dust emissions might be much higher after rain storms when dirt is  
5 tracked from unpaved areas onto paved roads.

6 Many fugitive dust sources are episodic rather than continuous emitters. For example,  
7 Engineering Science (1988) based windblown dust estimates for Phoenix, AZ, on high wind  
8 speeds that occur 5 to 10 times per year. Though windblown dust emissions are low on an  
9 annual average, they can be quite large during those few episodes when wind speeds are  
10 high. Construction activities are also episodic in nature. Reeser et al. (1992) reported  
11 fugitive dust emissions during wintertime in Denver, CO to be 44% higher than those found  
12 in the annual inventory using standard emissions inventory methods. In Coachella Valley,  
13 CA, the South Coast Air Quality Management District (SCAQMD) (1994) calculated 24-h  
14 emissions based on a worst windy day. When wind gust speeds exceeded 96 km/h, fugitive  
15 dust emissions could account for 20% of the entire annual average emission rates.

16 As noted earlier, many fugitive dust emitters are included in the inventories. For  
17 example, Chow et al. (1992) identified two cement plants and many roads with unpaved  
18 shoulders near the Rubidoux, CA, site. The cement plants were not included in the  
19 SCAQMD emissions inventory, and there is no distinction in any of the inventories between  
20 curbed and swept roads and those with no shoulders that may be dirtier than others.

21 Finally, the spatial disaggregation for fugitive dust emissions is poorer than that for all  
22 other source categories. Whereas most mobile sources are confined to established roadways  
23 and most area sources correspond to population density, suspendable dust is everywhere.  
24 Most fugitive dust emissions are compiled on a county-wide basis and are not allocated to  
25 specific fields, streets, unpaved roads, and construction sites possibly contributing to high  
26 airborne PM concentrations. Several of these limitations may be impossible to overcome,  
27 but many result from old methods being applied to the problem. Modern data bases,  
28 computer systems, and information management software can be applied to improve existing  
29 inventories without major additional costs beyond initial investments in establishing an  
30 inventory methodology.

## 5.5.2 Mobile Source Emissions

Mobile sources are major emitters of primary particles, oxides of nitrogen, and VOCs. They are also minor emitters of sulfur dioxide and ammonia. On-road motor vehicles using gasoline- and diesel-fueled engines are by far the largest component of mobile source emissions, and the emissions estimation methods are most highly developed for these vehicles. The U.S. EPA (1994) has published the MOBILE model to estimate carbon monoxide, oxides of nitrogen, VOC, and primary particle emissions from on-road vehicles. The other model in common use is the California Air Resources Board's Emissions FAcTor (EMFAC) model (CARB, 1993). These models use as their inputs variables such as vehicle speed, vehicle age distribution, vehicle classification, ambient temperature, and laboratory emissions test data. The laboratory test data generally use dynamometers with Federal Test Procedure (FTP) driving cycles.

MOBILE and EMFAC model estimates of carbon monoxide, oxides of nitrogen, and VOC emissions are variable as a function of the input variables. Primary particle emissions from tire and brake wear and from exhaust are constant, however, regardless of assumed driving conditions. Emissions estimates from these models have recently been called into question by a series of on-road emissions measurement experiments, which consist of measurements made in tunnels, along roadsides, and by pulling over vehicles for on-road inspection and dynamometer testing.

The Southern California Air Quality Study (SCAQS) Van Nuys Tunnel Study (Ingalls et al., 1989), conducted in October and December, 1987 in the Sherman Way tunnel under the Van Nuys Airport, first called modeled emissions into question by noting that the emissions models underestimated measured VOC emissions by nearly a factor of four. Nitrogen oxide emissions in the tunnel, however, were consistent with those calculated by the models. Pierson et al. (1990) concluded that the results were, in the main, correct. Even if the absolute values of the emission factors determined were somewhat biased due to inaccurate air flow measurements (one of the major difficulties pointed out by Pierson et al.) the emission factor ratios are still valid.

Other tunnel experiments were carried out in the Ft. McHenry Tunnel in Baltimore, Maryland, in June 1992 and in the Tuscarora Mountain Tunnel on Interstate 76 in south-central Pennsylvania, in September 1992 (Pierson et al., 1995). Both tunnels have

1 considerable fetches of freeway before them; thus, all vehicles should have been in the hot-  
2 stabilized mode when they entered. In both tunnels the traffic maintained steady speeds with  
3 low run-to-run and vehicle-to-vehicle variability. This is in distinct contrast to the Van Nuys  
4 tunnel where there was considerable variation in vehicle speeds and many different speeds.

5 Both MOBILE4.1 and MOBILE5 modeled running losses fell within the range of  
6 source contributions determined by the CMB model from VOC source profiles for tailpipe  
7 exhaust and gasoline headspace (Gertler et al., 1995) For the driving mode in these tunnels,  
8 failure to model hydrocarbon emissions is not exclusively due to the method which estimates  
9 running loss evaporative emissions. Fuel volatilities were lower at both Ft. McHenry and  
10 Tuscarora than during the Van Nuys tunnel experiment. While this may lower evaporative  
11 emissions, it is not enough to account for the discrepancy between the observed and modeled  
12 emission factors at Van Nuys.

13 The emissions models tend to overestimate at Tuscarora and only slightly underestimate  
14 emissions at Ft. McHenry, which are reasonable results given the sources of the emission  
15 factors in the models and traffic conditions at each tunnel. As stated previously, the models  
16 derive their emission factors from the FTP, which has many accelerations and decelerations  
17 and very little steady-speed driving. At Tuscarora, there was little acceleration or  
18 deceleration. The tunnel is virtually flat and contains no turns. It is more than 10 km from  
19 the nearest interchange and many, if not most, commuter vehicles travel for much longer  
20 distances. These vehicles were relatively new (median model year was 1989 during the 1992  
21 experiment) and presumably well maintained. The average speed of light-duty vehicles in the  
22 tunnel (determined by a hand-held radar gun) was 59.4 mph with a vehicle-to-vehicle  
23 variability of 5.6 mph, which is negligible variability compared to that seen at the Van Nuys  
24 tunnel. Traffic in the Tuscarora tunnel is expected to emit at low levels because of:  
25 (1) a flat roadway, (2) steady driving speeds, (3) relatively new and well maintained  
26 vehicles, and (4) vehicles in hot-stabilized driving mode. These conditions are consistent  
27 with basic assumptions of the emissions models.

28 The Ft. McHenry tunnel is a different situation, with up- and down-grades reaching  
29  $\pm 3.76\%$  and more speed variability. The vehicle average speeds were 51 mph upon entering  
30 the tunnel and 43 mph at the exit. The median model year was 1989 for automobiles, and  
31 given the tunnel's location on a major freeway, it is assumed that all vehicles were in hot-

1 stabilized driving mode. Though Ft. McHenry is a more complex driving situation than  
2 Tuscarora, it is still considerably less complex than the Van Nuys situation. At Ft.  
3 McHenry, MOBILE4.1 underestimates and MOBILE5 overestimates emissions, but only  
4 slightly in either case. None of the discrepancies are as severe as the underestimates at Van  
5 Nuys. The models agree well with the Tuscarora and Ft. McHenry tunnel observations,  
6 even when deviations from assumptions such as road grades are significant, but when  
7 challenged by a complex urban driving situation such as Van Nuys, it is uncertain at this  
8 time how well the models perform.

9 Stedman et al. (1994) and Ashbaugh et al. (1992) conducted a study in the Los Angeles  
10 area in 1991 using remote sensing devices for the detection of VOC and carbon monoxide  
11 emissions from individual vehicles. During the study, more than 60,000 vehicles' VOC and  
12 CO emissions were measured by remote sensing. Of that group, more than 300 high-  
13 emitting vehicles were identified by the remote sensors and pulled over for inspection.  
14 Sixty-seven percent of the inspected vehicles had emission control systems that were  
15 defective or had been tampered with; more than 90% of them failed the Smog Check  
16 inspection.

17 During the same time, approximately 80 of those inspected vehicles were given an  
18 IM240 test (a 240 second, loaded mode test on a dynamometer). These vehicles previously  
19 had been stopped because of high remote sensing CO and/or VOC readings. All but one of  
20 the tested vehicles exceeded the California certification emission standards. The ten highest  
21 CO and VOC emitters had mass emission rates that were 24 to 70 times higher than the  
22 standards. NO<sub>x</sub> emissions also were measured in the IM240 tests, and three of the vehicles  
23 had NO<sub>x</sub> mass emission rates greater than 10 g/mi. Even though the vehicles had been  
24 stopped because of their CO or VOC remote sensing readings, high NO<sub>x</sub> emitters were  
25 encountered. This unexpected finding suggests the presence of high NO<sub>x</sub> emitters in the fleet  
26 (Knapp, 1992) and has important implications for the accuracy of NO<sub>x</sub> emissions in the  
27 mobile source emissions inventory. Though particle emissions were not measured in these  
28 experiments, it is likely that inefficient combustion and pollution controls on these vehicles  
29 enhance the production of carbonaceous aerosols.

30 Ashbaugh and Lawson (1991) analyzed data collected in 1985, 1987 and 1989 random  
31 roadside surveys and showed that, for the low-idle test, 20% of the vehicles were responsible

for 80% of the CO emissions and 20% (not necessarily the same vehicles) were responsible for 80% of the VOC hydrocarbon (HC) emissions.

While several tests have examined on-road emissions of both nitrogen oxide and VOC precursors, only Hansen and Rosen (1990) report individual on-road vehicle measurements of particulate emissions. They measured the ratio of light-absorbing carbon to CO<sub>2</sub> in the exhausts of 60 gasoline-fueled vehicles in Berkeley, CA. The ratio of carbon to excess CO<sub>2</sub> above background provides an estimate of emissions per unit of fuel combusted. By making reasonable assumptions about speed and gasoline mileage, these ratios can be translated into grams/vehicle mile traveled. Their experiment found a factor of 250 between the highest and lowest ratio of light-absorbing carbon to CO<sub>2</sub> for the 60 vehicles tested. This is at odds with use of a single value for primary particle emissions, regardless of vehicle type or operating condition, typically employed in current emissions models.

These studies show that while vehicle emissions models may function well under idealized conditions, they underestimate the effects of high emitting vehicles that may be major sources of VOCs. Though data are lacking to verify the primary particle emissions in these models, it is very unlikely that the values currently in use account for the variability in emissions from different types of vehicles.

## **5.6 SIZES DISTRIBUTIONS OF PRIMARY PARTICLE EMISSIONS**

Recent measurements of the size distributions of primary particles confirm U.S. Environmental Protection Agency (1982a) conclusions that most fugitive dust emissions are in particles larger than 2.5  $\mu\text{m}$  and that the majority of emissions from combustion sources are in sizes smaller than 2.5  $\mu\text{m}$ . Figures 5-6 and 5-7 from Houck et al. (1989, 1990) were derived from a major characterization of different source emissions in California conducted during 1986. Hot exhaust samples were diluted to ambient temperatures prior to sampling onto filter media through impactor inlets with 50% cut-points of 1, 2.5, 10, and  $\sim 30 \mu\text{m}$ . These figures show that combustion products are nearly always less than 2.5  $\mu\text{m}$  in size.

Figure 5-8 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 the California study (Chow et al., 1994). This



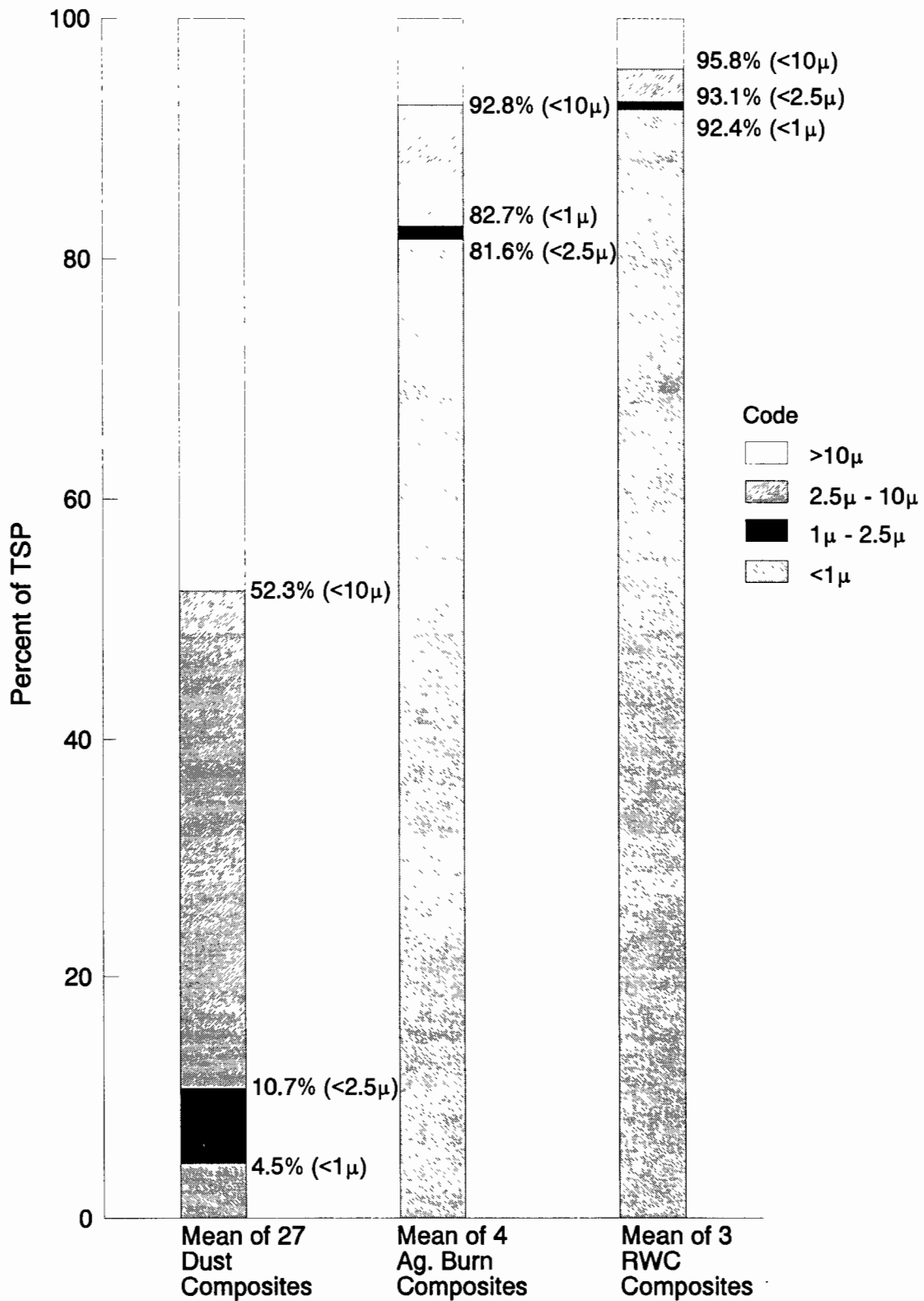


Figure 5-6. Size distribution of California source emissions, 1986.

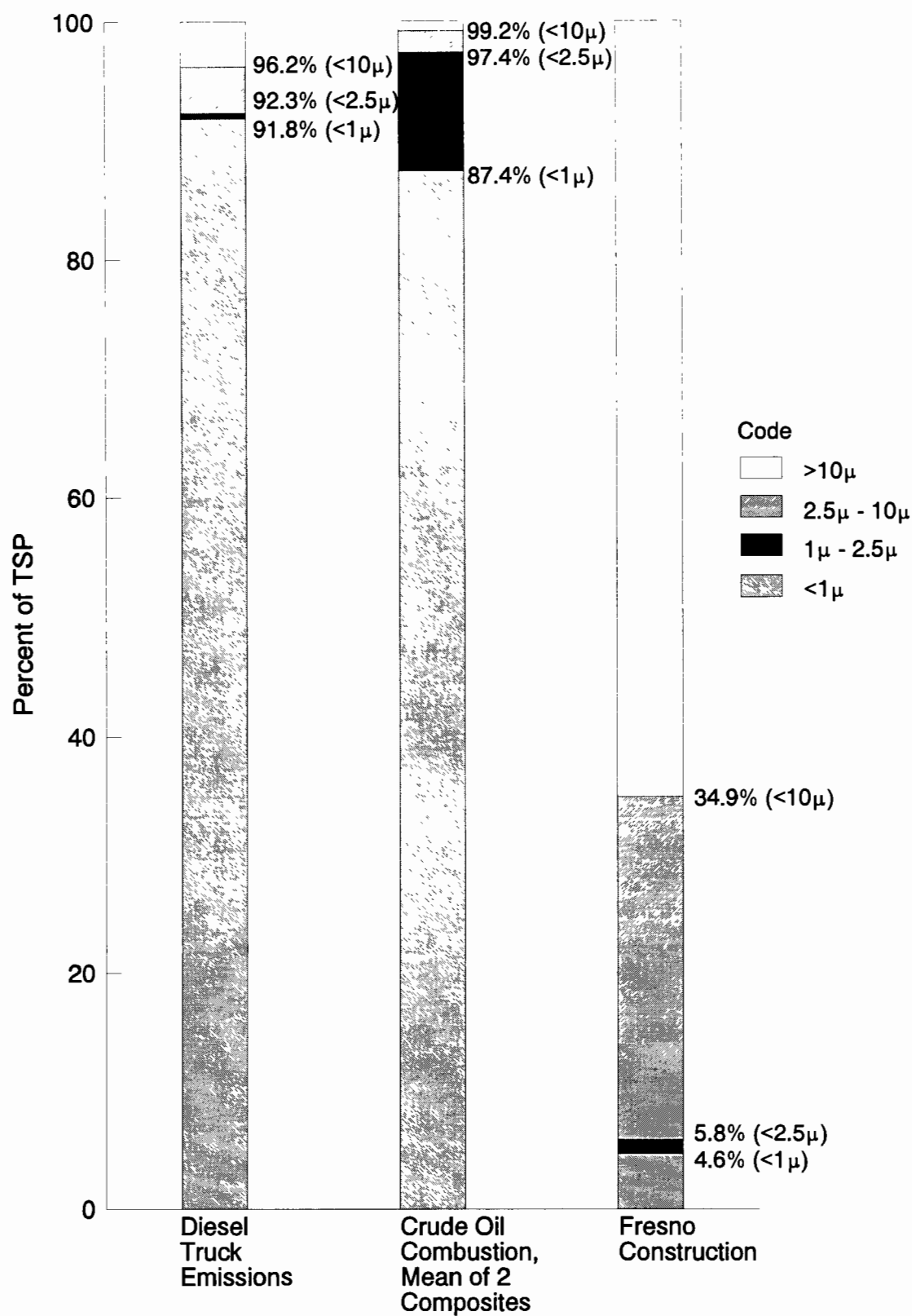
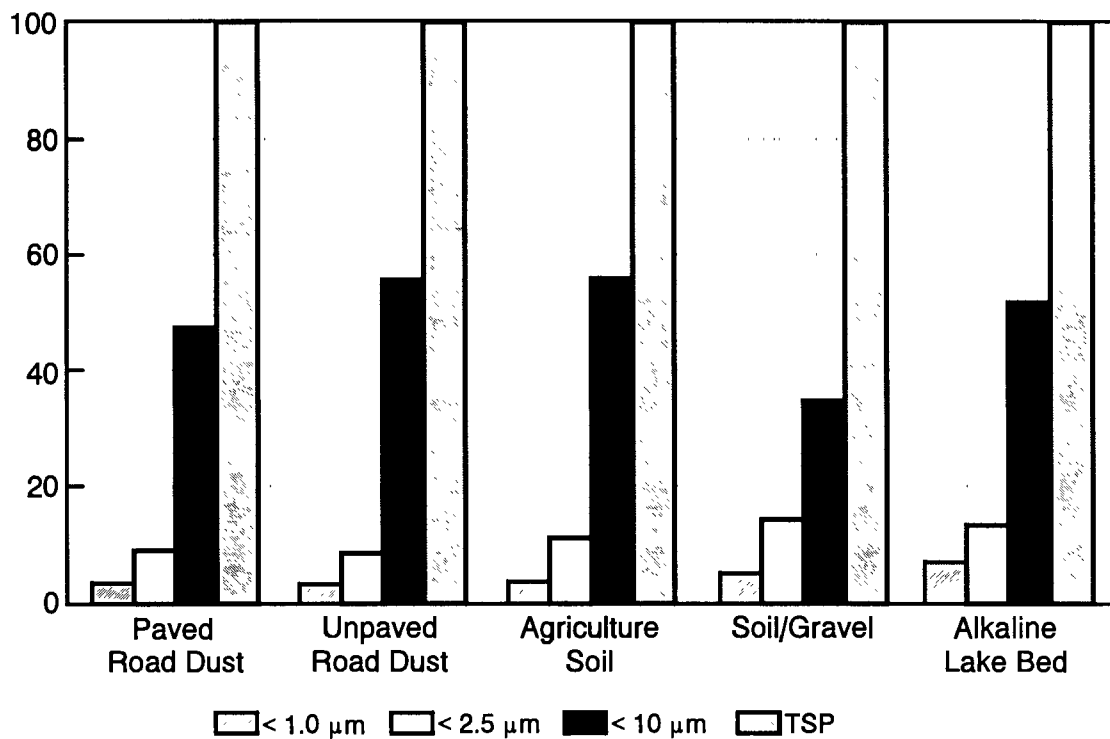


Figure 5-7. Size distribution of California particle emissions, 1986.



**Figure 5-8. Particle size distribution in laboratory resuspension chamber.**

figure shows substantial variation in primary particle size among some of these sources. The  $PM_{1.0}$  abundance (6.9%) in the alkaline lake bed dust is twice its abundance in paved and unpaved road dust. Approximately 10% of 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 consists of particles larger than the  $PM_{10}$  fraction. The  $PM_{2.5}$  fraction of TSP in alkaline lake beds and sand/gravel is approximately 30% to 40% higher than the other soil types. Particle emissions in the respirable fraction can be expected to vary substantially among these different fugitive dust sources.

## 5.7 CHEMICAL COMPOSITIONS OF PRIMARY PARTICLE EMISSIONS

The widespread use of receptor models since U.S. EPA (1982a) has resulted in many published chemical compositions for different particulate sources. Table 5-2 shows the relative amounts of different chemical species in the profiles from different source types. These are deduced from many different profiles compiled by Radian (1989) and by Chow et al. (1994) for EPA's SPECIATE source composition library.

Figures 5-9 through 5-12 show examples of the chemical abundances in specific  $PM_{2.5}$  profiles for paved road dust, motor vehicle exhaust, residential wood combustion, and a coal-fired power plants. These were measured in Denver, CO during 1987 (Watson and Chow, 1994). Substantial differences in chemical composition exist for these emitters, while these differ from site to site.

The road dust profile in Figure 5-9 contains large abundances of aluminum, silicon, potassium, calcium, and iron. Though total potassium is abundant in road dust, water-soluble potassium constitutes less than one-tenth of the total. Strontium and lead are also present at detectable levels. Paved road dust is much like an ambient  $PM_{10}$  sample, with a complex combination of particulate matter from a wide variety of sources, especially other geological source types. This complexity is evident in the comparison of a paved road dust profile reported by Chow et al. (1991) for Phoenix, AZ, with profiles from other geological sources in the area. Chow et al. (1991) noted that the abundance of organic carbon in the profile was  $11 \pm 9\%$ , larger and more variable than its abundance in profiles from agricultural land, construction sites, and vacant lots. The presence of tire wear, detritus, and engine oils can account for this enrichment. This organic carbon content places an effective upper limit on the contribution from tire wear and other carbon sources to suspendable paved road dust. Approximately 25% of tire material consists of styrene-butadiene rubber (SBR) (Pierson and Brachaczek, 1974). Ondov (1974) measured elemental components of tire material and found minor concentrations for most species, with S ( $\sim 2\%$ ), Cl ( $\sim 1.5\%$ ), and Zn ( $\sim 1\%$ ) being the most abundant components.

The abundances of Pb and Br in Phoenix paved road dust were more than double the concentrations in the other geological profiles, indicating the presence of tailpipe exhaust

TABLE 5-2. TYPICAL CHEMICAL ABUNDANCES IN SOURCE EMISSIONS.

Source Type	Dominant Particle Size	Chemical Abundances			
		< 0.1 %	0.1 to 1 %	1 to 10 %	> 10 %
Geological Material	Coarse	Cr, Zn, Rb, Sr, Zr	Cl <sup>-</sup> , NO <sub>3</sub> <sup>-</sup> , SO <sub>4</sub> <sup>=</sup> , NH <sub>4</sub> <sup>+</sup> , P, S, Cl, Ti, Mn, Ba, La	OC, EC, Al, K, Ca, K, Fe	Si
Motor Vehicle	Fine	Cr, Ni, Y <sup>+</sup>	NH <sub>4</sub> <sup>+</sup> , Si, Cl, Al, Si, P, Ca, Mn, Fe, Zn, Br, Pb	S, Cl, NO <sub>3</sub> <sup>-</sup> , SO <sub>4</sub> <sup>=</sup> , NH <sub>4</sub> <sup>+</sup>	OC, EC
Vegetative Burning	Fine	Ca, Mn, Fe, Zn, Br, Rb, Pb	NO <sub>3</sub> <sup>-</sup> , SO <sub>4</sub> <sup>=</sup> , NH <sub>4</sub> <sup>+</sup> , Na <sup>+</sup>	K <sup>+</sup> , K, Cl, Cl <sup>-</sup>	OC, EC
Residual Oil Combustion	Fine	K <sup>+</sup> , OC, Cl, Ti, Cr, Co, Ga, Se	Na <sup>+</sup> , NH <sub>4</sub> <sup>+</sup> , Zn, Fe, Si	Ni, OC, EC, V	S, SO <sub>4</sub> <sup>=</sup>
Incinerator	Fine	V, Mn, Cu, Ag, Sn	K <sup>+</sup> , Al, Ti, Zn, Hg	NO <sub>3</sub> <sup>-</sup> , Na <sup>+</sup> , EC, Si, S, Ca, Fe, Br, La, Pb	SO <sub>4</sub> <sup>=</sup> , NH <sub>4</sub> <sup>+</sup> , OC, Cl
Coal Fired Power Plant	Fine	Cl, Cr, Mn, Ga, As, Se, Br, Rb, Zr	NH <sub>4</sub> <sup>+</sup> , P, K, Ti, V, Ni, Zn, Sr, Ba, Pb	SO <sub>4</sub> <sup>=</sup> , OC, EC, Al, S, Ca, Fe	Si
Marine	Coarse	Ti, V, Ni, Sr, Zr, Pd, Ag, Sn, Sb, Pb	K, Ca, Fe, Cu, Zn, Ba, La, Al, Si	NO <sub>3</sub> <sup>-</sup> , SO <sub>4</sub> <sup>=</sup> , OC, EC	Na <sup>+</sup> , Na, Cl <sup>-</sup> , Cl

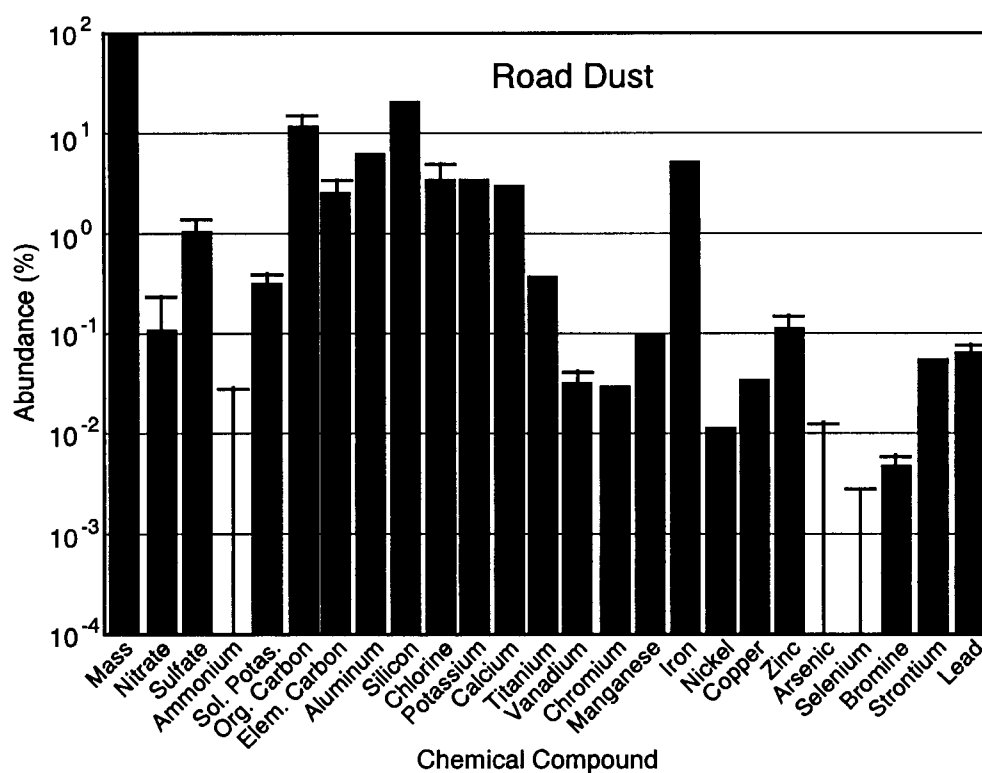


Figure 5-9. Chemical abundances for PM<sub>2.5</sub> profiles of road dust.

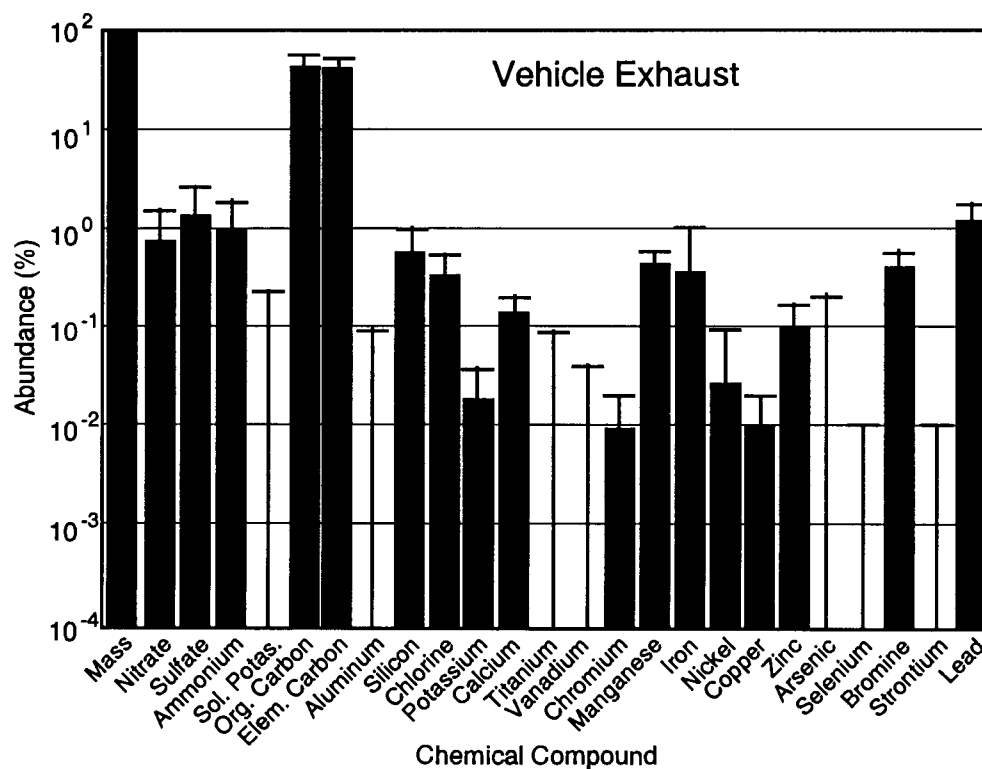


Figure 5-10. Chemical abundances for PM<sub>2.5</sub> profiles of vehicle exhaust.

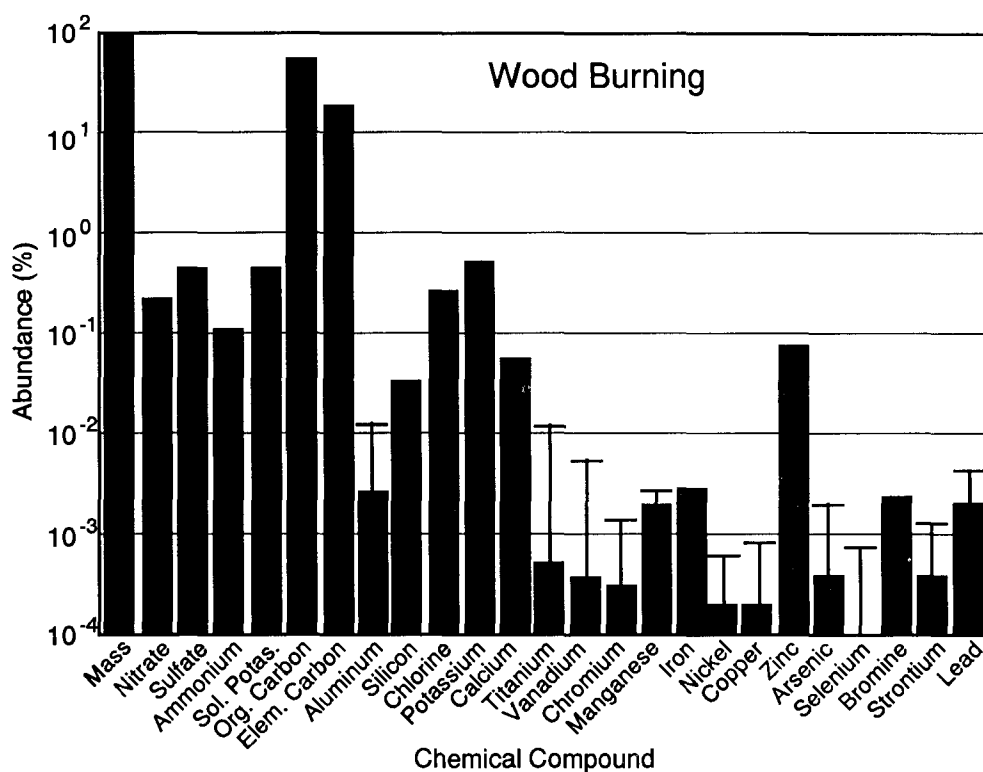


Figure 5-11. Chemical abundances for PM<sub>2.5</sub> profiles of wood burning.

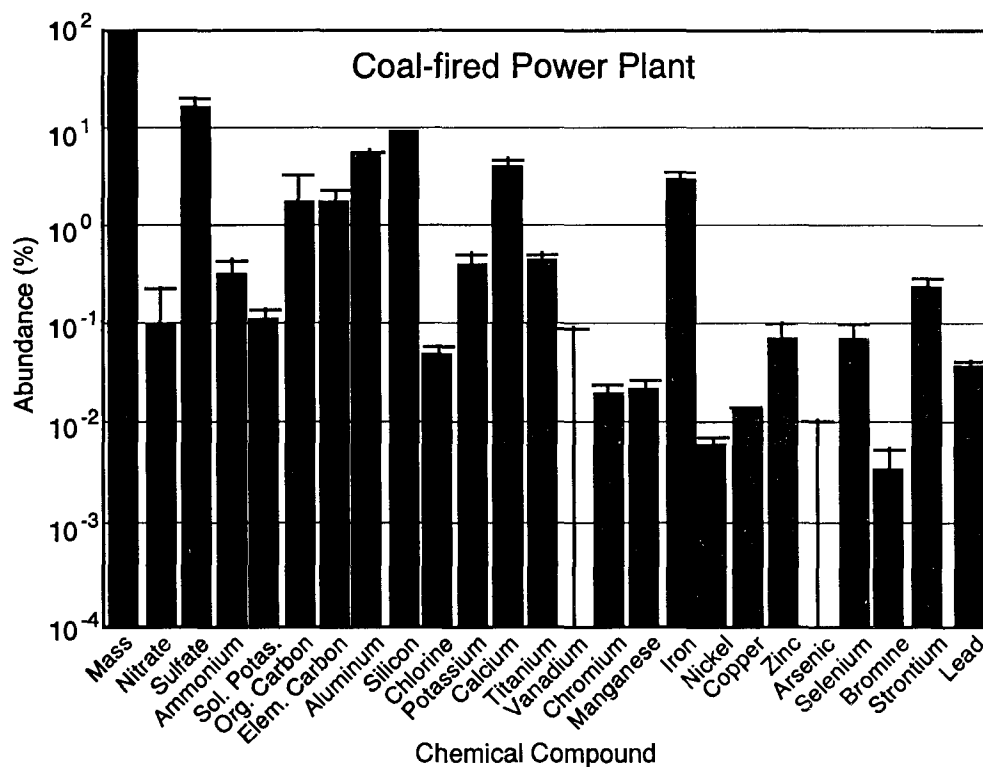


Figure 5-12. Chemical abundances for PM<sub>2.5</sub> profiles of coal-fired power plant.

1 from vehicles burning leaded fuels. These will not be good indicators of exhaust  
2 contributions today because tetraethyl lead is no longer used as a fuel additive. Enrichments  
3 in species from clutch and brake wear were absent in the Phoenix paved road dust profiles.  
4 These are often composed of asbestos and/or semi-metal carbon composites. Ondov (1974)  
5 measured abundances of ~14% Mg, ~2% Ca, ~4% Fe, and ~1% Ba in asbestos brake  
6 shoes, while Anderson et al. (1973) reported Si abundances of ~10%. Cooper et al. (1987)  
7 examined the elemental composition of semi-metal brake shoes and found abundances of  
8 ~45% Fe, ~2% Cu, ~0.5% Sn, ~3% Ba, and ~0.5% Mo. None of these species was  
9 found in the Phoenix paved road dust profiles at levels significantly in excess of their  
10 abundances in other geological sub-types.

11 The motor vehicle exhaust profile contains high concentrations of organic and elemental  
12 carbon; but their ratios are much different from those found in wood combustion with the  
13 abundance of elemental carbon being nearly equal to the organic carbon abundance. Bromine  
14 and lead are also much larger components in vehicle exhaust than in other source profiles.  
15 However, Br and Pb have been phased out of most U.S. gasolines, and this example does not  
16 represent current motor vehicle emissions profiles found in the United States today.

17 Pierson and Brachaczek (1976; 1983) pioneered the chemical characterization of  
18 particulate emissions from motor vehicles. These results, acquired from 1970 through 1981,  
19 were used extensively in the early days of CMB modeling of total suspended particulate  
20 matter (e.g., Watson, 1979; Kowalczyk et al., 1978). Little additional work on the chemical  
21 characterization of particulate motor vehicle emissions was conducted until promulgation of  
22 the PM<sub>10</sub> NAAQS in 1987. It was soon recognized that fleet composition, emissions  
23 controls, fuels, engine designs, and vehicle maintenance had changed considerably since the  
24 tests of Pierson and Brachaczek (1976; 1983), and that new tests, and types of testing, were  
25 needed to obtain chemical source profiles.

26 Watson et al. (1988b) obtained six roadside samples under a freeway overpass, in a city  
27 bus yard, and near busy intersections in Reno, NV, in 1986 and 1987 as part of the State of  
28 Nevada Air Pollution Study (SNAPS) (Chow et al., 1988). Cooper et al. (1987) and NEA  
29 (1990a; 1990b; 1990c), in studies conducted for SCAQMD (Gray et al., 1988; Zeldin et al.,  
30 1990), measured exhaust from eleven unleaded-gasoline-fueled vehicles, 3 leaded-gasoline-  
31 fueled vehicles, and 2 heavy-duty diesel-fueled trucks operating on laboratory dynamometers



1 in 1986. The FTP and a steady-state test at 35 mph were followed for the gasoline-fueled  
2 vehicle tests. Diesel-fueled trucks were tested under modified FTP and steady-state  
3 conditions. Cooper et al. (1987) also took three roadside samples in a tunnel under the Los  
4 Angeles Airport.

5 Watson et al. (1990b; 1990c) report the results from dynamometer tests of eight  
6 unleaded-gasoline-fueled vehicles, three leaded-gasoline-fueled vehicles, and three light- to  
7 medium-duty diesel-fueled vehicles conducted in 1988 during a Denver visibility study. The  
8 FTP was applied to vehicles under conditions (temperatures  $< 40^{\circ}\text{F}$ ) similar to those found  
9 in wintertime Denver. In 1987, Houck et al. (1989) took three samples of heavy-duty diesel-  
10 fueled truck exhaust at a roof monitor over the Wheeler weigh station near Bakersfield, CA.  
11 These measurements were used with SCAQMD source profiles for  $\text{PM}_{10}$  source  
12 apportionment in California's San Joaquin Valley (Chow et al., 1992; 1993d). The TOR  
13 method described by Chow et al. (1993b) was applied in all of these tests except that of  
14 Cooper et al. (1987). The Cooper et al. (1987) carbon analysis monitored light transmission  
15 instead of reflectance to implement the pyrolysis correction (Cary, 1990). Watson et al.  
16 (1994) report profiles derived in Phoenix, AZ during 1989.

17 There are significant similarities and differences among the chemical compositions of  
18 these different motor vehicle profiles measured in different areas, at different times, and by  
19 different methods. The Denver diesel-fueled profiles have a much higher abundance of  
20 elemental carbon ( $74 \pm 21\%$ ) than the SCAQMD ( $52 \pm 5\%$ ), Wheeler Station ( $43 \pm 8\%$ ), or the  
21 PHDIES ( $33 \pm 8\%$ ) profiles. The organic carbon in these profiles is  $23 \pm 8\%$  for Denver,  
22  $36 \pm 3\%$  for SCAQMD,  $49 \pm 13\%$  for Wheeler Station, and  $40 \pm 7\%$  for PHDIES.

23 For leaded-gasoline-fueled vehicles, the OC and EC abundances were found to be  
24  $67 \pm 23\%$  and  $16 \pm 7\%$  in the Denver tests,  $52 \pm 4\%$  and  $1.3 \pm 1\%$  in the SCAQMD steady-  
25 state tests, and  $31 \pm 20\%$  and  $15 \pm 2\%$  in the SCAQMD FTP tests, respectively. For  
26 unleaded-gasoline-fueled vehicles, the OC and EC abundances were found to be  $76 \pm 29\%$   
27 and  $18 \pm 11\%$  for Denver tests,  $93 \pm 52\%$  and  $5 \pm 7\%$  for SCAQMD steady-state tests, and  
28  $49 \pm 10\%$  and  $39 \pm 8\%$  for SCAQMD FTP tests, respectively. These compare to OC and EC  
29 abundances in PHAUTO of  $30 \pm 12\%$  and  $14 \pm 8\%$ , respectively.

30 In roadside and tunnel tests which included mixtures of diesel-, leaded-, and unleaded-  
31 fueled vehicles, Watson et al. (1988a; 1990c) found abundances of  $50 \pm 24\%$  OC and

1 28 ± 19% EC, and Cooper et al. (1987) found abundances of 38 ± 6% OC and 38 ± 5%  
2 EC. These are similar to the 39±19% OC and 36±11% EC abundances found in this study.

3 All of these profiles represent emissions from a small number of vehicles relative to the  
4 entire vehicle population. In each of these studies, as in this one, there were individual  
5 samples which deviated in their compositions from the majority of profiles. Further study is  
6 needed to determine why these deviations exist and how they are related to the mixture of  
7 vehicles tested. For wood burning in fireplaces and stoves, organic carbon is by far the most  
8 abundant constituent, followed by elemental carbon. Chlorine and potassium also approach  
9 an abundance of 1% in these emissions, as do sulfate and nitrate. The water soluble  
10 potassium equals total potassium in wood burning emissions.

11 The coal-fired power plant profile in Figure 5-12 has several chemical abundances that  
12 are similar to those of the road dust profile. The sulfate level is much higher in these  
13 emissions than in the other profiles, and the organic and elemental carbon fractions are much  
14 lower. Selenium is clearly detectable in the power plant profile, whereas it is below  
15 quantifiable limits in the other profiles.

16 The chemicals identified in Figures 5-9 through 5-12 represent the major components  
17 that contribute to atmospheric light extinction (i.e., crustal, sulfate, nitrate, ammonium,  
18 organic carbon, elemental carbon) as well as chemical patterns that help to distinguish one  
19 source of primary emissions from others (e.g., selenium, potassium, aluminum, silicon,  
20 organic carbon, elemental carbon). In addition to these commonly measured components, it  
21 is possible that isotopic ratios in source emissions may vary in an informative way with the  
22 nature of the combustion process and with the geologic age and character of the source input  
23 material. Carbon-14, for example, has been widely used to separate contemporary carbon  
24 due to vegetative burning from carbon emitted by fossil fuel combustion (Currie et al.,  
25 1984). Certain isotopic ratios might also distinguish coal-fired power plant emissions from  
26 other sources. Fuels from different mines may have isotopic differences that allow otherwise  
27 similar source emissions from different power plants to be distinguished.

## 5.8 EMISSIONS MODELS AND EMISSIONS INVENTORIES

As noted above, major discrepancies exist between relative amounts of emissions and contributions to suspended particles found in many areas. Major re-design is needed to create more accurate emissions models to improve quantification of source-receptor relationships.

Emissions models are intended to estimate the emissions rates as a function of space and time of selected pollutants from point, area, and mobile sources. In contrast to an emissions inventory, which is a static catalogue of emissions estimates for a given geographical area and averaging time, an emissions model is capable of accessing activity data bases from a multitude of information-gathering agencies and determining actual emissions for relatively small regions and averaging times.

Emissions models have, at their base, several activity surrogates that are considered to have some relationship to emissions. Activities relevant to the major source contributions identified in Table 5-1 include: (1) number of acres burned, locations, and durations of wildfires and prescribed burns; (2) cords of wood and tons of coal sold for residential heating; (3) vehicle miles traveled for mobile source emissions; (4) heads of livestock, pounds of fertilizer, and number sewage treated for ammonia; and (5) amount of product produced for industrial sources (e.g. power generated for power plant emissions; tons of coke produced for a coke oven). Wherever possible, different activity data for the same sources and emitted species are used to evaluate uncertainties. For example, Watson et al. (1990) showed for Denver, CO, that proportional differences between gasoline and diesel powered mobile source activities might be separately estimated from vehicle counts at selected roadways, areawide fuel sales, and vehicle registrations. Differences between separate activity estimates can be used to quantify the uncertainty of emissions rates.

Upon these activity data are imposed emissions/activity relationships (commonly termed "emissions factors") that may require meteorological inputs such as temperature, relative humidity, or wind speed. These relationships are easily replaceable and include the ability to propagate the precisions specified for the input data. The emissions/activity relationships are specific for different source sub-types. As an example, certain roads may have greater or lesser proportions of diesel truck traffic, older and newer vehicles, and vehicles which were recently started and ones which are fully warmed up. In the idealized emissions model, each

road segment is assigned a classification for a specific distribution of vehicles, and a separate emissions/activity relationship is determined for each classification.

Emissions models should have several attributes, i.e., they should: (1) be based on documented scientific and engineering principles; (2) be composed of special purpose modules which can be updated with new information and new science when available; (3) have activity levels and emissions/activity relationships specific to a non-attainment area; (4) contain error propagation algorithms to provide precision estimates on outputs; (5) use independent activity data bases and emissions/activity relationships of equivalent quality to estimate accuracy; (6) adjust the emissions/activity relationship in response to environmental variables, especially meteorology; (7) allow the addition, subtraction, or modification of emissions for special events; (8) retain traceability of all information to allow quality auditing; (9) provide output displays, statistics, and data bases which can be used for modeling, data analysis, control strategy development, and quality assurance; and (10) calculate the effects of changes, such as population growth, implementation of PM<sub>10</sub>, control measures, and changes in land use.

Unfortunately, there are no emissions models used or even currently available that attain all these attributes. Attempts have been made to improve the current state of the art with creation of the Flexible Response Emissions Data System (FREDS) (Lebowitz et al., 1987) for the National Acid Precipitation Assessment Program (NAPAP) and the Emissions Preprocessor System (EPS) for the Urban Airshed Model (SAI, 1990). The closest approach is the Geographical Emissions Modeling and Assessment Program (GEMAP; Dickson and Oliver, 1993) developed for the San Joaquin Valley Air Quality Study and Atmospheric Utility Signatures, Predictions and Experiments (SJVAQS/AUSPEX) in California (Solomon, 1994).

Assumptions inherent in using a static emissions inventory to represent short-term events are: (1) emissions rates are constant, typically averaged over a year and sometimes over a season; (2) emissions factors relating activities to emissions apply to all emitters at all locations at all times; (3) the values of activity variables are highly correlated with actual emissions; and (4) all major emitters have been identified and included.

It is not difficult to find major deviations from these assumptions, even in a small area over a short time period. As might be expected averaging over large spatial scales and time

1 periods evens out much of the variability inherent in applying these assumptions to individual  
2 episodes and locations. However, short-term episodes of a few hours or a few days duration  
3 and source influences over spatial scales of less than 100 km are exactly what is needed to  
4 evaluate source contributions to excessive 24-h values of particulate concentrations in non-  
5 attainment areas.

6 Emissions inventories are often used to develop emissions reductions strategies by the  
7 process of linear rollback Barth (1970). This approach assumes that pollutant concentrations  
8 and the effects of those concentrations (e.g., health effects) are directly proportional to  
9 emissions within a selected geographical region. For this approach, an area is defined that  
10 receives emissions from the sources to be controlled and ambient concentrations of the  
11 pollutants of interest are measured within and outside this area. If there are contributions  
12 from the suspected sources, the within-area concentrations will be significantly higher than  
13 the outside-area concentrations, and the outside-area concentrations are subtracted to obtain  
14 the incremental amount contributed by in-area sources. Emissions of the pollutant or the  
15 precursor within the study area are reduced by an amount proportional to the desired  
16 reduction in ambient concentrations.

17 The linear rollback method is simple and its application in urban areas has resulted in  
18 reduced ambient concentrations for primary particles when emissions estimates are accurate,  
19 spatial scales are large, and averaging times are long. It is currently being tested for U.S.  
20 utility sulfur dioxide emissions that are to be reduced to 8.95 million tons per year (by more  
21 than 50% from current emissions) by the year 2002. The rollback method, however, has not  
22 been proven to be accurate for short duration events over small spatial scales for secondary  
23 aerosol when emissions estimates are uncertain.

## 26 **5.9 SUMMARY AND CONCLUSIONS**

27 The ambient atmosphere contains both primary and secondary particles; the former are  
28 emitted directly by sources, and the latter are formed from gases ( $\text{SO}_2$ ,  $\text{NO}_x$ ,  $\text{HN}_4$ , VOCs)  
29 that are directly emitted by sources. Fugitive dust is a primary pollutant, and also has a role  
30 in secondary particle formation. Major sources of particle emissions are classified as major

1 point sources, mobile sources, and area sources; these are anthropogenic. Natural sources  
2 also contribute to ambient concentrations.

3 The 1982 Criteria Document emphasized emissions from industrial sources, especially  
4 primary particles.  $\text{SO}_2$  was the only precursor of secondary particles considered. Since  
5 1982, many of these sources have been controlled, yet particle standards are exceeded in  
6 many areas.

7 Source and receptor models are used to quantify major contributions to excess  $\text{PM}_{10}$   
8 concentrations. Source models use emissions inventories and meteorological data to product  
9 particle dispersion and  $\text{PM}_{10}$  concentrations measured at receptors. Receptor models use  
10 chemical composition of emissions and receptor concentrations to estimate the contribution of  
11 sources. The latter are more appropriate to identify sources in non-contaminant areas.

12 Fugitive dust is a major contribution to  $\text{PM}_{10}$  at nearly all sampling site, although the  
13 average fugitive dust source contribution is highly variable among sampling sites within the  
14 same areas, and is highly variable between seasons.

15 Primary motor vehicle exhaust makes up as much as 40% of average  $\text{PM}_{10}$  at many  
16 sampling sites. Vegetative burning outdoor and residential wood burning are significant  
17 sources in residential areas. Fugitive dust from paved and unpaved roads, agricultural  
18 operations, construction, and soil erosion constitute ~90% of nationwide primary emissions.  
19 All of the emissions have remained relatively constant over the 8-year period except for those  
20 from soil erosion.

21 The majority of wind erosion occurs in the dustbowl region; estimates are influenced by  
22 annual precipitation and wind-speed distribution. The major non-fugitive dust emitters are  
23 other industrial processes and exhaust from highway vehicles. Fuel combustion from  
24 utilities, industrial, and other sources together contribute between 1 to 2% to total primary  
25 particle emissions. Industrial fuel combustion emissions were reduced by one-third and other  
26 fuel combustion emissions were reduced by one half between 1983 and 1992. On high-way  
27 vehicle emissions increased by 50%, primarily due to large increases in the number of  
28 vehicle miles traveled. Electric utilities account for the largest fraction of sulfur dioxide,  
29 nearly 70% of total emissions. These emissions have not changed substantially over the 10  
30 years reported. Annual averages do not reflect the seasonality of certain emissions,  
31 residential wood burning in fireplaces and stoves, for example. Cold weather also affects

1 motor vehicle exhaust emissions, both in terms of chemical composition and emission rates.  
2 Planting, harvesting, and fertilizing and harvesting are also seasonal. Fugitive dust consists  
3 of geological material that is suspended into the atmosphere by natural wind and by  
4 anthropogenic activities from sources such as paved and unpaved roads, construction and  
5 demolition of buildings and roads, storage piles, wind erosion, and agricultural tilling. There  
6 are obvious discrepancies between the proportion of fugitive dust in primary emissions and  
7 geological contributions to  $PM_{10}$  calculated by receptor models, due to contributions from  
8 secondary aerosols, which are not included in the primary  $PM_{10}$  emission estimates. Even  
9 when secondary aerosol is subtracted, however, other sources such as vegetative burning and  
10 wood combustion make larger relative contributions to ambient concentrations than is  
11 indicated by the emissions inventories. Fugitive dust estimates are especially affected by the  
12 general limitations of emissions inventories. Annual and spatial averages do not reflect the  
13 seasonality of certain emissions. Planting and harvesting are seasonal, as are high winds  
14 which might cause erosion. Paved road dust emissions might be much higher after rain  
15 storms when dirt is tracked from unpaved areas onto paved roads. The spatial disaggregation  
16 of fugitive dust emissions is poorer than that for all other source categories. Whereas most  
17 mobile sources are confined to established roadways, and most area sources correspond to  
18 population density, suspendable dust is everywhere. Modern data bases, computer systems,  
19 and information management software could be applied to improve existing inventories  
20 without major additional costs after the initial investment in establishing an inventory  
21 methodology. Mobile sources are major emitters of primary particles, oxides of nitrogen,  
22 and volatile organic compounds. They are also minor emitters of sulfur dioxide and  
23 ammonia. On-road motor vehicles using gasoline- and diesel-fueled engines are by far the  
24 largest component of mobile source emissions, and the emissions estimation methods are  
25 most highly developed for these vehicles. Studies show that while vehicle emissions models  
26 may function well under idealized conditions, they underestimate the effects of high emitting  
27 vehicles that may be major sources of VOCs. Motor vehicle exhaust contains high  
28 concentrations of organic and elemental carbon, but their ratios are much different from  
29 those found in wood combustion with the abundance of elemental carbon being nearly equal  
30 to the organic carbon abundance. There are major discrepancies between the relative  
31 amounts of emissions and contributions to suspended particles found in many areas. Some

1 major re-design is needed to create more accurate emissions models that can improve the  
2 quantification of source-receptor relationships. Emissions models are intended to estimate  
3 the emissions rates as a function of space and time of selected pollutants from point, area,  
4 and mobile sources. In contrast to an emissions inventory, which is a static catalogue of  
5 emissions estimates for a given geographical area and averaging time, an emissions model is  
6 capable of accessing activity data bases from a multitude of information- gathering agencies  
7 and determining actual emissions for relatively small regions and averaging times.  
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## 6. ENVIRONMENTAL CONCENTRATIONS

### 6.1 BACKGROUND, PURPOSE AND SCOPE

This chapter summarizes the concentrations of particulate matter over the United States, including the spatial, temporal, size and chemical aspects. This chapter is aimed to support the quantification of particulate matter effects and to aid the PM standard setting process. The information needs for assessing the major aerosol effects of concern is summarized in Table 6.1. Depending on the effect, different aspects (dimensions) of aerosol concentrations are important. The effects on human health are considered most serious and this chapter is to provide relevant aerosol concentration information to help in quantifying these effects. Concern also exists for aerosol effects on visibility as well as damage to manmade materials.

Health effects are concerned with people, and the geographic areas of importance are those with high population densities. The spatial resolution and detail needed for health effect assessment is rather high, because of strong gradients in population densities. Health effects are believed to occur both as a consequence of short-term acute episodic exposure, as well as through cumulative chronic long-term exposure. The relevant particle sizes are in the inhalable size range ( $< 10 \mu\text{m}$ ), but it is known that submicron particles penetrate deeper into the lungs. It is not well known which ambient aerosol chemical species are most potent in causing health effects. However, sulfates, particularly in acidic form are believed to be important along with toxic trace metals and carcinogenic organic substances. Also, health damage is usually the consequence of the combined influence of multiple, coexisting pollutants, weather, and other environmental conditions.

Preventing the degradation of visibility, particularly in pristine national parks has been one of the provisions of the Clean Air Act. The main cause of visibility degradation is atmospheric haze that is contributed mainly by fine particles, except during dust events. Sulfates, organics, nitrates, absorbing carbon and to some extent dust particles are the contributors to visibility degradation. Both short term fine particle episodes, seasonal pattern and long term fine particle trends are relevant to visibility degradation. The potential climatic effects of aerosols are influenced by roughly the same factors that determine the visibility degradation except on a global scale.



**TABLE 6.1 AEROSOL INFORMATION NEEDS FOR ASSESSING EFFECTS**

	Health	Visibility	Materials Damage
Concern	People	National Parks	Costs
Space Resolution	Local	Regional	Local
Time Resolution	Short, Long	Short, Long	Long
Particle Size	Inhalable (Fine?)	Fine	Fine
Chemistry	Acidity, Toxicity	SO <sub>4</sub> , NO <sub>3</sub> , Organics	Acidity, Soot

Aerosol effects on man-made materials include soiling and corrosion. These materials are located mainly in populated areas and high spatial resolution for concentrations is needed. Soiling is due to carbonaceous smoke and soot and settling dust while corrosion increases are due to acidifying sulfurous aerosols. The materials damage occurs over the period of years, but daily and seasonal cycles are also important. The quantification of materials damage is particularly sensitive to the interaction with weather elements, particularly moisture.

Other regional and global aerosol effects include acid deposition and effects on climate. Acid deposition and its relationship to aerosols is treated extensively elsewhere (NAPAP, 1991). Direct aerosol perturbation of the radiative climate and the indirect aerosol influence through changing the cloud properties and pattern is beyond the scope of this chapter.

The commonality among these effects (Table 6.1) is that the overall damage is driven by the concentration of relevant aerosol parameters, the spatial pattern and density of receptors and by the receptors' sensitivity. The receptor densities, e.g. population densities, national parks, etc. are not discussed here. The sensitivity (damage functions) are treated in the respective chapters on aerosol effects.

### **6.1.1 Dimensionality and Structuring of the Aerosol Data Space**

Aerosol concentration patterns contain endless detail and complexity in space, time, size, and chemical composition. Chemically analyzed aerosol samples over the conterminous United States reveal the coexistence of sulfates, secondary organics, nitrates, smoke, soot, soil dust, sea salt, and trace metals in most aerosol samples. Each of these chemicals is also distributed in different size particles. This chemically rich aerosol mix arises from the

1 multiplicity of contributing aerosol sources, each having a unique chemical mixture for the  
2 primary aerosol at emission time. The primary aerosol chemistry is further enriched by the  
3 addition of species during atmospheric chemical processes. Finally, the immensely effective  
4 mixing ability of the lower troposphere stirs these primary and secondary particles into a  
5 mixed batch with various degrees of homogeneity, depending on location and time. The  
6 result is a spatial temporal, size, and chemically heterogeneous aerosol pattern that is  
7 probably unparalleled in the domain of atmospheric sciences.

8 In order to characterize the aerosol pattern that is useful for effects assessment, it is  
9 necessary to organize and structure the aerosol pattern analysis. This “user-driven” aspect of  
10 aerosol concentration structuring demands that it be consistent with the information needs  
11 stated in Table 6.1.

12 Another consideration in structuring the aerosol pattern analysis is that it has to be  
13 consistent with physical and chemical processes that determine the concentrations. The  
14 principles of atmospheric sciences state that the concentration of particulate matter, (C) at  
15 any given location and time is determined by the combined interaction of emissions, (E),  
16 dilution, (D), and chemical transformation and removal, (T), processes expressed as:

$$C = f(D, T, E)$$

19  
20 Dilution, transformation/removal and emissions, D,T,E are generic operators and can,  
21 in principle, be determined from suitable measurements and models. However, for  
22 consideration of aerosol pattern analysis it is sufficient to recognize and separate these three  
23 major causal factors influencing the aerosol concentration pattern.

24 This section outlines the main organizing principles for the analysis of PM pattern. It  
25 is convenient to categorize the highly variable aerosol signal along the following major  
26 dimensions: space, time, size and chemical composition. The space and time dependence of  
27 concentrations are common to all pollutants. However, both the distribution with respect to  
28 particle size as well as the chemical distribution within a given size range constitute unique  
29 dimensions of particulate matter that is not present for other pollutants. The concentration of  
30 single-compound gaseous pollutants can be fully characterized by their spatial and temporal  
31 pattern. This classification by dimensions is consistent with the size-chemical composition

distribution function introduced by Friedlander (1976). It could be said that particulate matter is a composite of hundreds of different pollutants having a distribution in space and time.

### 6.1.2 Spatial Pattern and Scales

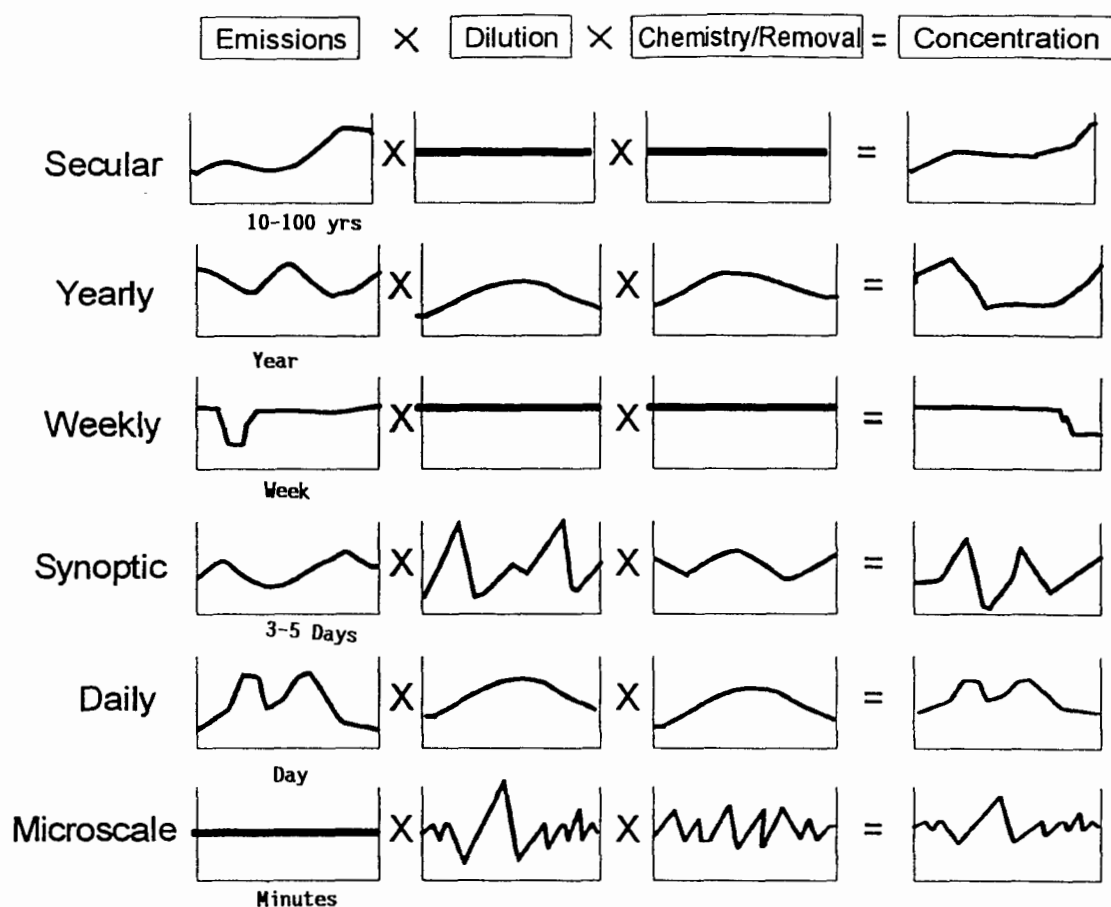
The spatial dimension covers the geographic scale and pattern of aerosols. Based on consideration of emissions, meteorology, and political boundaries, the spatial dimension can be classified as global, national, regional-synoptic, meso, urban, and local. Some of the characteristics of these spatial scales are illustrated in Table 6-2.

**TABLE 6-2. SPATIAL REGIONS AND SCALES**

Global	National	Regional	Meso	Urban	Local
Continent	Country	Multi-state	State	County	City-center
10,000 - 50,000 km	5,000 - 10,000 km	1,000 - 5,000 km	100 - 1,000 km	10 - 100 km	1 - 10 km

### 6.1.3 Temporal Pattern and Scales

The time dimension of aerosols extends over at least six different scales (Figure 6-1). A significant, unique feature of the temporal domain is the existence of periodicities. The secular time scale extends over several decades or centuries. Given climatic and chemical stability of the atmosphere the main causes of secular concentration trends are changes in anthropogenic emissions. The yearly scale is imposed by seasonal variation of solar radiation. Emissions, atmospheric dilution, as well as chemical/removal processes are influenced by the seasonal cycle. The weekly periodicity is unique among the time scales in that it is imposed exclusively by human-induced emission changes. The synoptic scale covers the duration of synoptic meteorological events (3-5 days). Its role is primarily reflected in dilution and chemical/removal processes. The daily cycle is again imposed by solar radiation and it strongly influences the emissions, dilution, and chemical/removal processes. Microscale defines variation of the order of an hour caused by short-term atmospheric phenomena. In the analysis that follows we will emphasize secular trends and



**Figure 6-1. Time scales for particle emissions.**

yearly cycles, with some consideration of daily aerosol pattern. The microscale patterns will be largely ignored.

#### 6.1.4 Space-Time Relationships

The spatial time scales of aerosol pattern are linked by the atmospheric residence time of particles. Short residence times restrict the aerosol to a short transport distance from a

1 source, causing strong spatial and temporal gradients. Longer residence times yield more  
2 uniform regional pattern caused by long range transport. The relationship between spatial  
3 and temporal scales for coarse and fine particles is illustrated in Figure 6-2.

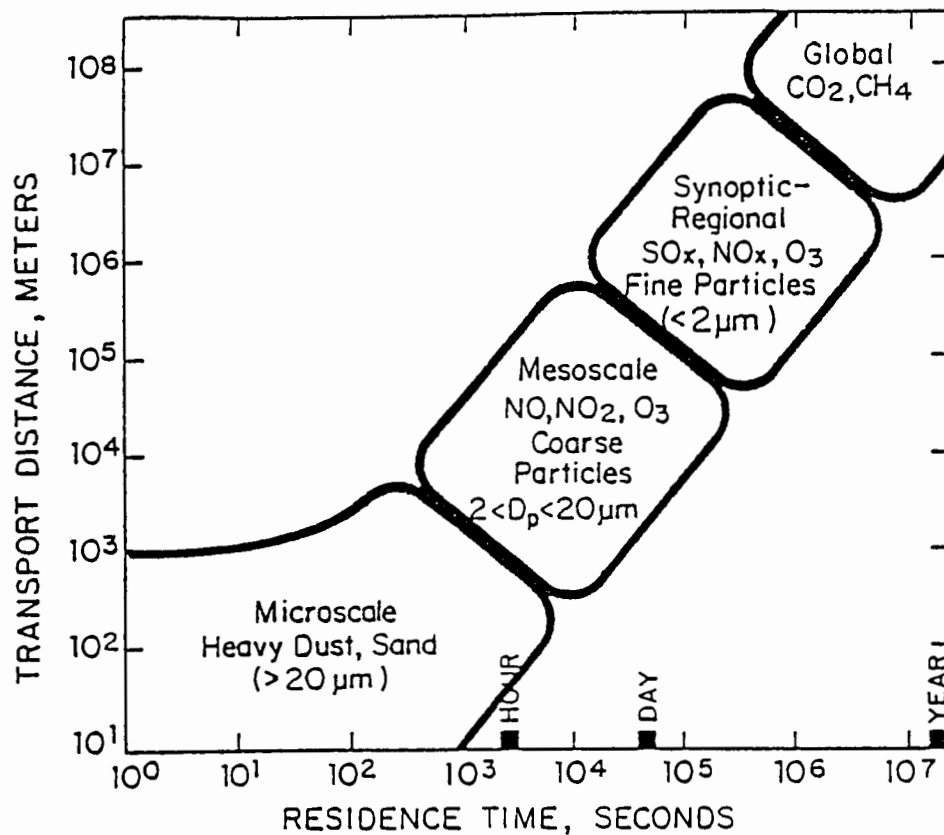
4 The aerosol residence time itself is determined by the competing rates of chemical  
5 transformations and removal rates. Secondary aerosol formation tends to be associated with  
6 multi-day long range transport because of the time delay necessary for the formation. For  
7 sulfates, for example, the residence time is 3-5 days. For fine particles, 0.1  $\mu\text{m}$  and above,  
8 the main removal mechanism involves cloud processing, while coarse particles above 10  $\mu\text{m}$   
9 are deposited by sedimentation. Ultrafine particles, below 0.1  $\mu\text{m}$  also coagulate to form  
10 particles in the 0.1 to 1.0  $\mu\text{m}$  size range. As a consequence of low removal rates, aerosols  
11 in 0.1-1.0  $\mu\text{m}$  size range reside in the atmosphere for longer periods than either smaller or  
12 larger particles (Figure 6-3). If aerosols are lifted into the mid- or upper-troposphere their  
13 residence time will increase to several weeks. Large scale aerosol injections into the  
14 stratosphere through volcanoes or deep convection extend their atmospheric residence to 1-2  
15 years.

16 In the context of the specific analysis that follows, the space-time-concentration  
17 relationship in urban and mountainous areas is of particular importance (Figure 6-4). Urban  
18 areas have strong spatial emission gradients and also corresponding concentration gradients,  
19 particularly in the winter under poor horizontal and vertical transport conditions. In the  
20 summer most urban areas have similar concentrations to their non-urban background.

21 In mountainous regions, the strong concentration gradients are caused by both  
22 topography that limits transport as well as the prevalence of emissions in valley floors.  
23 Strong wintertime inversions tend to amplify the valley-mountain top concentration  
24 difference. Fog formation also accelerates the formation of aerosols in valleys.

### 25 26 **6.1.5 Particle Size Distribution**

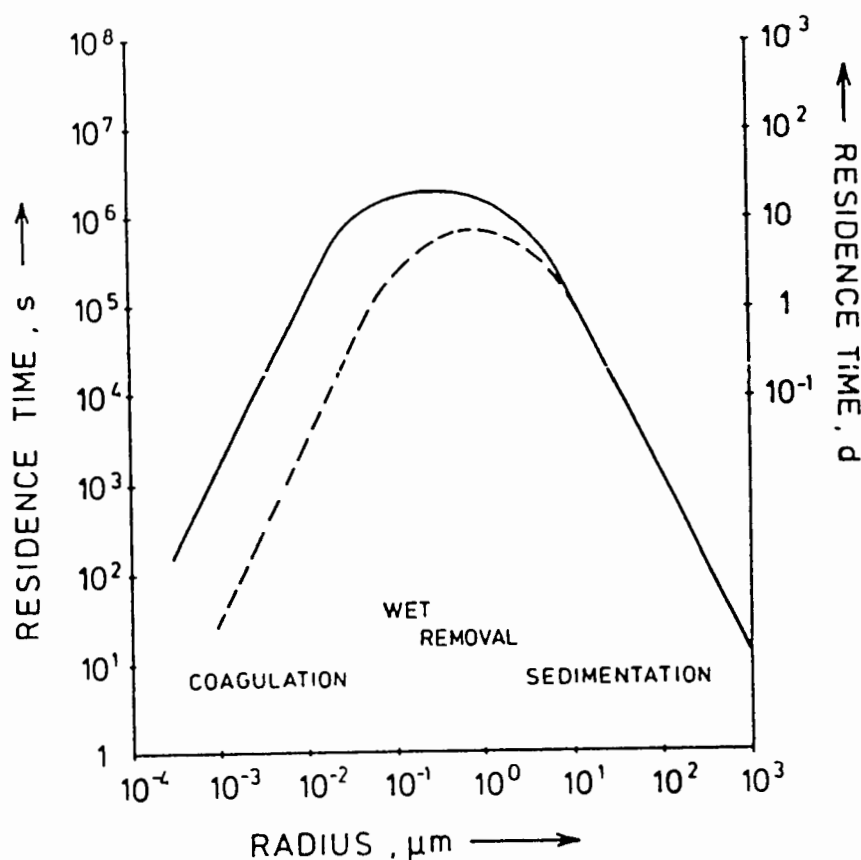
27 The aerosol size distribution is of importance in quantifying both the formation  
28 (generation) as well as the effects of aerosols. Condensation of gaseous substances during  
29 combustion in the atmosphere generally produces fine particles below 1  $\mu\text{m}$  in diameter.  
30 Forced resuspension of soil dust and dispersion of sea spray produces coarse particles above  
31 1  $\mu\text{m}$ .



**Figure 6-2. Relationship of spatial and temporal scales for coarse and fine particles.**

The size distribution of particles also influences both the atmospheric behavior and the effects of aerosols. Atmospheric coagulation, cloud scavenging, and removal by impaction and settling are strongly size dependent. The effects on human health depend on size-dependent lung penetration. Light scattering in visibility and climatic effects is also strongly dependent on particle size.

Measurements over the past decades (Whitby et al, 1972, Whitby 1978) show that atmospheric aerosols may be classified as fine or coarse particles. The size distribution of atmospheric particles is discussed in Section 3.7. The sources, formation mechanisms, and the chemical composition of these two aerosol modes are different. In general, the two aerosol size modes have independent spatial and temporal pattern as described throughout this chapter. Coarse, dust particles tend to be more variable in space and time and can be suspended through natural or human-induced activities. Fine particles are largely of



**Figure 6-3. Residence time in the lower troposphere for atmospheric particles between 0.1 and 1.0  $\mu\text{m}$ .**

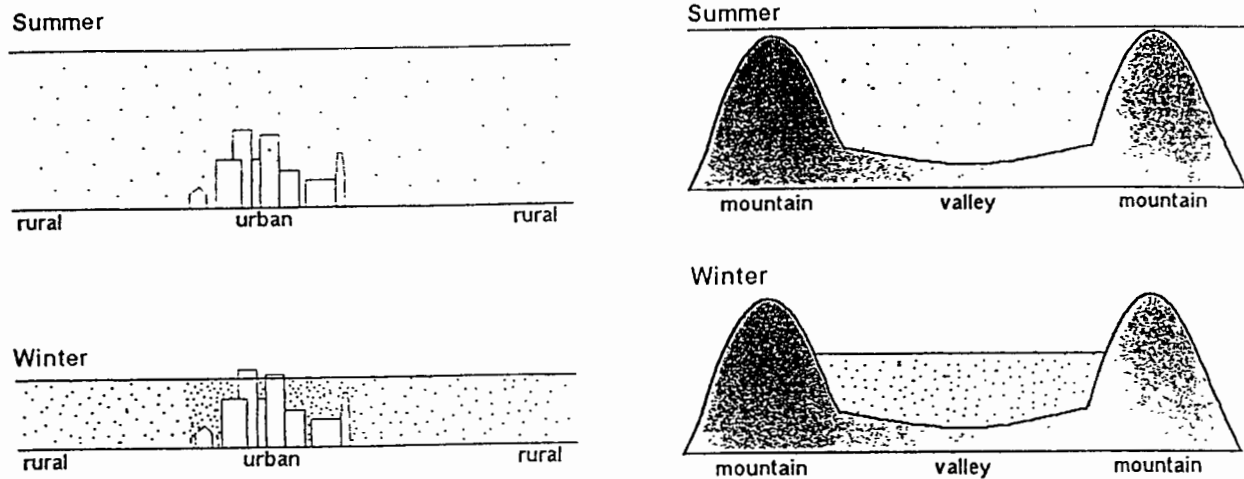
Source: Jaenicke, 1980

secondary origin and their spatial-temporal pattern is more regional. Notable exceptions are urban-industrial hotspots and mountain valleys where primary submicron size smoke particles can prevail.

### 6.1.6 Aerosol Chemical Composition

The chemical composition of atmospheric aerosol is believed to influence the effect on human health. While the causal mechanisms are not fully understood, the acidity, carcinogenicity, and other forms of toxicity are chemical properties considered relevant to human health.

The aerosol chemical composition has also become an important property for identifying source types based on chemical “fingerprints” in the ambient aerosol. Since



**Figure 6-4. Space-time relationship in urban and mountainous areas.**

aerosols reside in the atmosphere for days and weeks, there is a substantial amount of mixing that takes place among the contributions of many sources. At any given “receptor” location and time, the aerosol is a mixture of tens or hundreds of source contributions each having a chemical signature for possible source type identification.

Fine particles are generally composed of sulfates, organics, nitrates, elemental carbon (soot), as well as trace metals (Section 6.6). Each major chemical species have sub-species such as acidic and neutral sulfates, light and heavy organics, ammonium and sodium nitrates, etc.

The chemical composition of coarse particles is dominated by the elements of the earth crust, Si, Al, Fe, suspended from soil. Near roadways, coarse particles may be contaminated by lead and other trace metals. At ocean shores, coarse particles may consist of sea salt arising from breaking of waves. Both resuspended dust and sea salt are primary particles, carrying the chemical signature of their sources.



## 6.1.7 Chapter Organization and Approach

The general approach in preparing this chapter was to organize, evaluate, and summarize the existing large scale aerosol data sets over the United States. Emphasis was placed on complete national coverage as well as the fusion and reconciliation of multiple data sets. The aerosol concentrations are considered from the point of view of spatial, temporal, size and chemical pattern.

The main organizing dimension used to structure this chapter is space. The concentrations are presented on global, continental, national, regional, and sub-regional/urban scales. Within each spatial domain, the spatial-temporal structure, aerosol size and chemical composition is presented. The presentation of aerosol pattern begins with a global and continental perspective (Section 6.2). Next, the national aerosol patterns are examined (Section 6.3) as derived from non-urban and urban  $PM_{10}$  and  $PM_{2.5}$  monitoring networks. In Section 6.4 the aerosol characteristics over seven subregions of the conterminous United States are examined in more detail. The ten year trends, seasonal patterns, as well as the  $PM_{2.5}/PM_{10}$  relationship and fine particle chemical composition is examined for each region. Section 6.5 focuses further on the sub-regional and urban-scale aerosol pattern over representative areas of the United States.

The aerosol concentration pattern over the United States has been reported by many aerosol researchers over the past decade. In particular the research groups associated with the IMPROVE aerosol monitoring networks have been prolific producers of high quality data, reports, and analysis of non-urban data. This section draws heavily on their contribution but the maps, charts, and computations have been re-done for sake of consistency with other (urban) data from the AIRS network. Each of the sections are augmented by suitable but not complete references to the pertinent literature.

## 6.2 CONTINENTAL AND GLOBAL AEROSOL PATTERNS

There are two data sets which can be used to provide information on fine particles concentration patterns on a continental and global scale. Routine visibility distance observations, recorded hourly at many U. S. airports by the U. S. Weather Service, provide an indication of fine particles pollution over the United States. The visibility distance data has been converted to aerosol extinction coefficient and used to access patterns and trends of aerosol pollution over the U.S. (Husar et al., 1994). Routine satellite monitoring of backscattered solar radiation over the oceans by the Advanced Very High Resolution Radiometer sensors on polar orbiting meteorological satellites provides a data set which can be used to give an indication of aerosol pollution over the world's oceans (Husar and Stowe, 1994).

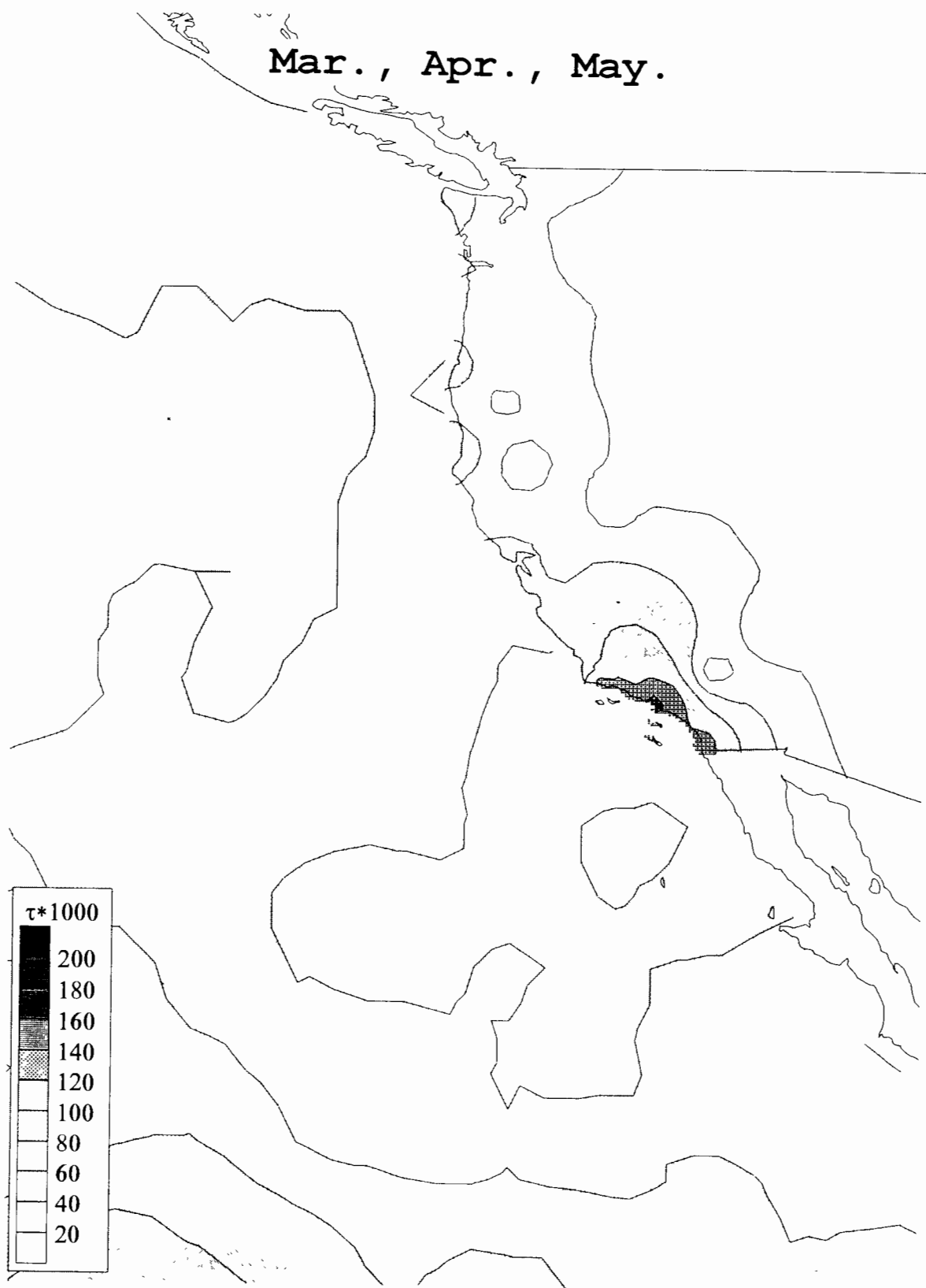
Aerosol detection over the oceans is facilitated by the fact the ocean reflectance at 0.6  $\mu\text{m}$  is only 2%. Hence, even small backscattering from aerosols produces a measurable aerosol signal. The backscattering is converted to a vertically integrated equivalent aerosol optical thickness assuming a shape for the aerosol size distribution or phase function. Clouds are eliminated by a cloud mask, so the data are biased toward clear-sky conditions. The oceanic aerosol maps represent a two-year average (July 1989-June 1991) prior to the eruption of Mt. Pinatubo, while the stratosphere was unusually clear from aerosol. Consequently, the images represent the spatial pattern of tropospheric aerosol.

These two data sets may then be merged to provide a continental-scale perspective. Some results for North America are shown in Figures 6-5a, 6-5b, and 6-5c. The oceanic aerosol for the entire globe is shown seasonally in Figure 6-6. The average aerosol map of Eastern North America for June, July and August (Figure 6-5a) shows areas of high optical depth over the Mid-Atlantic States and over the Atlantic Ocean. The oceanic aerosol concentration is higher near the coast and declines with distance from the coast. This indicates that the aerosol is of continental origin and represents the plume of Eastern North America heading north-east across the Atlantic ocean. This plume can also be seen in the spring and summer season oceanic aerosol patterns shown in Figure 6-6.



**Figure 6-5a. Continental scale pattern of aerosols derived from visibility observations over land and satellite monitoring over the oceans: Eastern North America.**

Source: Husar and Stowe, 1994



**Figure 6-5b. Continental scale pattern of aerosols derived from visibility observations over land and satellite monitoring over the oceans: Western North America.**

Source: Husar and Stowe, 1994

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6-14

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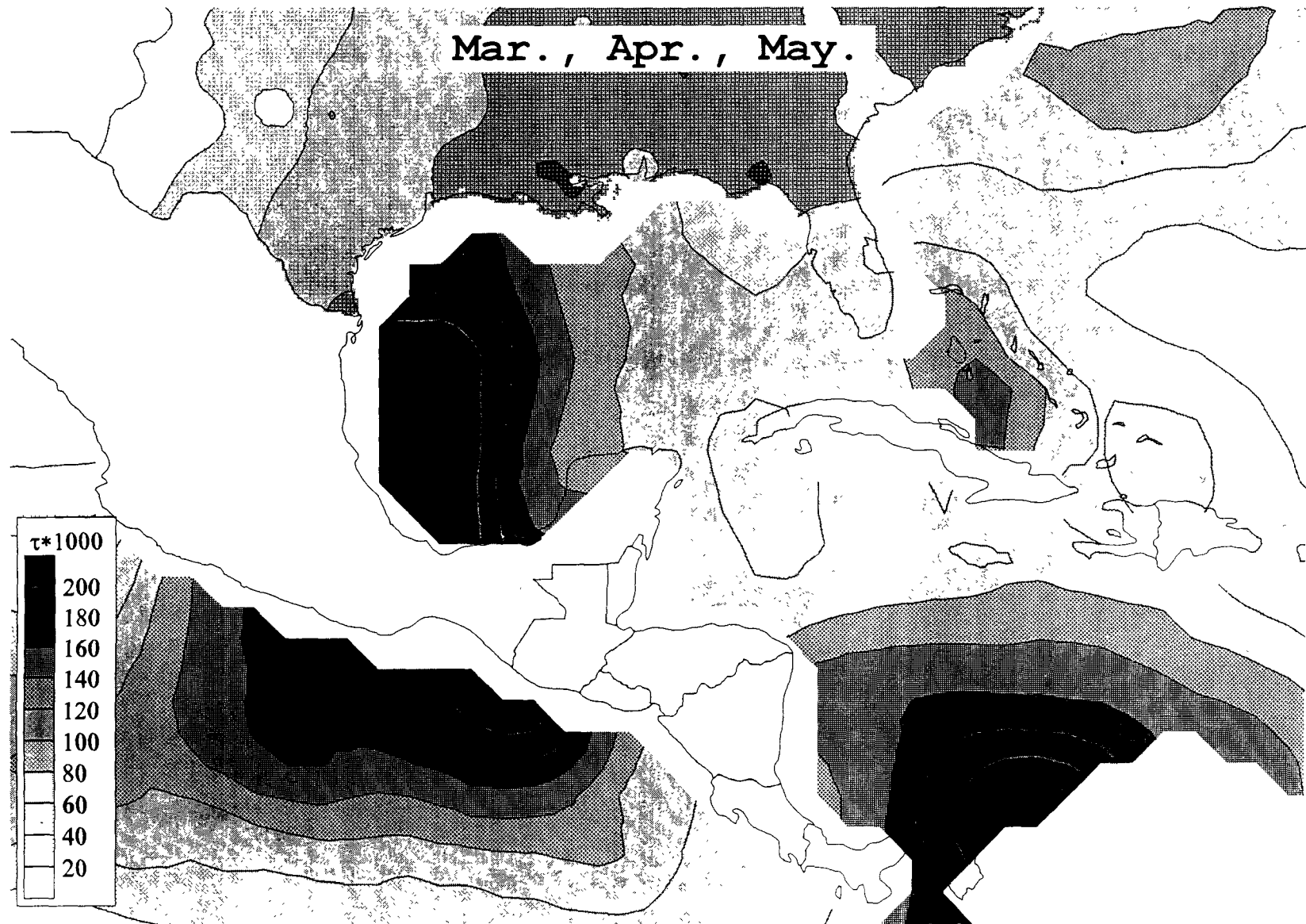


Figure 6-5c. Continental scale pattern of aerosols derived from visibility observations over land and satellite monitoring over the oceans: Southern North America.

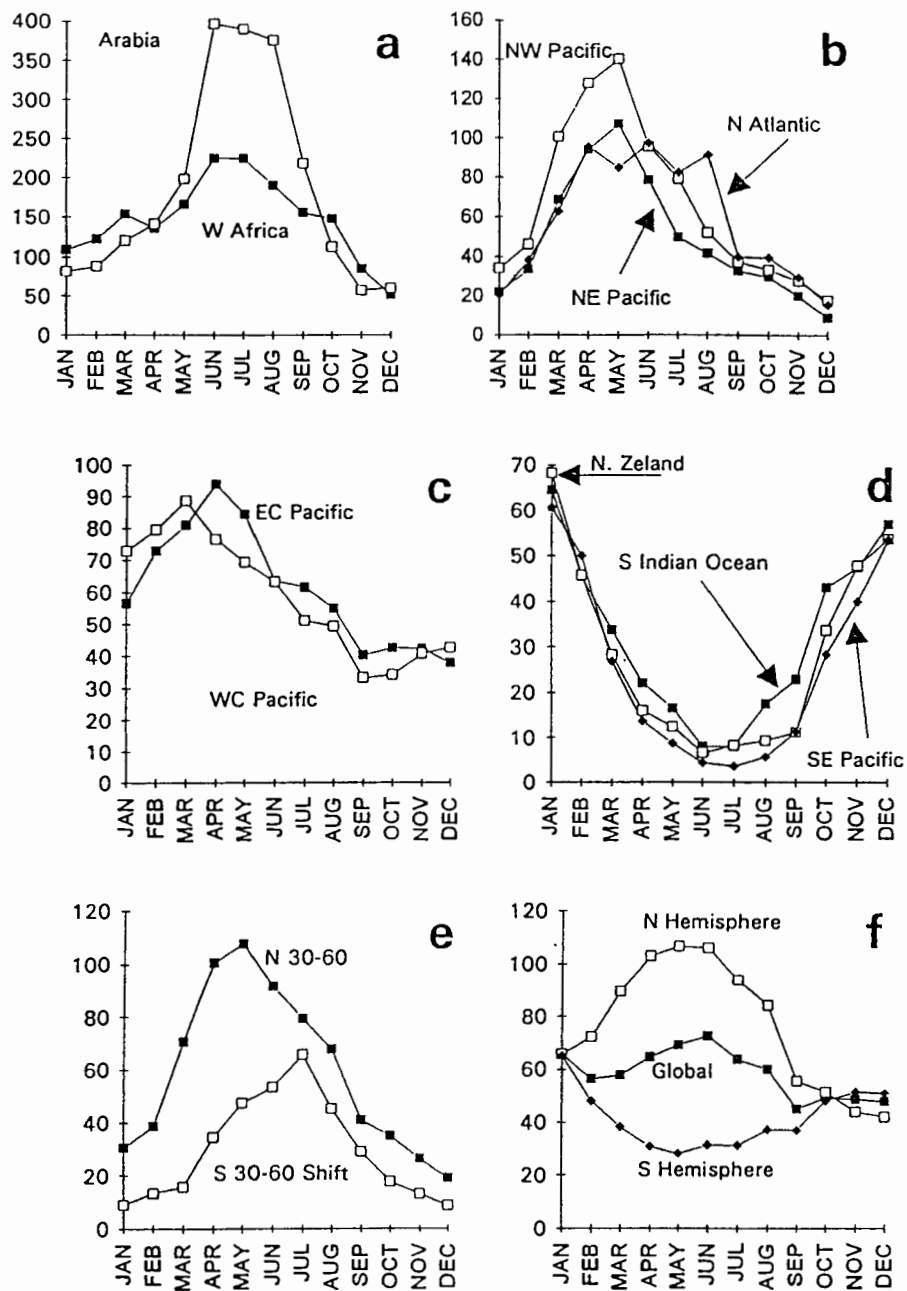
Source: Husar and Stowe, 1994

1           The continental aerosol extinction coefficient data for the southwest coast of North  
2 America indicate elevated aerosol extinction over southern California. The area includes  
3 the hazy South Coast and the San Joaquin Valley air basins. It is interesting to note that  
4 somewhat elevated aerosol optical thickness is also recorder over the Pacific near  
5 Southern California. However, the low aerosol signal and the semi-quantitative satellite  
6 data preclude a clear cause-effect association.

7           The average aerosol map for Southern North America (Figure 6-5c) April, May  
8 and June shows that the oceans adjacent to southern Mexico have high aerosol optical  
9 thickness, both on the Gulf side and the Pacific side. The aerosol concentration is higher  
10 near the coasts and declines toward the sea. This indicates that the aerosol is of  
11 continental origin, over southern Mexico. The haze off the Mexican coasts is most  
12 pronounced in the spring season. Visibility observations at meteorological stations also  
13 indicate a spring maximum in horizontal extinction. The region is known for extensive  
14 springtime slash burning. Photographs taken by astronauts show numerous areas of  
15 biomass burning in the spring season. Visible geostationary satellite images taken in the  
16 spring also show the haze plumes emanating from southern Mexico. However the  
17 composition and sources of the Mexican haze are not established.

18           The seasonal aerosol pattern over the oceans reveals that the highest aerosol  
19 signal is near the tropics, where wind-blown dust and biomass combustion from Africa  
20 and southern Asia produce 5,000 km long aerosol plumes (Figure 6.6). Further aerosol  
21 belts of marine origin are observed just north of the Equator and at 30 to 60° latitudes  
22 in both hemispheres. The backscattering in the summer hemispheres exceed the winter  
23 values by a factor of 5 to 10. There is a pronounced seasonality in each aerosol region  
24 (Figure 6-7); the higher aerosol levels appear in the summer hemispheres although  
25 many continental and marine aerosol regions show a spring maximum. Thus, the global  
26 tropospheric aerosol is a dynamic collection of independent aerosol regions, each having  
27 unique sources and temporal pattern.

28           The seasonal oceanic aerosol maps show two distinctly different spatial patterns:  
29 aerosol plumes originating from continents, and oceanic aerosol patches that are  
30 detached from the continents. The continental aerosol plumes are characterized by high



**Figure 6-7. Seasonal pattern of oceanic aerosols derived from satellite observations.**

Source: Husar and Stowe, 1994

values near the coastal areas and a decline with distance from the coast. The most prominent aerosol plume is seen over the equatorial Atlantic, originating from West Africa and crossing the tropical Atlantic. It is the well known Sahara dust plume. Additional continental plumes emanate from Southwest Africa, Indonesia, China-Japan, Central America and eastern North America. Aerosols of marine origin dominate large zonal belts (30 to 60° N and S) in the summer hemispheres as well as near the Equator. In summary, the global tropospheric aerosol is a collection of largely independent aerosol regions, each having a bio-geochemically active source and unique spatial temporal pattern.

Based on the above global and continental-scale observations, it can be concluded that the continental plume from eastern North America is not as intense as those from other industrial and non-industrial regions of the world. However, quantitative aerosol comparisons of global regions are not available.

## **6.3 U.S. NATIONAL AEROSOL PATTERN AND TRENDS**

Our current understanding of the U.S. national aerosol pattern arises from non-urban, regional background monitoring networks the Interagency Monitoring of Protected Visual Environments (IMPROVE) and the Northeast States for Coordinated Air Use Management (NESAUM) and from the mainly urban network, the Aerometric Information Retrieval System (AIRS). The non-urban and urban networks yield markedly different national patterns, particularly over the western US. For this reason the results from the two sets of observations are presented separately and the differences between two networks are evaluated.

An early compilation of the chemical and size resolved aerosol studies list 31 aerosol data sets gathered since the 1970's. However, these databases are widely dispersed, and are not generally available for study or evaluation (Chow and Watson, 1988).

### **6.3.1 Non-Urban National Aerosol Pattern**

Non-urban aerosol concentrations are measured at remote sites, away from urban-industrial activities. Size-segregated aerosol mass and chemical composition data are available for 50 sites, through the IMPROVE (Eldred et al, 1988) and NESAUM (Poirot



et al., 1990; Flocchini et al., 1990) networks. These are located mostly in national parks and wilderness areas. The  $PM_{10}$  and  $PM_{2.5}$  mass concentrations are sampled and analyzed on separate filters. The sampling frequency was generally twice a week (Wednesdays and Saturdays) for 24-hours. The  $PM_{2.5}$  samples are analyzed for chemical composition which make the data sets suitable for chemical mass balance computations (e.g. Sisler et al., 1993). The IMPROVE/NESCAUM aerosol data are available from 1988 through 1993.

The results of the national spatial and temporal pattern analysis are presented in quarterly contour maps and monthly seasonal time charts. The contours drawn for the eastern United States are derived from only 15 to 20 stations. As a consequence, these contour lines are to be taken as guides to the eye and not as actual pattern. The quarters of the year are calendrical.

#### 6.3.1.1 Non-urban $PM_{2.5}$ Mass Concentrations

Maps of seasonal average non-urban  $PM_{2.5}$  concentrations are shown in Figure 6-8. The maps show that the country can be divided roughly into east and west halves. The eastern United States is covered by large, contiguous  $PM_{2.5}$  concentrations that range from  $10 \mu\text{g}/\text{m}^3$  in Quarter 1, and  $17 \mu\text{g}/\text{m}^3$  in Quarter 3. During the transition seasons (Quarters 2 and 4) the eastern U.S. non-urban  $PM_{2.5}$  concentrations are at about  $12 \mu\text{g}/\text{m}^3$ . Within the eastern US, there are subregions such as New England that have lower concentrations ranging between 8 to  $12 \mu\text{g}/\text{m}^3$ .

The lowest non-urban  $PM_{2.5}$  concentrations are measured over the central mountainous western states. The low winter concentrations are at about  $3 \mu\text{g}/\text{m}^3$ , while the summer values are around  $6 \mu\text{g}/\text{m}^3$ . Somewhat elevated  $PM_{2.5}$  concentrations are observed over the southwestern border adjacent to Mexico as well as in California and the Pacific Northwest.

The non-urban fine particle mass clearly show multiple aerosol regions over the conterminous US, each exhibiting a unique spatial and seasonal characteristics.

#### 6.3.1.2 Non-urban $PM_{\text{Coarse}}$ Concentrations

The non-urban coarse aerosol mass concentration in the size range 2.5 to  $10 \mu\text{m}$  is given in the seasonal maps Figure 6-9. It is plotted on the same scale as the non-urban  $PM_{2.5}$  and  $PM_{10}$  maps to show that the non-urban coarse mass concentration is less than the

fine mass concentration over most of the country. The lowest non-urban coarse particle concentration is recorded during the first and fourth calendar quarters when virtually the entire conterminous United States showed values  $< 10 \mu\text{g}/\text{m}^3$ . It is remarkable that during the quarters 1 and 4, the industrialized Midwest, adjacent to the Ohio River shows low PMCoarse concentration ( $< 10 \mu\text{g}/\text{m}^3$ ) comparable to the pristine mountainous Rocky Mountains states. The highest non-urban coarse mass concentrations is shown during quarters 2 and 3. In quarter 2, the southwestern United States adjacent to the Mexican border shows the highest non-urban coarse mass concentrations. In quarter 3, the monitoring sites in Florida and Great Smoky Mountains exhibit high concentrations ( $> 12 \mu\text{g}/\text{m}^3$ ).

### 6.3.1.3 Non-urban PM<sub>10</sub> Mass Concentrations

Maps of seasonal average non-urban PM<sub>10</sub> concentrations are shown in Figure 6-10. PM<sub>10</sub> is the sum of the PM<sub>2.5</sub> and PMCoarse. The spatial pattern, including the delineation of aerosol regions is similar to the PM<sub>2.5</sub>. However, the PM<sub>10</sub> concentrations exceed the PM<sub>2.5</sub> by up to factor of two depending on region and season.

The eastern U.S. PM<sub>10</sub> concentrations range between  $12 \mu\text{g}/\text{m}^3$  in Quarter 1, and  $25 \mu\text{g}/\text{m}^3$  in Quarter 3. During the transition seasons (Quarters 2 and 4) the eastern U.S. non-urban PM<sub>10</sub> concentrations are at about  $15 \mu\text{g}/\text{m}^3$ , except in New England. The lowest non-urban PM<sub>10</sub> concentrations are measured over the central mountainous states,  $5 \mu\text{g}/\text{m}^3$  in Quarter 1,  $10 \mu\text{g}/\text{m}^3$  in Quarter 3, and  $7 \mu\text{g}/\text{m}^3$  during the transition seasons. Higher PM<sub>10</sub> concentrations, between 10 to  $20 \mu\text{g}/\text{m}^3$  were measured over the southwestern United States as well as over the Pacific states from California to the Northwest.

### 6.3.1.4 PM<sub>2.5</sub>/PM<sub>10</sub> Ratio at Non-urban Sites

The PM<sub>10</sub> aerosol mass is composed of fine mass (PM<sub>2.5</sub>) and coarse mass, below  $10 \mu\text{m}$  (Figure 6-10). Both the sources and the effects of fine particles differ markedly from those of coarse particles. For this reason it is beneficial to examine the relative contribution of PM<sub>2.5</sub> and PM<sub>10</sub> concentrations. Figure 6-11 shows the seasonal fine mass as a fraction of PM<sub>10</sub>.

Nationally, the fine fraction at non-urban sites ranges between 0.4 and 0.8. The highest fine fraction is recorded east of the Mississippi River, where 75% of the PM<sub>10</sub> mass

1 is in particles  $<2.5\ \mu\text{m}$  in size. This is also the region that shows the highest  $\text{PM}_{10}$   
2 concentrations, thus fine particles dominate the non-urban aerosol concentrations east of the  
3 Mississippi River. The fine fraction also exceeds the coarse fraction at the non-urban  
4 northwestern sites. The fine fraction is the lowest in the southwestern United States  
5 ( $< 50\%$ ) particularly in the spring season (Quarter 2). Evidently, the southwestern  $\text{PM}_{10}$  is  
6 dominated by coarse particles in the spring season.

7 Spatial and seasonal variation of the fine fraction is a further indication for the  
8 existence of different aerosol regions over the conterminous US. This is further illuminated  
9 in Section 6.4 where the aerosol characteristics over different regions of the United States are  
10 discussed.

### 11 12 **6.3.1.5 Non-urban Fine Particle Chemistry**

13 The chemical composition of non-urban fine particles over the conterminous United  
14 States is now reasonably well understood. The IMPROVE/NESCAUM network provides  
15 over 5 years of aerosol mass and chemical composition data. The detailed and almost  
16 complete fine particle chemistry data from these networks allows the chemical apportionment  
17 of the fine particle mass into aerosol types such as sulfates, nitrates, organics, soot, and fine  
18 soil (Schichtel and Husar, 1992; Sisler et al., 1993, Sisler and Malm, 1994). The  
19 quantification of these aerosol types is relevant to both the determination of the aerosol  
20 effects as well as for source apportionment of fine particle species. It should be emphasized  
21 that the chemical composition as well as the absolute concentrations of the chemical species  
22 is likely to be different in urban areas and mountain valleys, than at the remote monitoring  
23 sites. Also, the quantification of organics, nitrates, and other metastable species is subject to  
24 major uncertainties.

25 The following discussion is a summary of the national fine particle chemistry derived  
26 from non-urban monitoring networks. The national spatial pattern for fine particle sulfate,  
27 nitrate, organics and soot will be presented. These aerosol types along with wind blown dust  
28 account for virtually all aerosol fine mass in the conterminous US. Presentation of the  
29 detailed chemical pattern in urban-industrial areas as well as in poorly ventilated air sheds  
30 over the mountainous western states would be desirable but it is unavailable at this time.

1 In the non-urban East the fine aerosol is dominated by sulfur aerosol types (sulfate and  
2 ammonium ions and associated water) and organics which together constitute approximately  
3 80% of the fine particulate mass. Over the Northeast, organics dominate the fine particle  
4 mass, particularly during the winter season. In the Southwest, fine soil is also a major  
5 component accounting for 25 to 30% of fine mass while sulfates are a less dominant  
6 component (as shown in Figure 6-12) (Schichtel and Husar, 1992).

7 The national pattern of annual fine particle sulfate, nitrate, organics, and soot  
8 concentrations from the IMPROVE network is shown in Figure 6-13 (Sisler et al., 1993).  
9 The station density, particularly over the eastern United States is limited. The contour lines  
10 in the annual average maps are to be used as guides to the eye, rather than actual values.  
11 The eastern U.S. sulfate (Figure 6-13a) exceeds the concentrations over the mountainous  
12 western states by factor of five or more. Elevated sulfate in excess of  $1 \mu\text{g}/\text{m}^3$  is also  
13 reported over the Pacific coast states. Sulfates also contribute over 50% of the eastern fine  
14 particulate mass, while in the West sulfates contribute 30% or below.

15 Fine particle nitrates (Figure 6-13b) are most prevalent over California, exceeding  $4$   
16  $\mu\text{g}/\text{m}^3$  at most sites. Their share of the fine mass at several California sites exceeds 20%. It  
17 is well known, however, that accurate measurement of nitrate concentration has been plagued  
18 by numerous sampling problems, and uncertainties in chemical analysis.

19 Organic carbon concentrations are high over California, northwestern sites, as well as  
20 at the eastern U.S. sites. Relative to fine particle mass organics contribute over 50% over  
21 the Northwest, and about 30% throughout the eastern US. Sampling and chemical analysis  
22 problems of organics are comparable to that of the nitrates. For this reason, the  
23 concentration estimates of these meta-stable species are continuously being revised.

24 Light absorbing elemental carbon/soot concentrations are high over the Northwest,  
25 southern California, as well as at the Washington DC site. In the Northwest, soot exceeds  
26 10% of the fine mass concentration, but over most of the country it is 5% or less.

27 The chemical composition of  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  aerosols in the IMPROVE network  
28 (Eldred et al., 1994) revealed that the average coarse mass does not differ significantly  
29 between the East and West, however, the fine mass is higher in the East. Also about 80% of  
30 soil elements and 20 % of sulfur were found in the coarse fraction. Most trace elements  
31 were found in the fine fraction, both in the East and in the West. The spatial and seasonal

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6-24b

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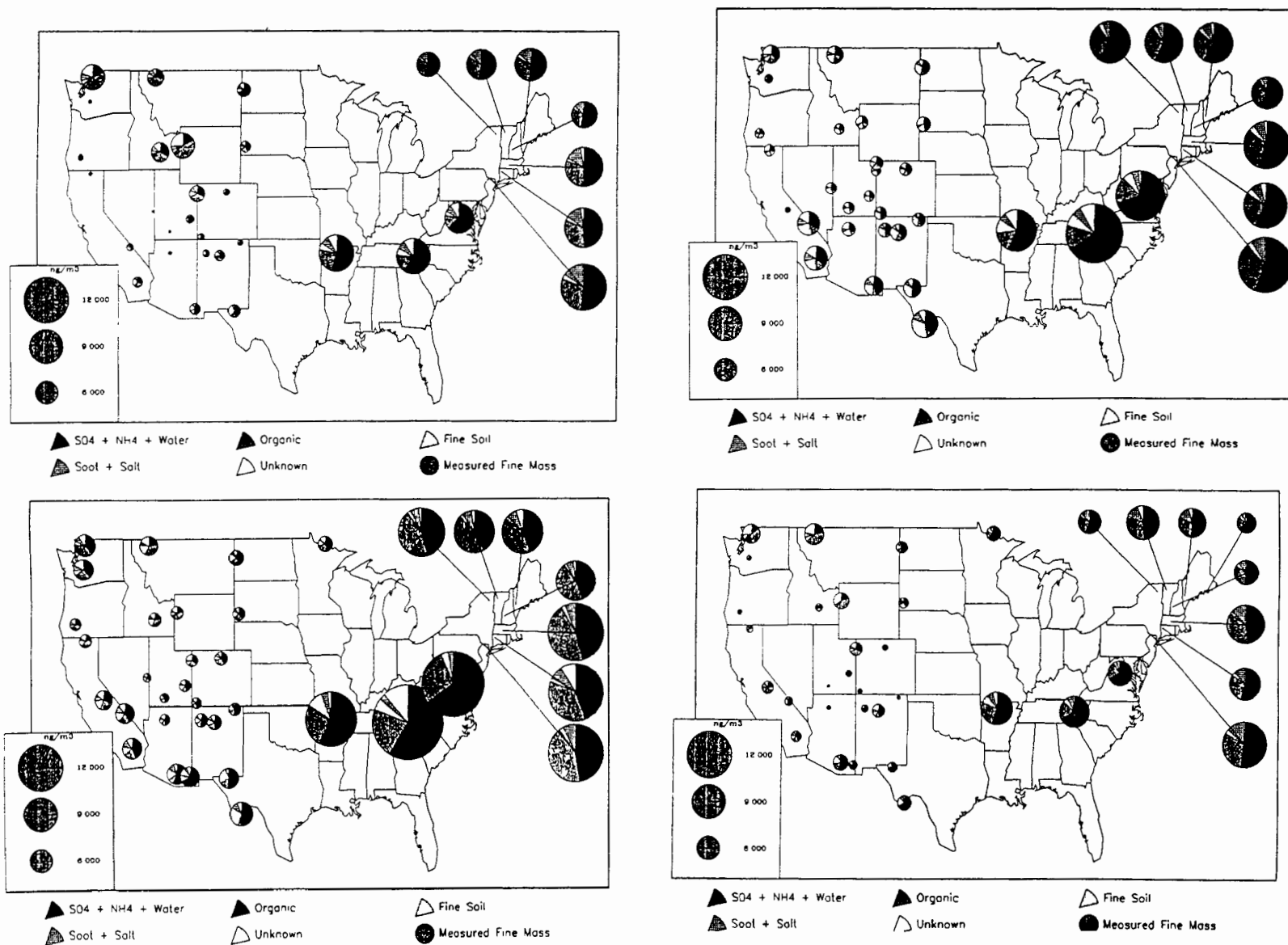
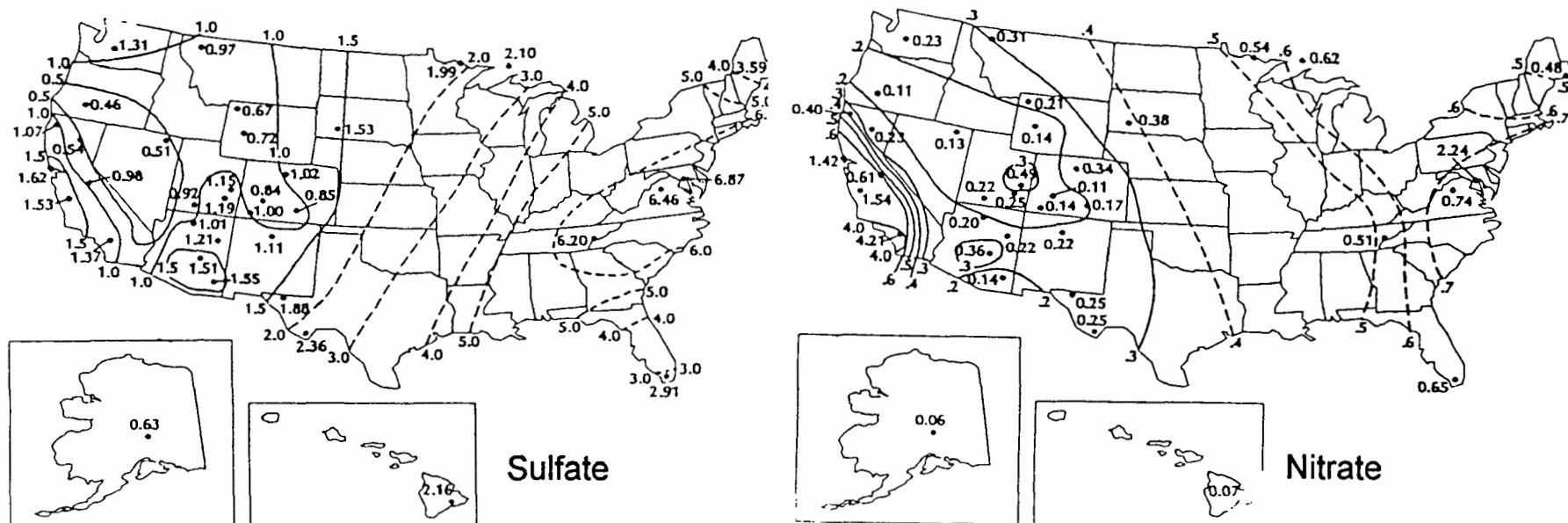


Figure 6-12 Chemical mass balance of fine particles derived from non-urban IMPROVE/NESCAUM networks.

Source: Schichtel and Husar, 1992

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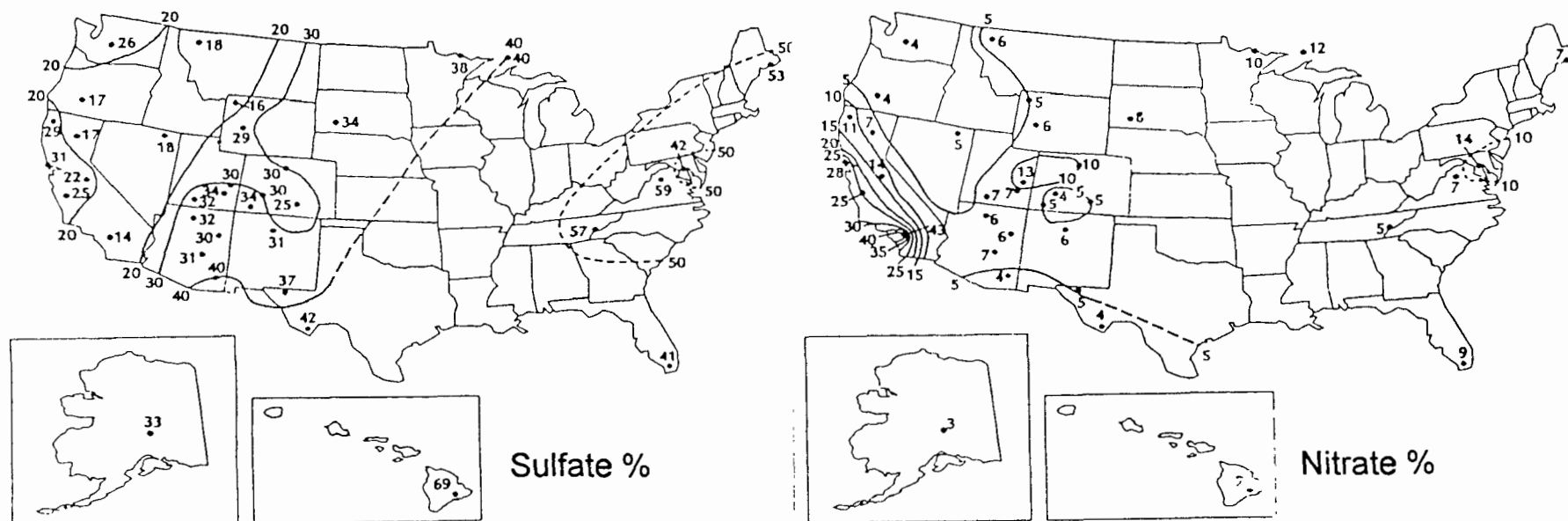


Figure 6-13a,b. Yearly average absolute and relative concentrations for sulfate, nitrate, organics, and soot.

Source: Sisler et al, 1993

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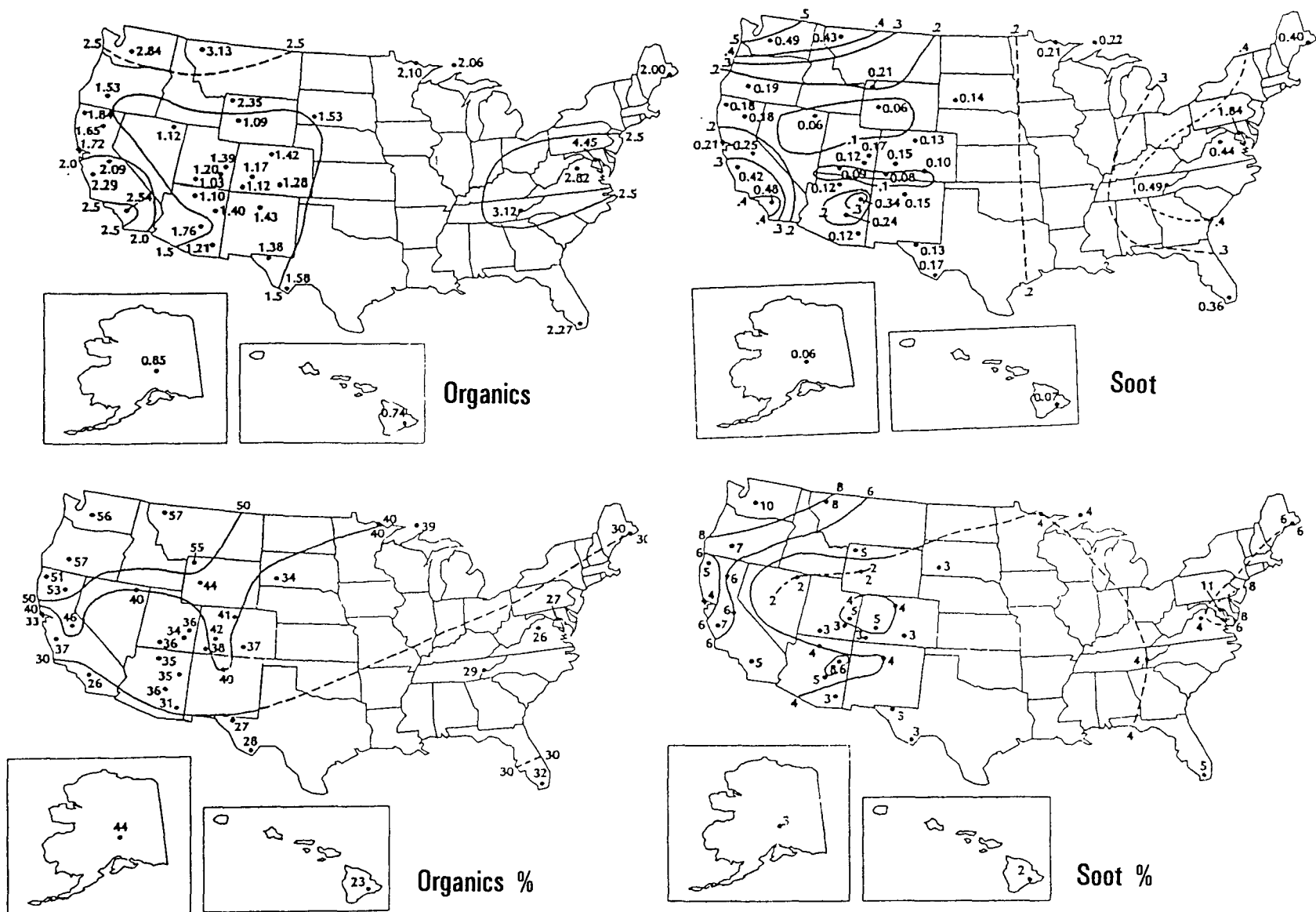


Figure 6-13c,d. Yearly average absolute and relative concentrations for sulfate, nitrate, organics, and soot.

Source: Sisler et al, 1993

1 pattern in particle concentration and optical extinction in the United States from the  
2 IMPROVE network were also summarized by Malm et al., 1994.

3 Studying the regional patterns of non-urban trace metals in the IMPROVE network  
4 (Eldred et al., 1994) found a good correlation between selenium and sulfur at all sites in the  
5 East. The correlation in the West is lower. Comparison of the S/Se ratios for summer and  
6 winter shows that there is approximately twice the sulfur relative to selenium in summer  
7 compared to winter. Zinc is highest at the sites in the central East. It does not correlate  
8 well with sulfur. Lead and bromine are relatively uniform, with slightly higher mean  
9 concentrations in the East. There is poor correlation between lead and bromine. Copper and  
10 arsenic are highest in Arizona copper smelter region. Copper is also higher in the central  
11 East.

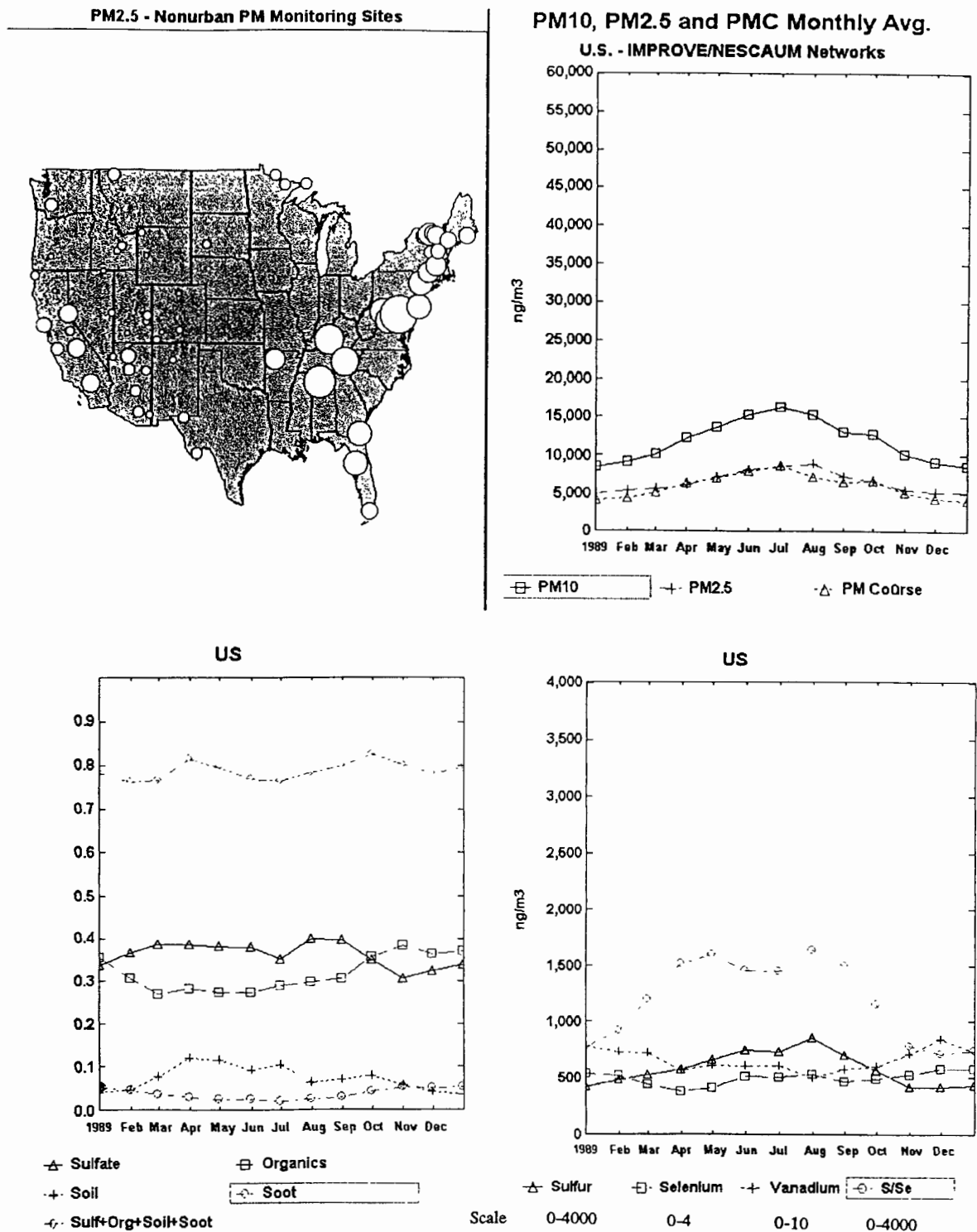
12 Trends (1982 to 1992) of non-urban fine particle sulfur, zinc, lead, and soil elements  
13 were reported by Eldred et al. (1994) using the IMPROVE network data. They observe that  
14 in the southwest, sulfur trends in spring, summer, and fall decreased, while most of the  
15 winter trends increased. The trends in the Northwest increase slightly. The two eastern sites  
16 (Shenandoah and Great Smokey Mountains), have increased almost 4% per year in summer,  
17 increased 1 to 3 % in spring and fall, and decreased 2% in winter. The annual increase was  
18 between 2 to 3%. Generally, there were no significant trends in zinc and the soil elements.  
19 Lead at all sites decreased sharply through 1986, corresponding to the shift to unleaded  
20 gasoline. The ten year trends reported by Eldred et al. (1994) have not been compared and  
21 reconciled with other compatible data.

#### 22 23 **6.3.1.6 Seasonality of the Non-urban Chemistry**

24 This section discusses the seasonality of size segregated chemical composition at  
25 non-urban monitoring sites (IMPROVE/NESCAUM) over the entire U.S. (Figure 6-14).

26 The nationally aggregated average  $PM_{10}$ ,  $PM_{2.5}$  and  $PM_{Coarse}$  is shown in Figure  
27 6-14b. The non-urban  $PM_{10}$  concentration ranges from  $8 \mu g/m^3$  in the winter, December  
28 through February to about  $15 \mu g/m^3$  in June to August. On the national scale the  $PM_{10}$   
29 seasonality is clearly sinusoidal with a peak. Fine particles over the non-urban conterminous  
30 United States account for about 50 to 60% of the  $PM_{10}$  mass concentration throughout the





**Figure 6-14.** Seasonal pattern of non-urban aerosol concentrations for the entire U.S. a) Average concentration. b) PM<sub>10</sub>, PM<sub>2.5</sub>, and PM<sub>Coarse</sub>. c) Chemical fraction of sulfate, soil, organics, and soot. d) Tracer concentrations.

1 year. The coarse mass accounts for 40 to 50% throughout the year. Hence, the fine-coarse  
2 aerosols ratio does not change dramatically for the average non-urban aerosol.

3 The relative chemical composition of the aggregated non-urban aerosol pattern is  
4 shown in Figure 6-14c, including sulfates, organics, soil, and soot as a fraction of the fine  
5 particle mass concentration. The Figure also shows the sum of these four aerosol species to  
6 indicate the fraction of the fine aerosol mass that is not accounted for. Most notable among  
7 the missing species is the contribution of nitrates.

8 Throughout the year, sulfate aerosol, including the ammonium cation accounts for  
9 30 to 40% of the fine mass. There is a remarkably mild seasonality in the nationally  
10 aggregated sulfate fraction. Organics also contribute 30 to 40% of the nationally averaged  
11 fine particle mass. Thus, sulfates and organics are the two dominant species contributing to  
12 about 70% of the fine aerosol mass.

13 The contribution of soil dust to the fine mass ranges between 4% in the winter months  
14 to 12% during April through July. Soot, i.e. elemental carbon is about 2% during the  
15 summer and 5% during the winter.

16 The sum of the four measured fine mass components, sulfates, organics, soil and soot  
17 add up to about 80% of the measured fine mass throughout the year. The remaining,  
18 unaccounted fine mass may be contributed by nitrates, trace metals (e.g. Pb, Br), sea salt  
19 (NaCl), etc.

20 The seasonal pattern of concentration of primary emission tracers, selenium, Se and  
21 vanadium, V is shown Figure 6-14d. Se is a known tracer for coal combustion (Miller and  
22 Friedlander, 1992?), while V is a trace constituent of fuel oil. The Figure also shows the  
23 monthly average concentration of fine particle sulfur as well as the S/Se ratio. If all the fine  
24 particle sulfur was contributed by coal combustion then S/Se ratio would be a measure of  
25 secondary sulfate formation.

26 The national average Se concentration is rather uniform over the seasons, ranging  
27 between 400 to 600 ng/m<sup>3</sup>. Since Se is a primary pollutant, the seasonal invariance means  
28 that the combined effect of emissions and dilution is seasonally invariant over the year.

29 The concentration of V is between 500 to 700 ng/m<sup>3</sup>, with the higher concentrations  
30 occurring in the winter season. Evidently, emission of V bearing fuel oil is more  
31 pronounced during the cold season. The monthly average sulfur aerosol exhibits the highest

1 concentrations  $1.5 \mu\text{g}/\text{m}^3$ , during June, July, and August, and the lowest values  $0.9 \mu\text{g}/\text{m}^3$ ,  
2 during November, December, and January.

3 The S/Se ratio is about 700 during November to January and climbs to about 1,500  
4 during April through September. The higher S/Se ratio during the warm season is an  
5 indication of secondary sulfate production. Alternatively, the summer sulfates could be  
6 contributed by sources other than coal combustion.

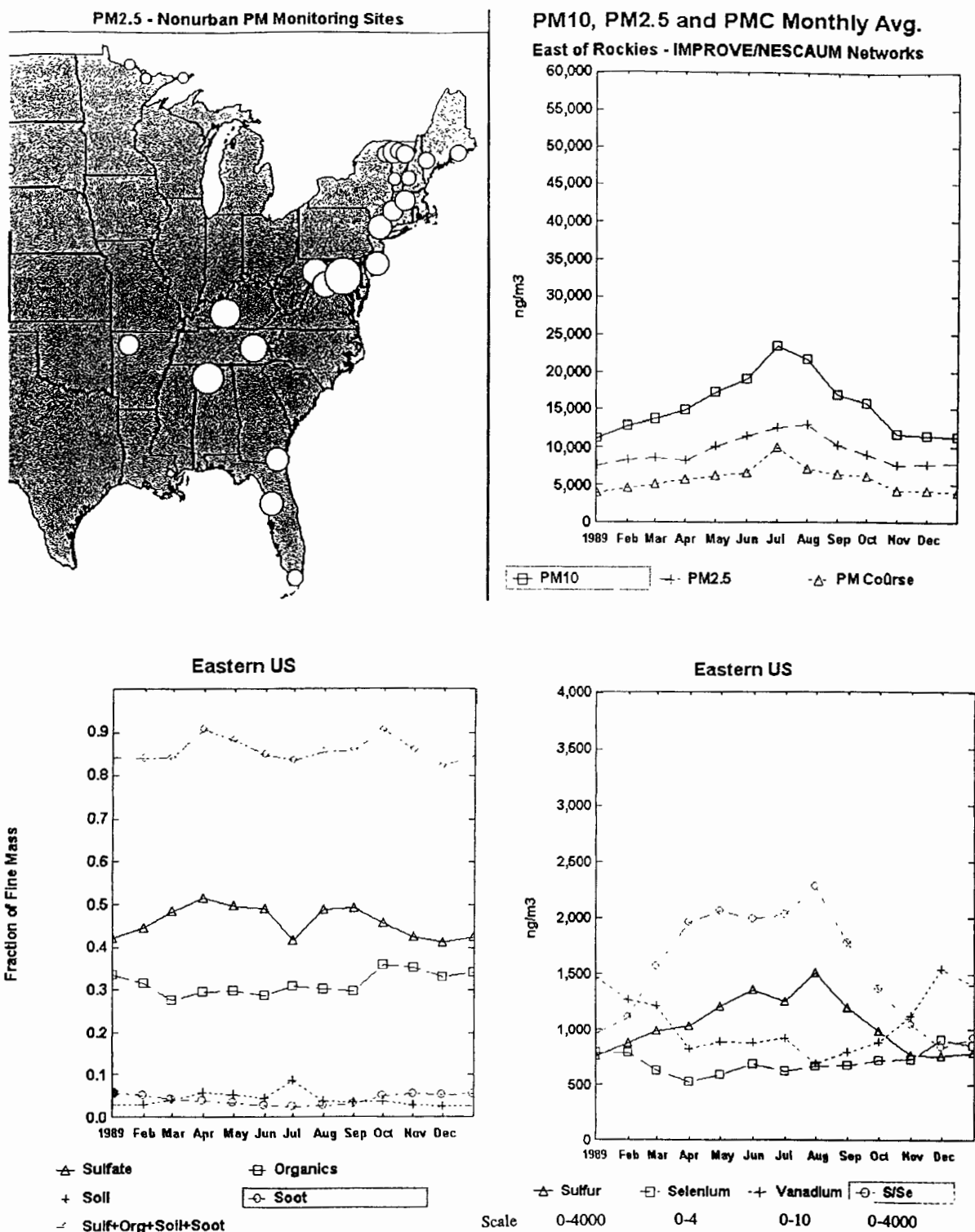
### 7 *Eastern United States*

9 The seasonal pattern of the eastern U.S. aerosol chemistry is shown in Figure 6-15.

10 The concentration of  $\text{PM}_{10}$ ,  $\text{PM}_{2.5}$ ,  $\text{PM}_{\text{Coarse}}$  (Figure 6-15b) indicates a similar  
11 seasonality, highest concentrations in the summer, and lowest in the winter. The  $\text{PM}_{10}$  levels  
12 range between 12 to  $24 \mu\text{g}/\text{m}^3$ , the  $\text{PM}_{2.5}$  are between 8 to  $12 \mu\text{g}/\text{m}^3$ , while  $\text{PM}_{\text{Coarse}}$  are 4  
13 to  $7 \mu\text{g}/\text{m}^3$ . The size segregated aerosol data for the non-urban East show that the fine mass  
14 concentration ( $8$  to  $12 \mu\text{g}/\text{m}^3$ ) is higher than the national average ( $4$  to  $8 \mu\text{g}/\text{m}^3$ ), while the  
15 coarse mass concentration is comparable to the national average. Consequently, eastern U.S.  
16 non-urban fine particles contribute 60 to 70% of the fine mass throughout the year.

17 The apportionment of the fine particle mass into its chemical components  
18 (Figure 6-15c) favors sulfates which amount to 40 to 50% of the fine mass throughout the  
19 year, compared to about 30% of organics. The contribution of soil dust is about 5%  
20 throughout the year, while soot is more important in the winter (6%) than in the summer  
21 (3%). The above three aerosol chemical components account for 85 to 90% of the measured  
22 fine particle mass, leaving only marginal contribution to nitrates, trace metals, and sea salt.

23 The coal tracer selenium (Figure 6-15d) exhibits a modest winter peaked seasonality  
24 between 600 to  $800 \text{ ng}/\text{m}^3$ . Vanadium on the other hand, is factor of two higher in the  
25 winter ( $1,500 \text{ ng}/\text{m}^3$ ) compared to the summer ( $750 \text{ ng}/\text{m}^3$ ). Evidently, the primary  
26 contribution from fuel oil is winter peaked. The S/Se ratio is about 1,000 in the winter, and  
27 it is over 2,000 in the summer months. This suggests the seasonality of secondary sulfate  
28 formation during the summer months, but other factors can not be excluded.



**Figure 6-15.** Seasonal pattern of non-urban aerosol concentrations for the Eastern U.S. a) Average concentration. b)  $PM_{10}$ ,  $PM_{2.5}$ , and  $PM_{Coarse}$ . c) Chemical fraction of sulfate, soil, organics, and soot. d) Tracer concentrations.

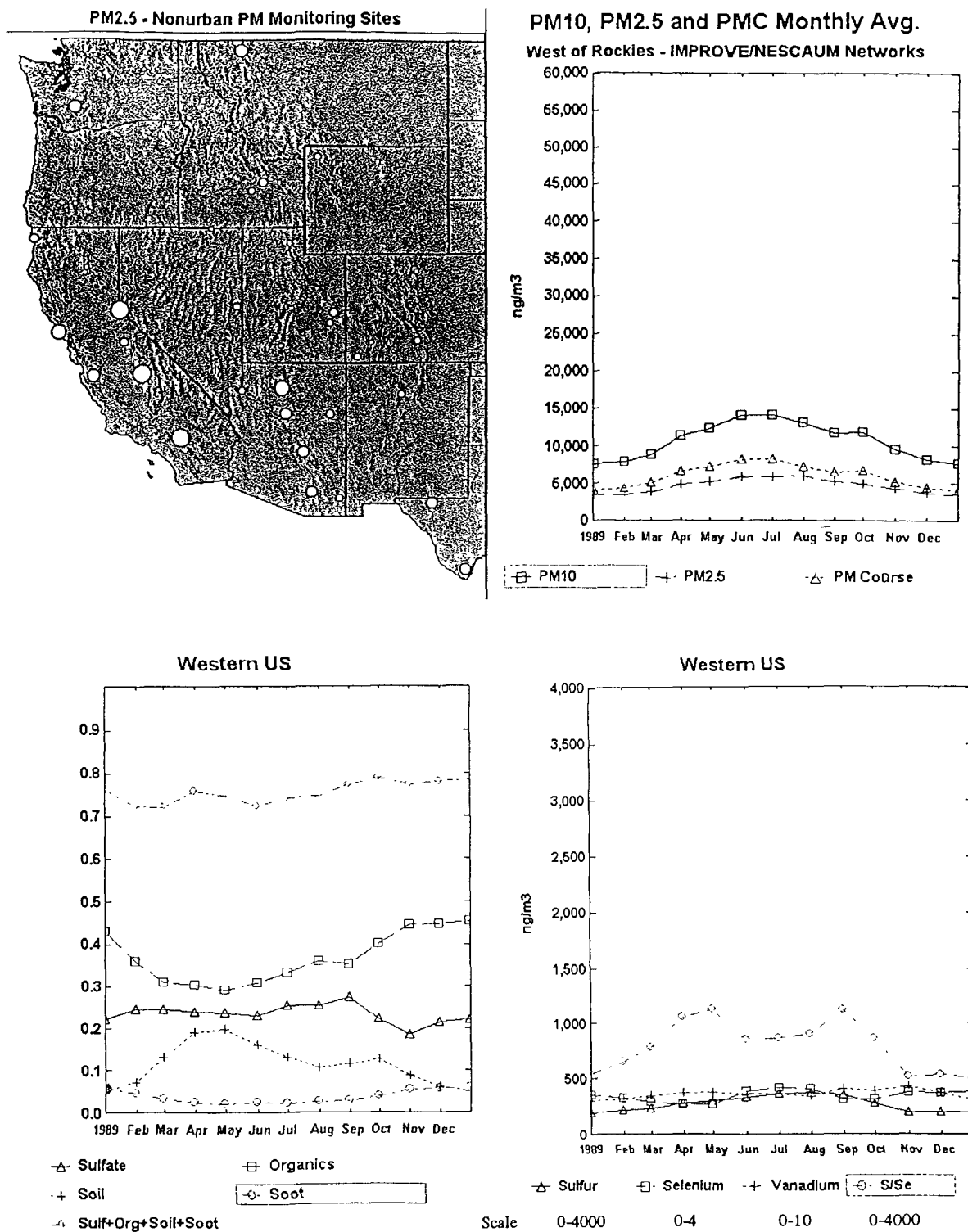
## *Western United States*

The aggregated western U.S. aerosol seasonality is presented in Figure 6-16. The non-urban aerosol concentrations for  $PM_{10}$ ,  $PM_{2.5}$ , and  $PM_{Coarse}$  are well below the concentrations over the eastern United States (Figure 6-16b). Evidently, the non-urban western United States differs from the eastern United States, having lower fine mass concentrations, which range between 3 to 5  $\mu\text{g}/\text{m}^3$ . The coarse mass concentration (4 to 8  $\mu\text{g}/\text{m}^3$ ) and seasonality is similar over the East and the West. It is worth emphasizing, however, that these measurements are at remote national parks and wilderness areas in both East and West. The examination of monitoring data in urban areas and confined airsheds (Sections 6.4 and 6.5) reveals a highly textured pattern in space and time.

The fine particle chemical mass balance (Figure 6-16c) for the aggregated western United States shows the dominance of organics, which account for 30 to 45% of the fine mass. The higher organic fraction occurs in the November through January season. Sulfates hover at 20 to 25% throughout the year. Soil dust plays a prominent role in the western fine mass balance, contributing 20% in April through May, but declining to 5% by January. Soot ranges between 5% in the winter and 2% during the summer. About 25% of the fine mass over the western United States is not accounted for by sulfates, organics, soil, and soot. It is known (Cahill???) that nitrates are major contributors to the fine particle mass in the South Coast Basin, as well as other western regions.

The concentration of the trace substances (Figure 6-16d) selenium and vanadium shows both low concentrations and weak seasonality. The sulfur concentrations are also less than half of the eastern U.S. values. The S/Se ratio is about 500 in the winter months and 1,000 during the summer. The low summer S/Se values would indicate less sulfate yield per selenium in the summer. However, these observations need to be tempered by the fact that selenium emitting coal-fired power plants are not the only sources of western U.S. sulfur. The S/Se ratio is included here for sake of completeness.

The above discussion of national pattern of chemical and size dependence hide a rich spatial and temporal texture of the U.S. aerosol pattern discussed in the following sections. However, it provides the national scale gross features and serves as a broader context for the more detailed examinations.



**Figure 6-16.** Seasonal pattern of non-urban aerosol concentrations for the Western U.S. a) Average concentration. b) PM<sub>10</sub>, PM<sub>2.5</sub>, and PMCoarse. c) Chemical fraction of sulfate, soil, organics, and soot. d) Tracer concentrations.

### 6.3.2 Urban National Aerosol Pattern - AIRS

The urban monitoring network is operated by state and local agencies as mandated by the Clean Air Act. The data from this network constitute the sensory input for the detection of exceedences over the particulate matter standards. Federal regulations also require that these monitoring data be submitted to the EPA Aerometric Information and Retrieval System (AIRS). In what follows, AIRS  $PM_{10}$  refers to the  $PM_{10}$  mass concentration extracted from the AIRS database.

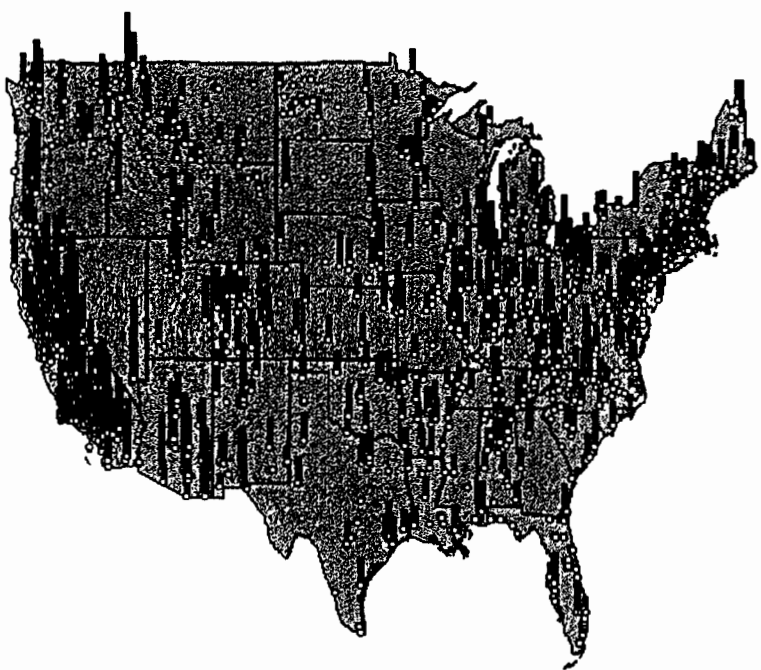
The AIRS  $PM_{10}$  stations are mostly in urban areas but some suburban and non-urban sites are also reported. The aerosol mass concentrations for  $PM_{10}$  and  $PM_{2.5}$  are sampled and weighed by a variety of devices. The sampling frequency is generally every sixth day for 24-hours. The analysis presented in this section is based on  $PM_{10}$  and  $PM_{2.5}$  data retrieved from AIRS in October 1994.

The  $PM_{10}$  station density has been increasing over time. Particulate matter sampling with the size cut-off of  $10\mu m$ ,  $PM_{10}$  begun in the early 1980s. By 1985 about 200 samplers were operational and the number of sampling stations has grown to 1,350 by 1994 as shown in Figure 6-17. The emergence of new stations appeared in rough proportion to the final station density shown in Figure 6-17. In other words, in 1985, the national coverage had a similar pattern to 1994, except less dense.

The results of AIRS  $PM_{10}$  aerosol pattern analysis are presented in quarterly contour maps, as well as seasonal time charts. For valid monthly and quarterly aggregation, it was required to have at least two samples a month, and six samples per quarter. For the seasonal maps all the available data between 1985 to 1994 were used.

The seasonal contour maps also show the location of the  $PM_{10}$  monitoring sites. The size of the rectangle at each site is proportional to the quarterly average  $PM_{10}$  concentration using all available data between 1985 to 1994. Hence, sampling biases due to station density that changed over time can not be excluded.

The quarterly concentration pattern of  $PM_{10}$  is shown in Figure 6-18. The high sampler density allows the resolution of spatial texture on the scale of 100 km, particularly over major metropolitan areas. However, remote regions in the central and western states have poor spatial density. In the absence of rural monitoring data computerized contour



Valid PM10 Stations

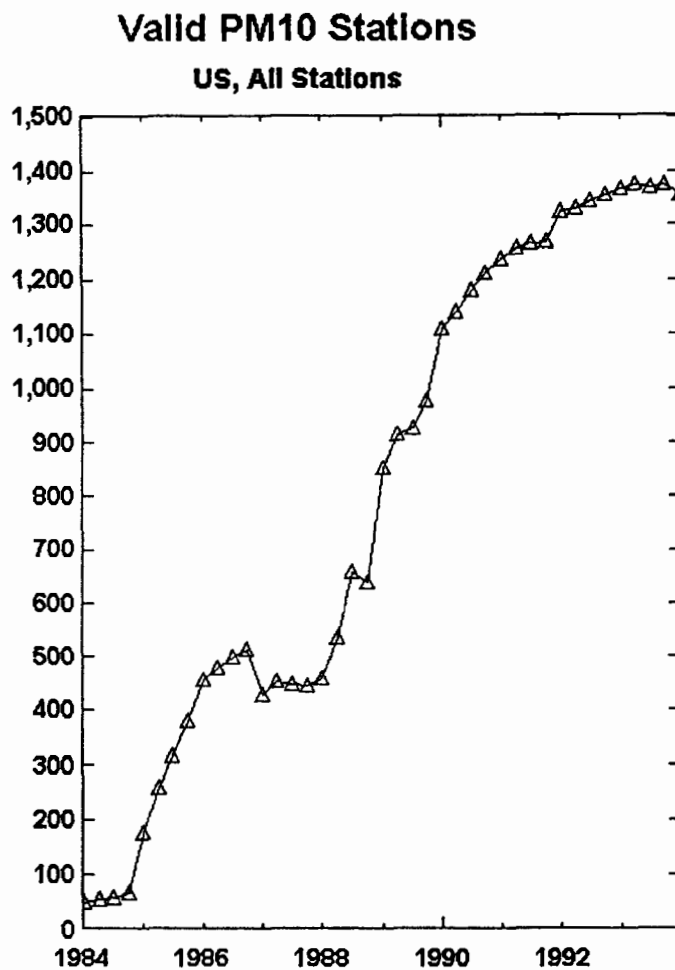


Figure 6-17. Trend of valid PM<sub>10</sub> monitoring stations in the AIRS database.



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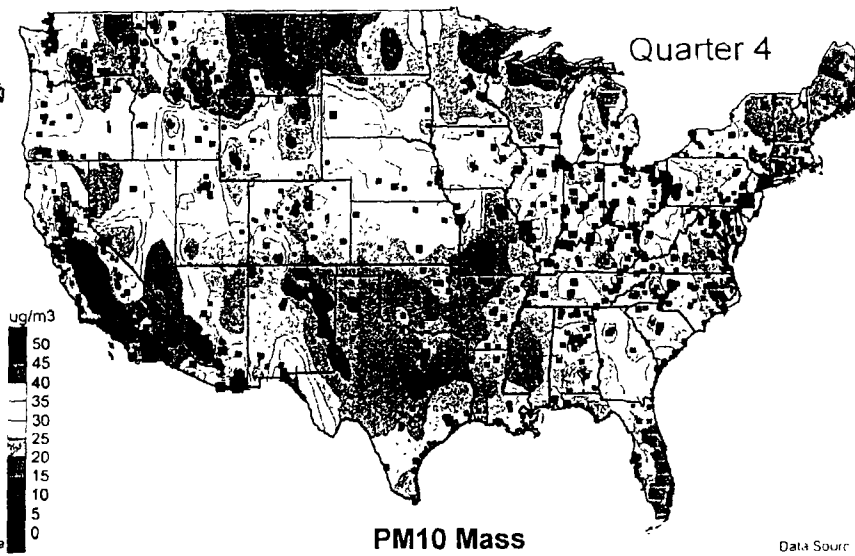
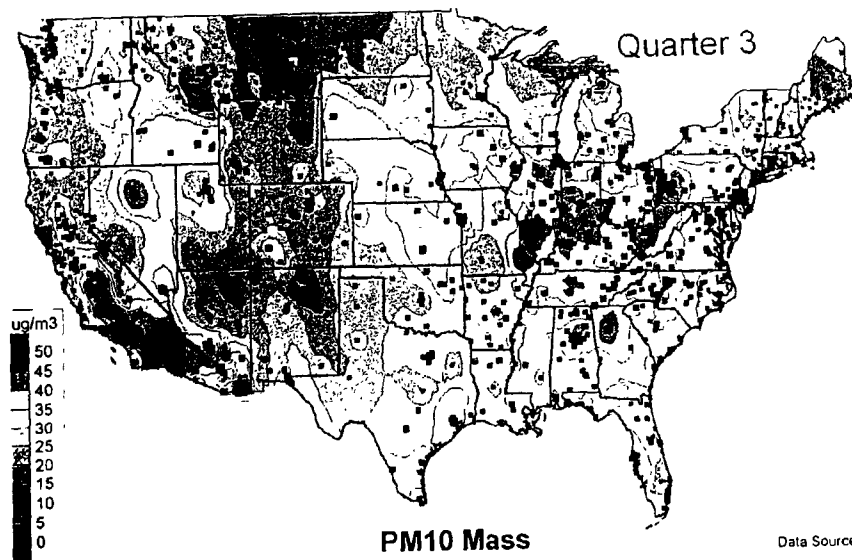
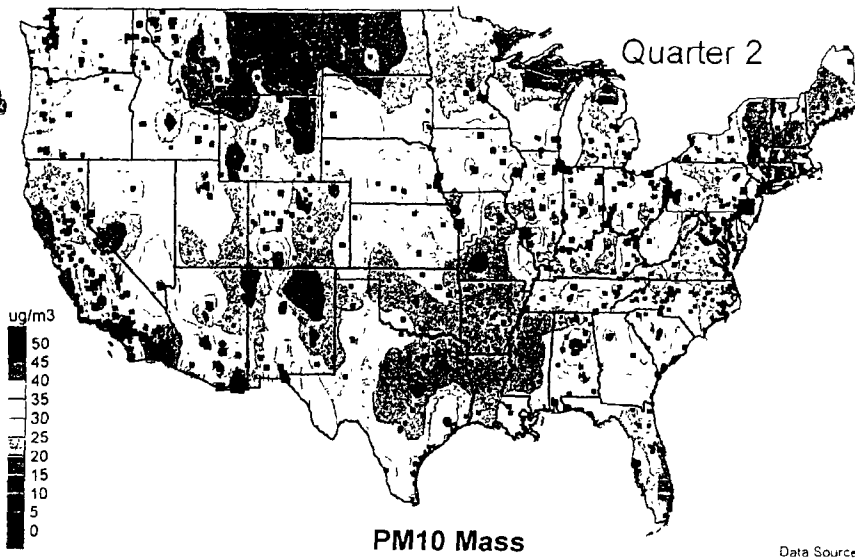
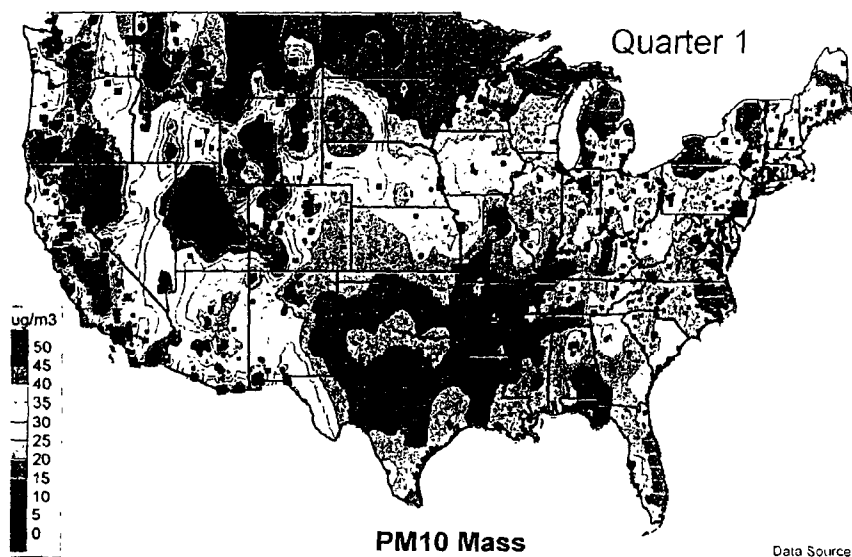


Figure 6-18. AIRS PM<sub>10</sub> quarterly concentration maps using all available data.

plotting of  $PM_{10}$  is biased toward extrapolating (spreading) high concentrations over large areas. This bias is particularly evident in the maps for Quarters 1 and 4 in the western states, where the area of high concentration hot spots is exaggerated.

The AIRS  $PM_{10}$  concentrations over the eastern United States are lowest during Quarter 1, ranging between 20 to 30  $\mu g/m^3$ . The higher concentrations exceeding 30  $\mu g/m^3$  are confined to metropolitan areas.

#### 6.3.2.1 National Pattern and Trend of AIRS $PM_{10}$

The trend (1985 to 1993) of national average  $PM_{10}$  concentrations is shown in Figure 6-19b. During the decade there was a remarkable reduction in  $PM_{10}$  concentrations from 48  $\mu g/m^3$  to 25  $\mu g/m^3$ . Between 1986 and 1993, the reduction was 38%. The Figure 6-19b also shows the standard deviation among the yearly average  $PM_{10}$  concentrations for each year. On the national scale the standard deviation of yearly average concentrations is about 40% of the mean.

The concentration of  $PM_{2.5}$  and  $PM_{10}$  are compared in the scatter chart in Figure 6-19c. Each point represents a pair of  $PM_{2.5}$ - $PM_{10}$  monthly average concentrations. The diagonal line is the 1:1 line and shows the fine particle concentration ranges between 20 and 85% of  $PM_{10}$ . The heavy solid line is derived from linear best fit regression. The detailed correlation statistics is reproduced in the upper-left corner of the scatter charts. The ratio of overall average  $PM_{2.5}$  and overall average  $PM_{10}$  is also indicated. For the data when both  $PM_{2.5}$  and  $PM_{10}$  data were available, nationally aggregated  $PM_{2.5}$  particles accounted for 57% of the  $PM_{10}$  mass.

The seasonal pattern of the national  $PM_{10}$  concentration is also depicted in Figure 6-19d, utilizing all available data in AIRS. The national average  $PM_{10}$  seasonality ranges between 27  $\mu g/m^3$  in March and April, and 33  $\mu g/m^3$  in July and August, yielding a modest 16% seasonal modulation. There is also evidence of slight bimodality with the December through January peak.

The seasonal chart also shows the annual variation of  $PM_{2.5}$ , and  $PM_{10}$ - $PM_{2.5}$  (i.e. coarse particles). The national fine particle concentration shows clear evidence of bimodality with peaks in July and December. It is shown below that the fine particle winter peak arises from western sites, while the summer peak is due to eastern U.S. contributions.

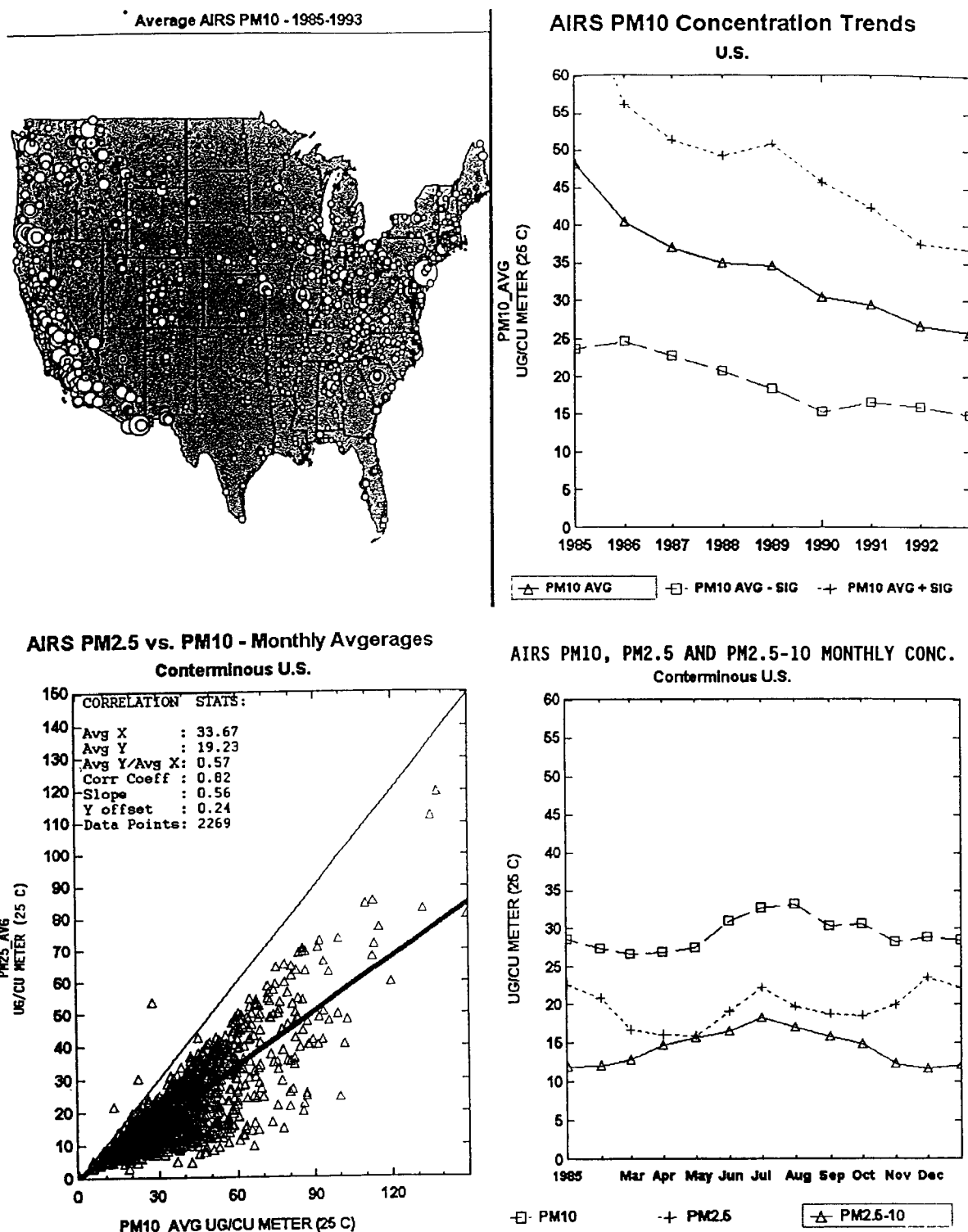


Figure 6-19. AIRS  $PM_{10}$  and  $PM_{2.5}$  concentration pattern for the conterminous US.

1 The national average coarse particle concentration has a 50 % yearly modulation with a  
2 single peak in July.

3 Summarizing the national PM<sub>10</sub> concentrations one can observe that the country has  
4 several major aerosol regions. Each region has a discernible geographic extent as well as  
5 seasonal pattern. Over the plains of the eastern United States the spatial texture of PM<sub>10</sub> is  
6 driven by the pattern of the emission fields, while the seasonality of concentrations is likely  
7 to be determined by the chemical transformation and removal processes, as well as by the  
8 regional dilution. In the mountainous western and Pacific states US, pockets of wintertime  
9 PM<sub>10</sub> concentrations exist that well exceed the eastern U.S. values. It is believed that haze  
10 and smoke in confined mountain valleys and air basins are strongly influenced by topography  
11 which in turn influences the emission pattern, dilution, as well as the chemical transformation  
12 and removal rate processes.

13 Given the regionality of the aerosol concentration pattern much of the discussion that  
14 follows will be focused on the characteristics of these aerosol regions. The Rocky Mountains  
15 produce a natural division between the eastern and western aerosol regimes which will be  
16 discussed next.

#### 18 **6.3.2.2 Eastern U.S. PM<sub>10</sub> Pattern and Trend**

19 The eastern U.S. PM<sub>10</sub> concentration (Figure 6-20b) shows a 29% downward trend of  
20 yearly average PM<sub>10</sub> concentrations from 35 µg/m<sup>3</sup> in 1985 to 25 µg/m<sup>3</sup> in 1993. The  
21 decline is rather steady over time.

22 The highest eastern U.S. AIRS PM<sub>10</sub> concentrations are recorded in Quarter 3 (Figure  
23 6-20d). The peak concentrations are over the Ohio River Valley stretching from Pittsburgh  
24 to West Virginia, southern Indiana and St. Louis. In this region, the PM<sub>10</sub> concentration  
25 over the industrialized Midwest exceeds 40 µg/m<sup>3</sup>. Additional hot-spots with > 40 µg/m<sup>3</sup>  
26 are recorded in Birmingham, AL, Atlanta, GA, Nashville, TN, Philadelphia, PA and  
27 Chicago, IL. The summer time PM<sub>10</sub> concentrations in New England and upstate Michigan  
28 are < 20 µg/m<sup>3</sup>.

29 The transition seasons Quarters 2 and 4 (Figure 6-20d) show about 30 µg/m<sup>3</sup> over  
30 much of the eastern US, with concentration hot-spots over the industrial Midwest as well as  
31 in the Southeast, Atlanta, GA and Birmingham, AL. It is quite remarkable, however,

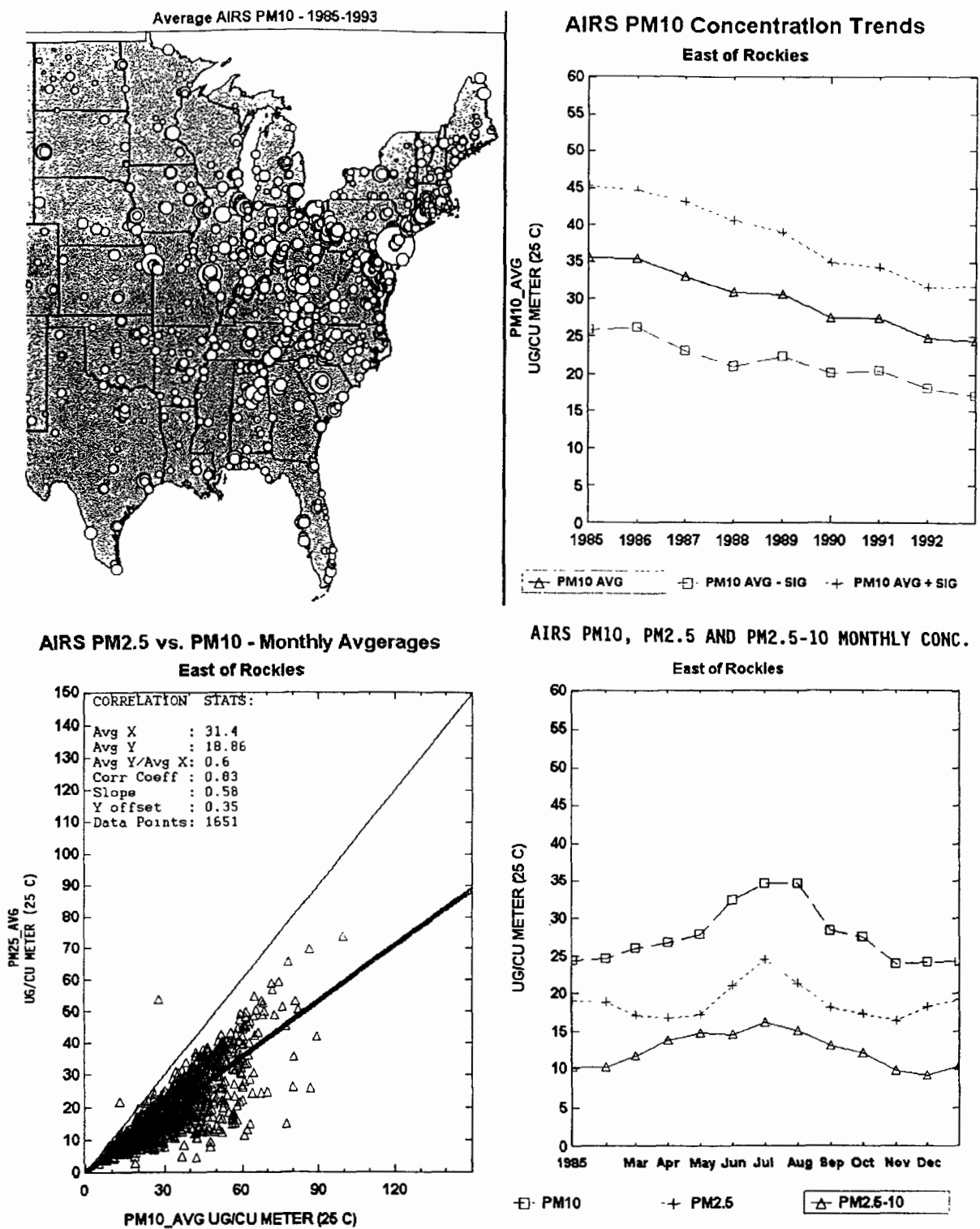


Figure 6-20. AIRS PM<sub>10</sub> and PM<sub>2.5</sub> concentration pattern for east of the Rockies.

1 that the  $PM_{10}$  concentrations in urban-industrial “hot-spots” exceed their rural surrounding  
2 by less than a factor of two.

3 The spatial variability of  $PM_{10}$  over the eastern United States is driven primarily by  
4 the varying aerosol emission density. This can be deduced from the coincidence of high  
5 concentrations within urban industrial areas. The atmospheric dilution, i.e. horizontal and  
6 vertical dispersion is not likely to be spatially variable. Also, the chemical aerosol formation  
7 and removal processes are likely to have weak spatial gradients when averaged over a  
8 calendrical quarter. Hence, the main factor that is believed to be responsible for the spatial  
9 variability is the emission field of primary  $PM_{10}$  particles and the precursors of secondary  
10 aerosols.

11  $PM_{10}$  concentration in excess of  $30 \mu\text{g}/\text{m}^3$  is recorded over the agricultural states of  
12 Iowa, Kansas, Nebraska, and South Dakota. The elevated  $PM_{10}$  concentrations over this  
13 region tend to persist over all four seasons. The spread of yearly average concentrations east  
14 of the Rockies is only 28%.

15 The eastern  $PM_{10}$  seasonality (Figure 6-20d) is rather pronounced, with winter  
16 concentrations (December through March) of  $24 \mu\text{g}/\text{m}^3$ , and July through August peak of  $35$   
17  $\mu\text{g}/\text{m}^3$ . The amplitude of the  $PM_{10}$  seasonal concentrations is about 30%.

18 The scatter chart of  $PM_{2.5}$ - $PM_{10}$  relationship shows significant amount of scatter, with  
19 a slope of 0.58. The ratio of the overall average  $PM_{2.5}$  and  $PM_{10}$  concentration is 0.6 such  
20 that 60% of  $PM_{10}$  in the sub  $2.5 \mu\text{m}$  size range. The seasonality of the fine particle  
21 concentration over the East is bimodal with a major peak in July and smaller winter peak in  
22 January. The coarse particle concentration shows a single broad peak over the warm season,  
23 April through October (Figure 6-20d). It is therefore evident that fine and coarse particles  
24 have different seasonal dynamics in the East.

### 25 26 **6.3.2.3 Western U.S. $PM_{10}$ Pattern and Trend**

27 The mountainous states, west of the Rockies (Figure 6-21) show high  $PM_{10}$   
28 concentrations ( $> 50 \mu\text{g}/\text{m}^3$ ) at localized hot-spots during the cold season, Quarters 1 and 4.  
29 These high concentrations occur over both metropolitan areas such as Salt Lake City, as well

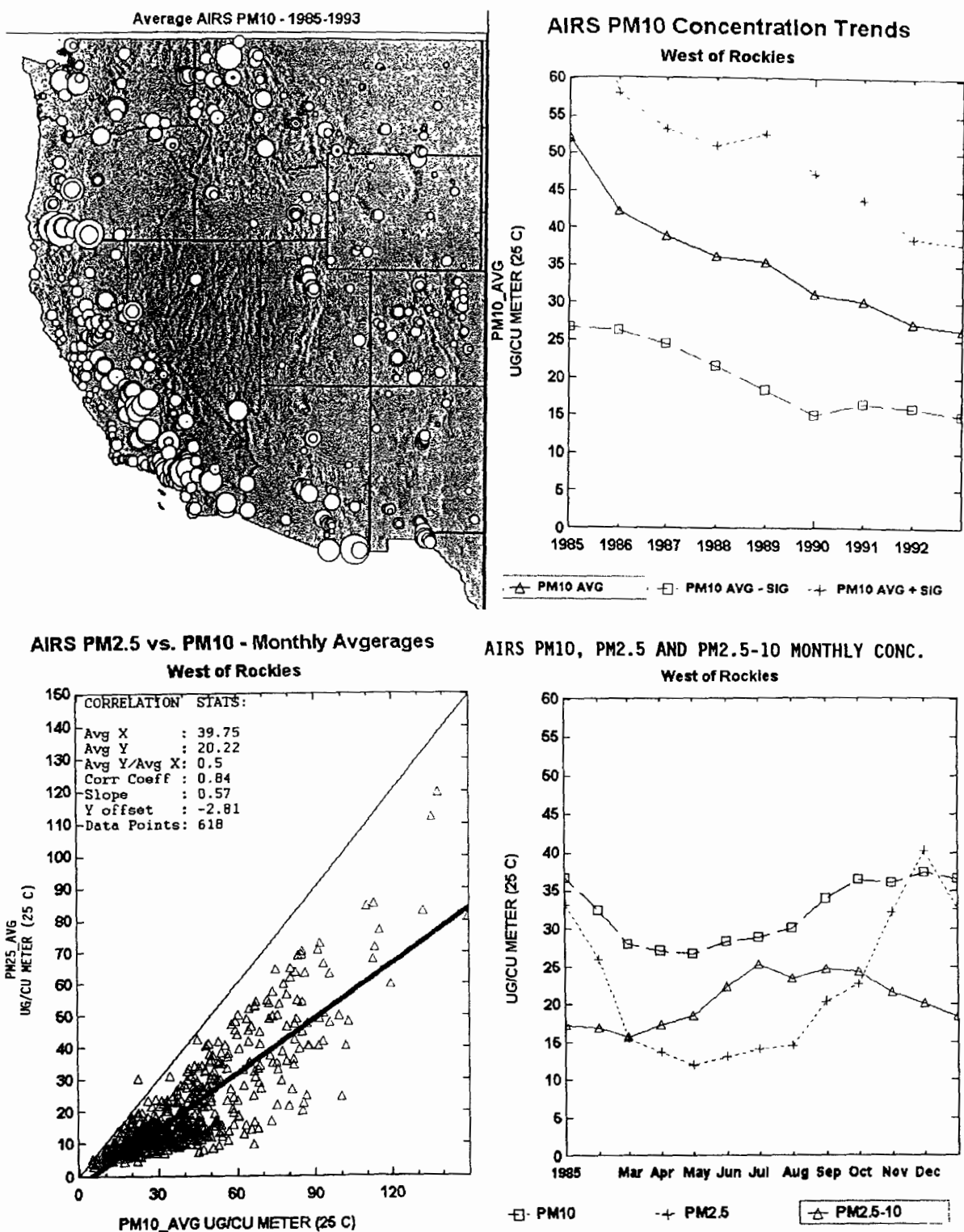


Figure 6-21. AIRS PM<sub>10</sub> and PM<sub>2.5</sub> concentration pattern for west of the Rockies.

1 as in smaller towns in mountain valleys of Colorado Wyoming, Montana, Idaho, Oregon,  
2 and Washington.

3 The main geographic features of California PM<sub>10</sub> aerosols are the Los Angeles basin  
4 and the San Joaquin Valley. Both basins show concentrations in excess of 50 µg/m<sup>3</sup>. These  
5 basins are also confined by surrounding mountains that limit the dilution, facilitate cloud  
6 formation, and have emissions that are confined to the basin floor. Accordingly, they  
7 represent airsheds with characteristic spatial and temporal pattern. It is likely that the actual  
8 spatial texture of the PM<sub>10</sub> concentration field in the mountainous western states has much  
9 higher texture than depicted in Figure 6-21a.

10 It appears that the spatial pattern of these high concentration hot spots is driven by  
11 both emissions as well as by the restricted wintertime ventilation due to mountainous terrain.  
12 Over the mountainous western states the atmospheric dilution by horizontal and vertical  
13 dispersion is severely restricted by mountain barriers and atmospheric stratification due to  
14 strong and shallow inversions. Radiative cooling also causes fog formation which enhances  
15 the production rate of aerosols in the valleys. As a consequence, mountain tops are generally  
16 extruding out of haze layers. Emissions arising from industrial, residential, agricultural,  
17 unpaved roadways and other sources are generally confined to mountain valleys. In the  
18 wintertime the mountain valleys are frequently filled with fog which also influences the  
19 chemical transformation and removal processes. As a consequence all three major factors  
20 that determine the ambient concentrations, i.e. emissions, dilution, and chemical rate  
21 processes are strongly influenced by the topography. For this reason, many of the maps  
22 depicting the regional pattern use shaded topography as a backdrop.

23 The western half of the US, west of and including the Rockies, show a more  
24 pronounced downward PM<sub>10</sub> concentration trend (Figure 6-21b). The reduction between  
25 1985 (57 µg/m<sup>3</sup>) and 1993 (26 µg/m<sup>3</sup>) is a remarkable 55%. The reduction between 1986  
26 (42 µg/m<sup>3</sup>) and 1993 (26 µg/m<sup>3</sup>) is 38%. Standard deviation among the western stations of  
27 yearly average PM<sub>10</sub> concentrations is about 40%.

28 The PM<sub>2.5</sub>-PM<sub>10</sub> relationship (Figure 6-21c) shows that on the average about 50% of  
29 the PM<sub>10</sub> is contributed by fine particles. The scatter chart (Figure 6-21c) also shows that  
30 during high concentration PM<sub>10</sub> episodes the fine fraction dominates.



1 The western  $PM_{10}$  seasonality (Figure 6-21d) is also rather pronounced, having about  
2 30% amplitude. However, the lowest concentrations ( $26 \mu\text{g}/\text{m}^3$ ) are reported in the late  
3 spring (April through June), while the highest values occur in late fall (October through  
4 January).

5 The seasonality of  $PM_{2.5}$  west of the Rockies (Figure 6-21d) is strongly peaked in  
6 November through January ( $40 \mu\text{g}/\text{m}^3$ ). In fact, it is about factor of four higher than the  
7 summertime values. On the other hand, the coarse fraction shows a broad peak during late  
8 summer, July through October. It is to be noted that in Figures 6-20 and 6-21, the fine and  
9 coarse particle concentrations do not add up to  $PM_{10}$ , because size resolved samples were  
10 only available for tens of sites, while the  $PM_{10}$  concentrations were obtained from hundreds  
11 of monitoring stations.

12 In summary, there is a remarkable 40 to 50% reduction of national  $PM_{10}$   
13 concentrations between 1985 and 1993. On the national average the  $PM_{10}$  seasonality is  
14 insignificant. Desegregation of the national averages into east and west of the Rockies,  
15 shows that the downward trend west of the Rockies is more pronounced than over the eastern  
16 half of the US. The east west desegregation also shows that the lack of national  $PM_{10}$   
17 seasonality arises from two strong seasonal signals that are phase shifted, the eastern United  
18 States has a summer peak, the West fall and winter peak, and the sum of two signals is a  
19 weakly modulated seasonal pattern. Nationally,  $PM_{2.5}$  mass accounts for about 57% of  $PM_{10}$   
20 mass. The East and West show comparable fine fraction (60% in the East and 50% in the  
21 West), and fine particles tend to dominate during the winter season particularly in the  
22 western US.

23 It is evident that further examination discussed in the next sections will show that the  
24 East-West division itself is rather crude and that dividing the conterminous United States into  
25 additional subregions is beneficial in explaining the  $PM_{10}$  concentration pattern and trends.

26 A cautionary note on a possible sampling bias is in order. The national average  
27 concentrations were calculated utilizing all of the available data since 1985, when more than  
28 200 monitoring stations were operational. Since that time, the number of monitoring stations  
29 has risen to more than 1,300. The implications of the changing stations density to the above  
30 described national  $PM_{10}$  trend is not well studied. Also, changes in sampling equipment and

monitoring protocols are also possible causes of systematic errors in the reported spatial pattern and trends.

#### **6.3.2.4 Short-term Variability of PM<sub>10</sub> Concentrations**

The previous aerosol concentration patterns were expressed as quarterly averages. However, for health and other effects, the variance of the concentration, in particular the occurrence of extreme high concentrations is of importance. The PM<sub>10</sub> concentrations exhibit marked differences in the shape of their distribution functions around the mean values. For example in Figure 6-22, the day to day variations of PM<sub>10</sub> concentrations in Knoxville, TN are about 40% of the mean value of 35  $\mu\text{g}/\text{m}^3$ . On the other hand, the concentration time series for Missoula, MT shows a coefficient of variation of 60% over the mean of 34  $\mu\text{g}/\text{m}^3$ . During the winter season the coefficient of variation is even higher. It is therefore evident, that for comparable mean concentrations the Missoula, MT site exhibits significantly higher short-term variations.

The variability of concentration is examined spatially and seasonally by computing logarithmic standard deviation (ratio of 84/50 concentration percentiles) for each monitoring site. These deviations were then contoured for each season. The results are depicted in the seasonal maps of the logarithmic standard deviation (Figure 6-23). The highest logarithmic standard deviation is recorded over the northern and northwestern states during the cold season, Quarters 1 and 4. Regionally, the logarithmic standard deviation in the north-northwest is about 2.0 with pockets of high winter variability such as Salt Lake City, UT and Missoula, MT. The lowest variability prevails over the warm season, Quarters 2 and 3, covering the southeastern and southwestern states. Over multistate regions in the southern states the summertime logarithmic standard deviation is below 1.5. This means that these areas are covered more or less uniformly by summertime PM<sub>10</sub>, while the northern states are more episodic.

#### **6.3.2.5 AIRS PM<sub>2.5</sub> Concentrations.**

The mass concentration of fine particles in urban areas is not well known. Sampling and analysis of PM<sub>2.5</sub> is limited by small number of stations (< 50), sampling period restricted to few years, and different, non-standard sampling equipment was utilized for

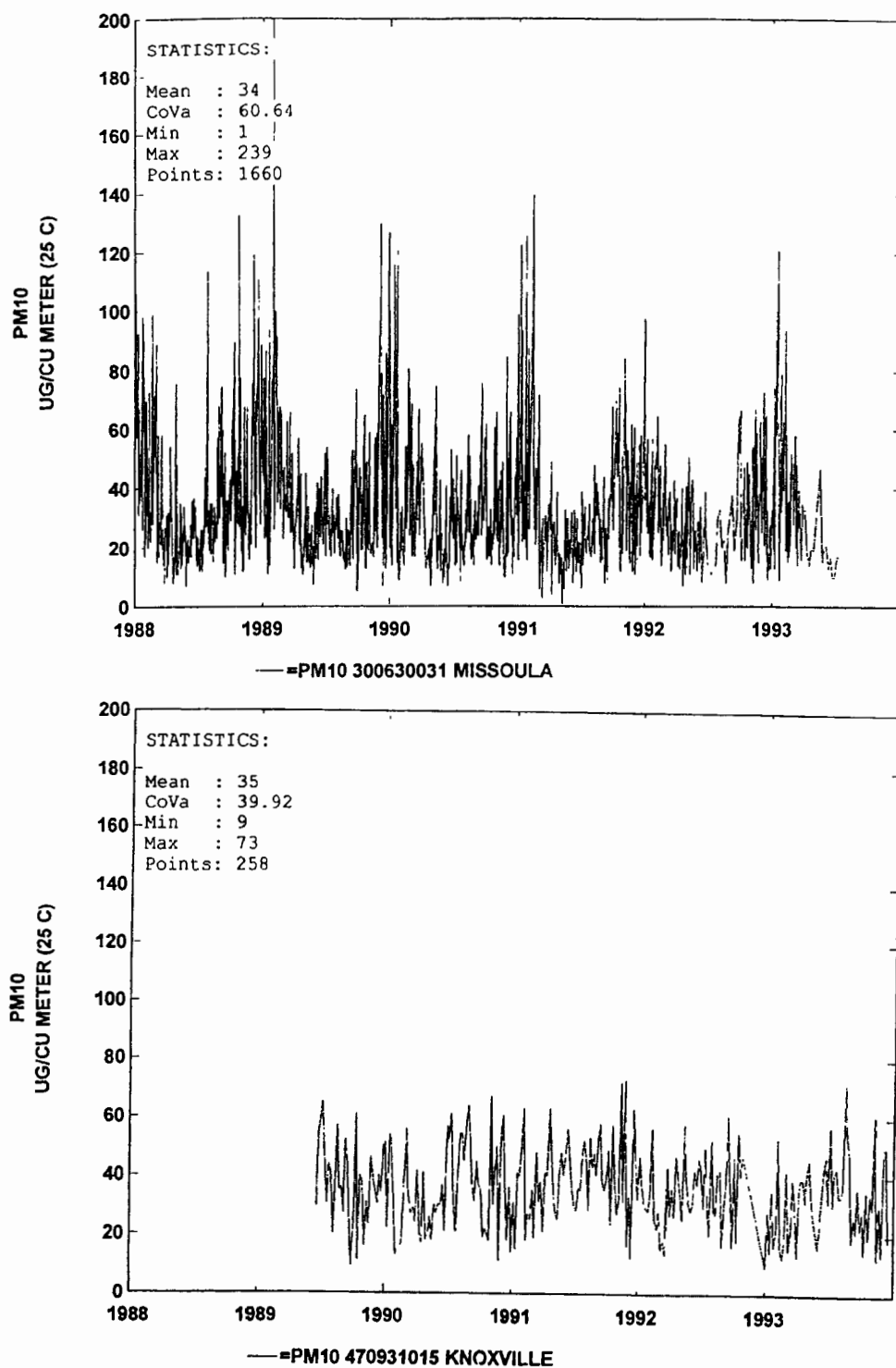
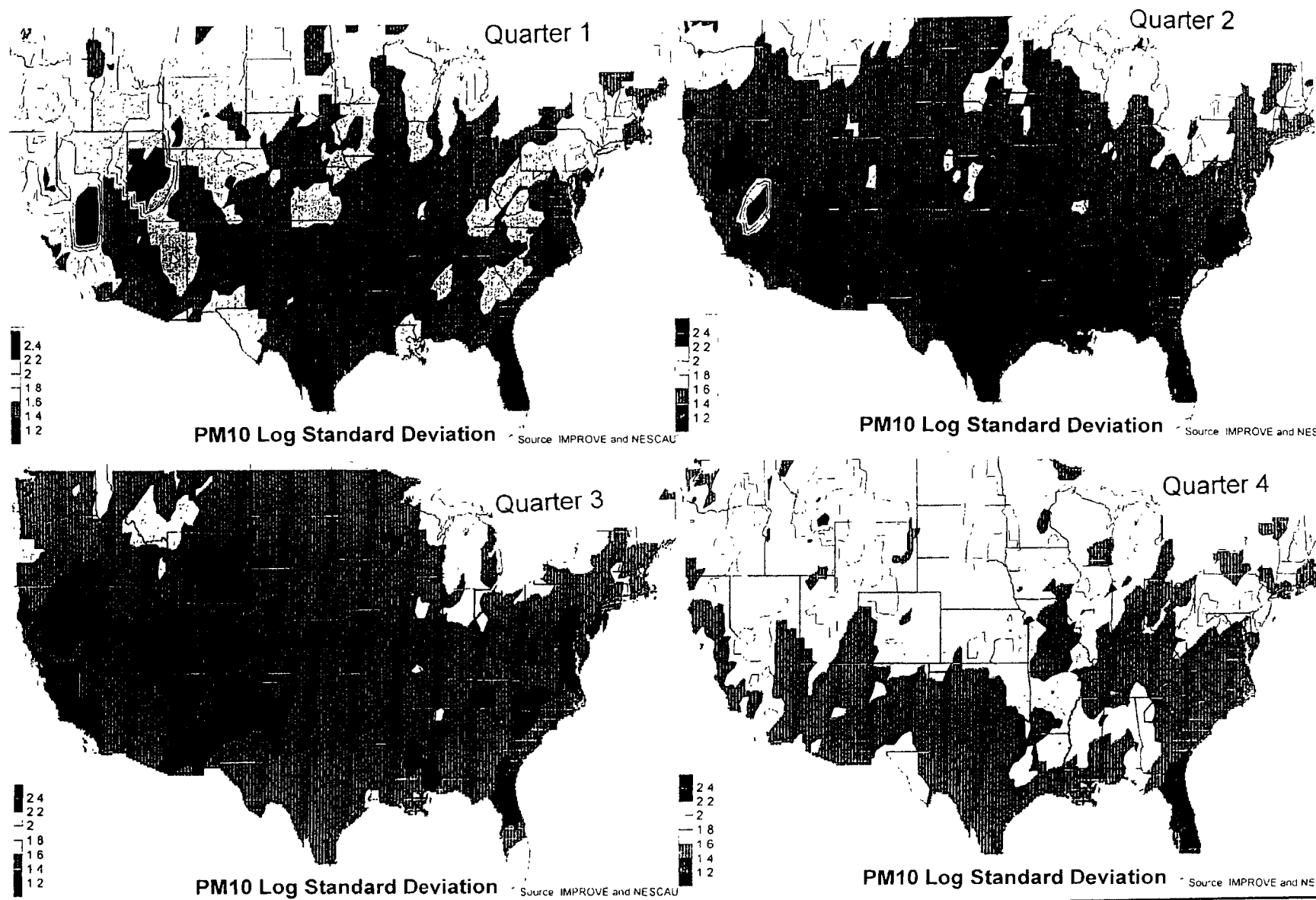


Figure 6-22. Short-term PM<sub>10</sub> concentration time series for Missoula, MT, and Knoxville, TN.

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Figure 6-23. Logarithmic standard deviation AIRS PM<sub>10</sub> concentrations.

PM<sub>2.5</sub> monitoring. Consequently, it is not possible to perform a detailed spatial and temporal mapping and trend analysis for AIRS PM<sub>2.5</sub>.

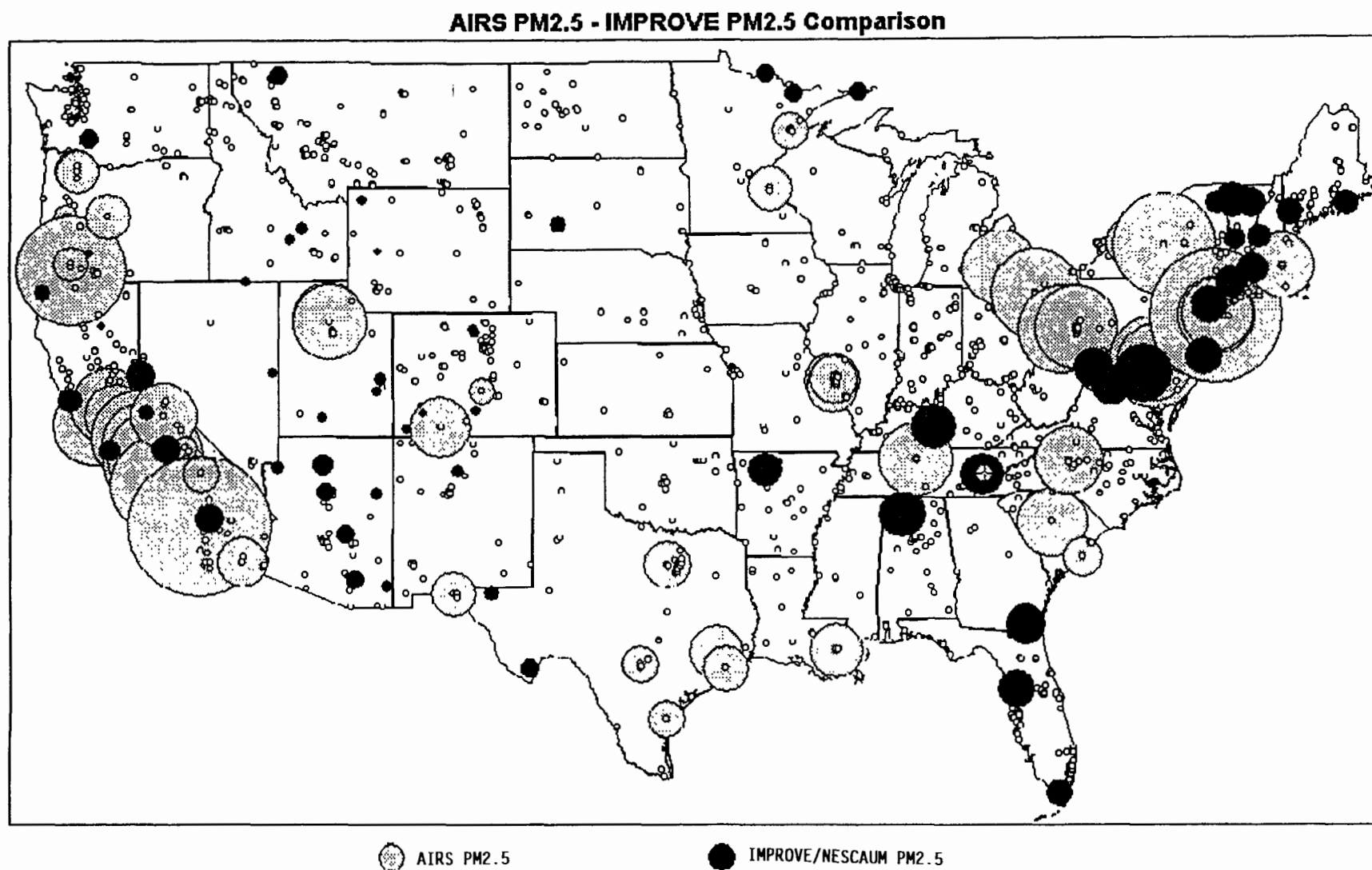
The yearly average AIRS PM<sub>2.5</sub> concentrations are shown in Figure 6-24. Figure 6-24 also shows the location and magnitude of PM<sub>2.5</sub> concentrations arising from the IMPROVE/NESCAUM monitoring networks. The fine particle data from the IMPROVE/NESCAUM shows a smooth pattern with uniformly high concentrations ( $> 15 \mu\text{g}/\text{m}^3$ ) occurring over the eastern United States and uniformly low concentrations of  $< 5 \mu\text{g}/\text{m}^3$  between Sierra and Cascade Mountains. This pattern of non-urban fine particle concentrations was discussed in Section 6.3.1.

#### 6.3.2.6 Other National Surveys

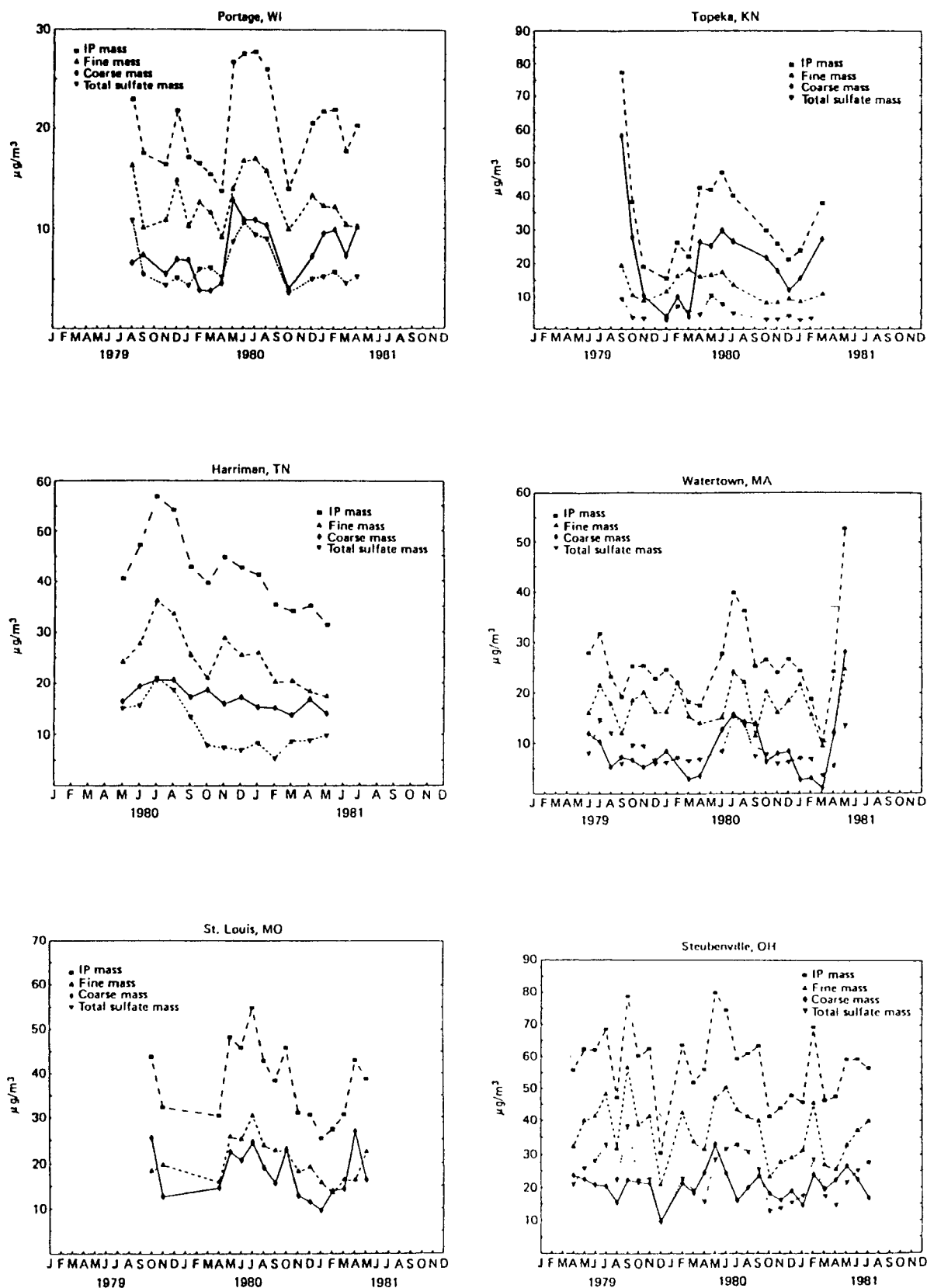
A summary of urban PM<sub>10</sub>, PM<sub>2.5</sub>, PMCoarse at eight urban areas, Birmingham, AL, Buffalo, NY, Houston, TX, Philadelphia, PA, Phoenix, AZ, Pittsburgh, PA, Rubidoux, CA and Steubenville, OH was reported by Rhodes and Evans (1985). The overall ratio of the 10  $\mu\text{m}$  fraction to Total Suspended Particulate (TSP) was 0.486. The relationships between PM<sub>10</sub> and the 15  $\mu\text{m}$  fraction (IP) are very linear for all sites. With exception of Phoenix, AZ and Houston, TX, PM<sub>2.5</sub> exceeded the PMCoarse mass concentration in all six urban areas.

Spengler and Thurston (1983) reported inhalable particulate matter (IP) concentrations in six United State cities, Portage, WI Topeka, KS, Kingston, TN, Watertown, MA St. Louis, MO and Steubenville, OH using dichotomous virtual impactors in the two size ranges, PM<sub>2.5</sub>, having  $d_p < 2.5 \mu\text{m}$  and PMCoarse with  $2.5 < d_p < 15 \mu\text{m}$ . All six cities displayed a seasonal trend of higher summertime and lower wintertime concentrations. Figure 6-25 displays the monthly mean concentrations ( $\mu\text{g}/\text{m}^3$ ) for total IP mass, FP mass, CP mass and S mass (assuming S as Ammonium sulfate) for the six cities. The seasonal pattern is more pronounced in St. Louis, Portage, and Harriman, where the July monthly mean FP concentration is 60%, 60%, and 40% higher than the January monthly concentration in each city, respectively. Sulfate has been noted to have similar variations in other locations (Altshuler, 1980).

The quartz content and elemental composition of aerosols from selected sites in the EPA Inhalable Particulate (IP) network were reported by Davis et al., 1984. For all IP



**Figure 6-24.** Annual PM<sub>2.5</sub> concentration pattern obtained from IMPROVE/NESCAUM and AIRS networks.



**Figure 6-25.** Monthly mean concentrations in ( $\mu\text{g}/\text{m}^3$ ) of IP, Fine Fraction, and S as  $(\text{NH}_4)_2\text{SO}_4$  in Portage, WI; Topeka, KS; Harriman, TN; Watertown, MA; St. Louis, MO; and Steubenville, OH.

Source: Spengler and Thurston, 1983

1 sites, an average of only 4.9 weight per cent of the coarse particle mass that was measured  
2 by the dichotomous samplers consists of quartz and 0.4 weight per cent as quartz in fine  
3 mass. Continental interior sites show the highest average quartz content as well as the  
4 greatest variability. The coastal regions and eastern interior sites reveal the lowest quartz  
5 concentrations. The complete X-ray spectra from some samples in Portland, OR, show that  
6 Si comes primarily from minerals such as feldspars, where the Si in the Buffalo, NY  
7 aerosols comes from quartz.

### 9 **6.3.3 Comparison of Urban and Non-Urban Concentrations**

10 Seasonal maps of the AIRS PM<sub>10</sub>-IMPROVE/NESCAUM PM<sub>10</sub> spatial concentrations  
11 are given in Figure 6-26. The AIRS PM<sub>2.5</sub> concentrations everywhere exceed their adjacent  
12 IMPROVE/NESCAUM concentrations. The highest AIRS PM<sub>2.5</sub> are reported over the  
13 eastern urban industrial centers, such as Philadelphia and Pittsburgh, where the  
14 concentrations of 50  $\mu\text{g}/\text{m}^3$  exceed their non-urban counterparts by a factor of 2 to 3.  
15 However, the excess urban PM<sub>2.5</sub> concentrations are evidently confined to the immediate  
16 vicinity of urban centers. The PM<sub>2.5</sub> concentrations at remote New England, over the  
17 southeastern US, and over the upper Midwest are within about 50% for AIRS PM<sub>2.5</sub> and  
18 IMPROVE/NESCAUM PM<sub>2.5</sub>. This indicates that over the eastern United States a  
19 regionally homogeneous background of PM<sub>2.5</sub> concentration exists that has smooth spatial  
20 gradients. Superimposed on the smooth regional pattern are local hot-spots with excess  
21 concentrations of factor of 2 to 3 that are confined to few miles of urban industrial centers.  
22 The regional homogeneity is an indication that the eastern U.S. PM<sub>2.5</sub> is composed of  
23 secondary aerosols that is produced several days after the emission of its gaseous precursors.  
24 The excess PM<sub>2.5</sub> concentration in urban centers suggests that primary emissions such as  
25 automobile exhaust, heating furnaces, and are responsible for much the urban PM<sub>2.5</sub>  
26 hot-spots.

27 The reported AIRS PM<sub>2.5</sub> concentrations over the Pacific states are generally higher  
28 and average at 20 to 50  $\mu\text{g}/\text{m}^3$ . This is 5 to 10 times higher than their companion  
29 IMPROVE PM<sub>2.5</sub> concentrations. The dramatic difference is attributable to the pronounced  
30 concentration differences between urban-industrial-agricultural centers that occur in



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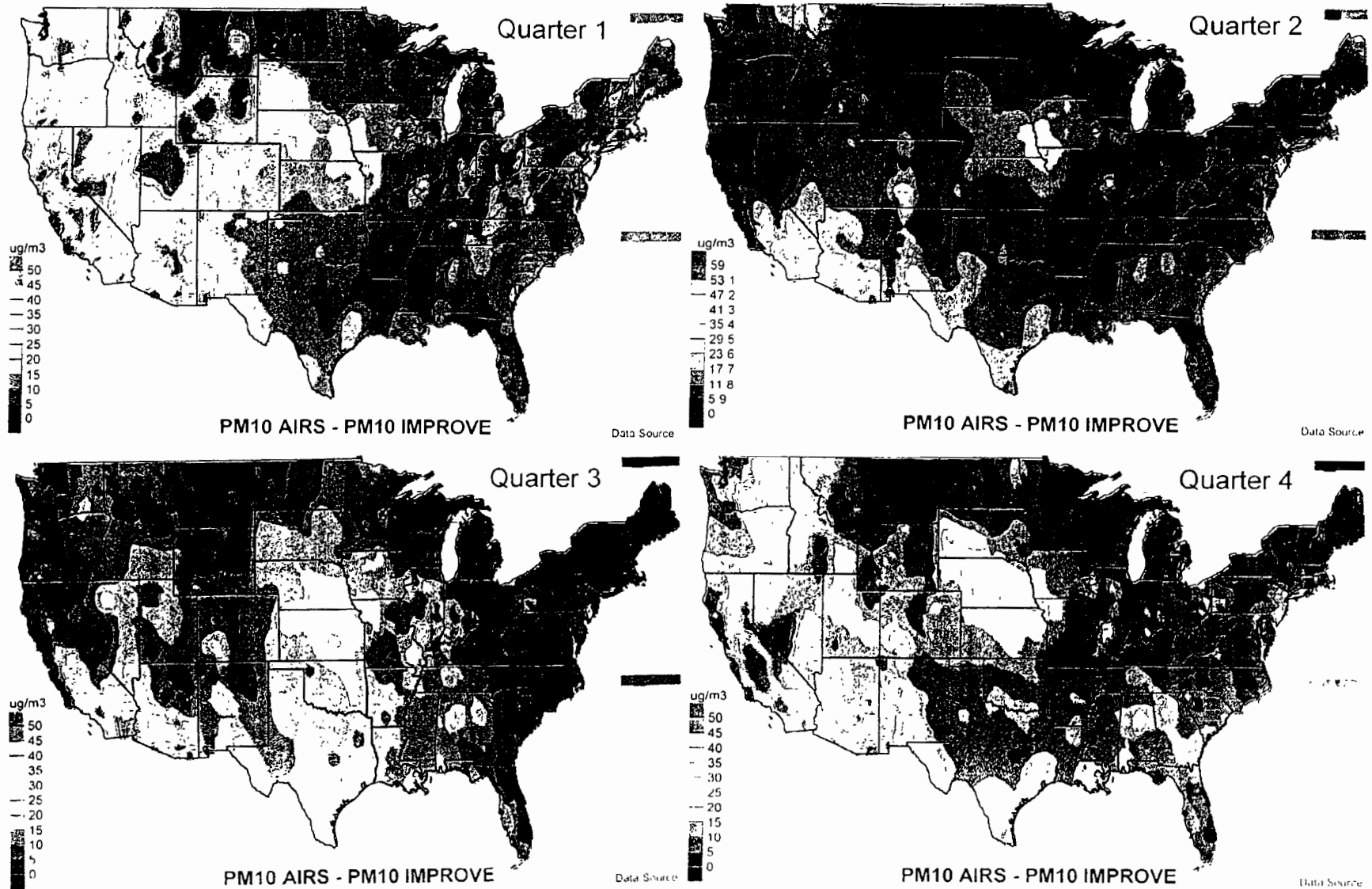


Figure 6-26. Spatial maps of PM<sub>10</sub> concentration difference between AIRS and IMPROVE/NESCAUM networks.

1 mountainous air basins and the concentrations monitored at remote national parks and  
2 wilderness areas that are generally at higher elevations. However, it is fair to presume that  
3 the AIRS and IMPROVE PM<sub>2.5</sub> data sets represent the extreme of aerosol concentration  
4 ranges that exist over the western US. The challenging task of filling in the details,  
5 i.e. spatially and temporally extrapolating the aerosol concentrations over the rugged western  
6 United States is discussed in further detail in later regionally and locally focused sections  
7 below.

8 It is also instructive to compare the seasonality of the urban (AIRS) concentrations to  
9 the non-urban (IMPROVE/NESCAUM) data. In Figure 6-27 the difference in PM<sub>10</sub>, PM<sub>2.5</sub>,  
10 and PMCoarse between AIRS and IMPROVE/NESCAUM sites, using all available data, is  
11 used to indicate the urban excess particle concentration compared to the rural concentration.

12 Nationally, the urban excess fine particle concentration ranges between 18 µg/m<sup>3</sup> in  
13 December through February and 10 µg/m<sup>3</sup> in April through June (Figure 6-27a). The urban  
14 excess coarse mass concentration is less seasonal ranging between 10 to 7 µg/m<sup>3</sup>. The sum  
15 of the fine and coarse national urban excess mass concentration is about 25 µg/m<sup>3</sup> in the  
16 winter season, and 18 µg/m<sup>3</sup> during spring season. Hence, the nationally aggregated urban  
17 and non-urban data confirm that urban area have excess concentrations on the order of 20  
18 µg/m<sup>3</sup>, and well over half is due to fine particles, particularly in the winter season.

19 The urban excess (AIRS-IMPROVE/NESCAUM difference) over the eastern United  
20 States (Figure 6-27c) shows fine particles excess of 8 to 12 µg/m<sup>3</sup>, with higher value  
21 occurring during both winter and summer. The urban excess coarse mass in the eastern  
22 United States is only 5 to 8 µg/m<sup>3</sup>, peaking during spring and summer. The sum of fine and  
23 coarse urban excess is 15 to 18 µg/m<sup>3</sup> throughout the year.

24 The excess urban (AIRS-IMPROVE/NESCAUM) aggregated over the western United  
25 States is much more pronounced in magnitude and seasonality. The urban excess fine mass  
26 is about 30 µg/m<sup>3</sup> in November through January and drops to 8 to 10 µg/m<sup>3</sup> in April through  
27 August. The urban excess coarse mass is less in magnitude and seasonality 15 to 18 µg/m<sup>3</sup>  
28 in July through December, and 10 to 12 µg/m<sup>3</sup> in March through May. The sum of the  
29 urban excess fine and coarse mass is 40 to 50 µg/m<sup>3</sup> in November through January and about  
30 20 µg/m<sup>3</sup> in the spring March through June. The urban AIRS and non-urban IMPROVE)  
31 networks in the western United States clearly monitor distinctly different aerosol types, as

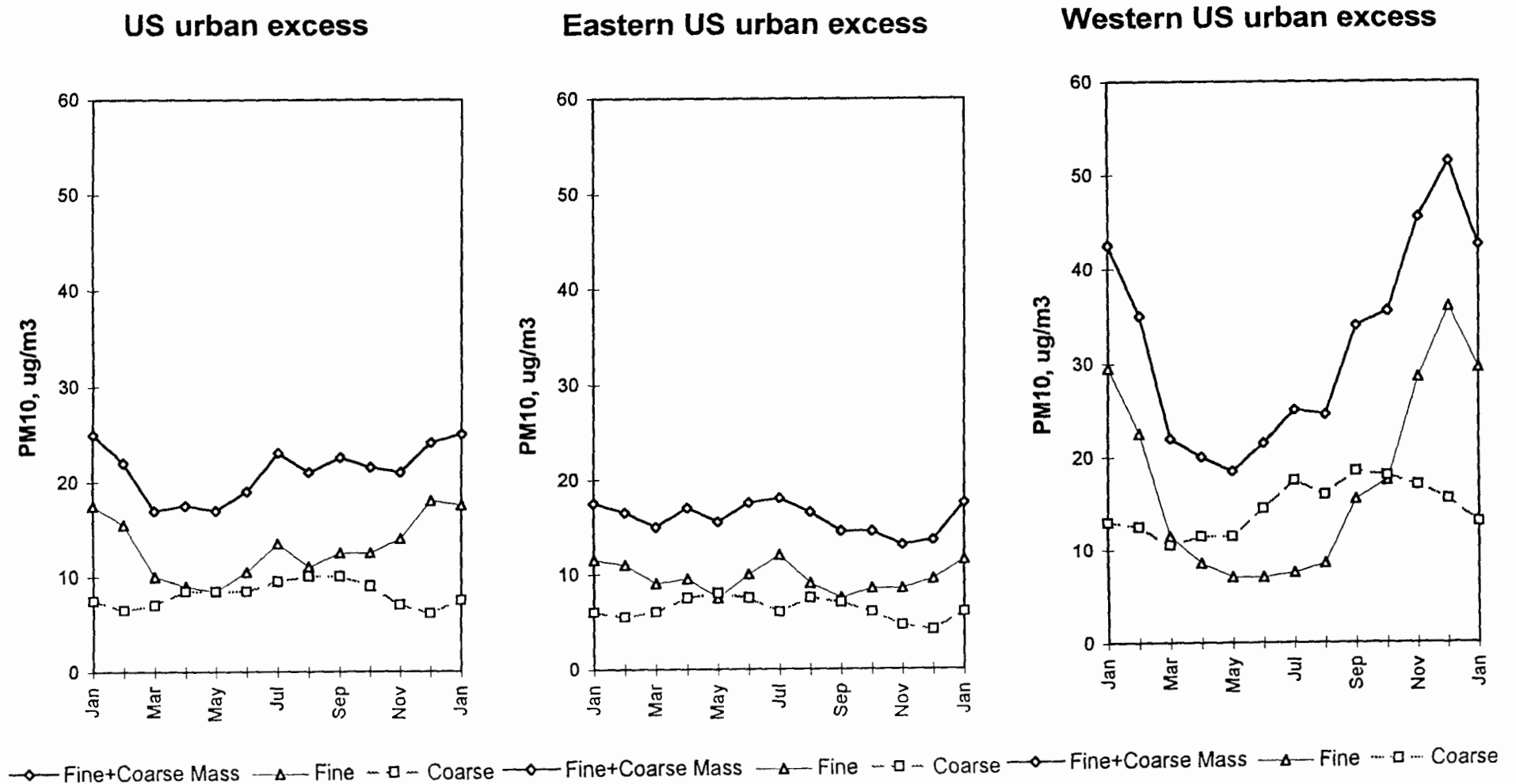


Figure 6-27. Urban excess concentrations (AIRS minus IMPROVE) for the U.S., Eastern U.S., and Western U.S.

1 stated by their respective goals and mandates. The urban non-urban difference is such that  
2 the western non-urban concentrations are virtually irrelevant for the much higher urban  
3 values, particularly in the winter season. On the other hand, the eastern urban sites are  
4 greatly influenced by the non-urban, regionally representative concentrations, particularly in  
5 the summer season.

## 6 7 8 **6.4 Regional Patterns and Trends**

9 This section describes the spatial, temporal, size, and chemical characteristics of seven  
10 aerosol regions of the conterminous US. The size and location of these regions were chosen  
11 based mainly on the characteristics of their aerosol pattern. The main criteria for delineating  
12 a region were 1) the region had to possess some uniqueness in aerosol trends, seasonality, size  
13 distribution, or chemical composition; 2) each territory of conterminous United States had to  
14 belong to one of the regions; 3) for reasons of computational convenience the shape of the  
15 regions were selected to be rectangular on unprojected latitude longitude maps. The resulting  
16 criteria yielded seven rectangular aerosol regions as shown in Figure 6-28. It is recognized  
17 that this selection is arbitrary and for future analysis additional regional definition criteria  
18 would be desirable.

19 For sake of consistency and intercomparisons each region is described using maps  
20 delineating the spatial pattern and the sampling locations (Figure section a). Monthly  
21 concentrations for a given region were computed by averaging all the available data for the  
22 specific month. In case of non-urban aerosol chemistry some regions only had 2 to 4  
23 monitoring stations. The monthly  $PM_{2.5}$ ,  $PM_{Coarse}$  and  $PM_{10}$  (Figure section b) over  
24 regions illustrate the relative seasonality of each aerosol type. The non-urban regional  
25 average chemical composition is presented as seasonal charts of chemical aerosol components  
26 as a fraction of the fine mass concentration (Figure section c). The role of some primary  
27 sources, such as coal and fuel oil combustion is indicated through seasonal charts of selenium  
28 (coal) and vanadium (fuel oil) trace metals (Figure section d).

29 In addition, for each region figures will be provided showing short term variability of  
30  $PM_{10}$  concentrations and  $PM_{10}$  urban excess.

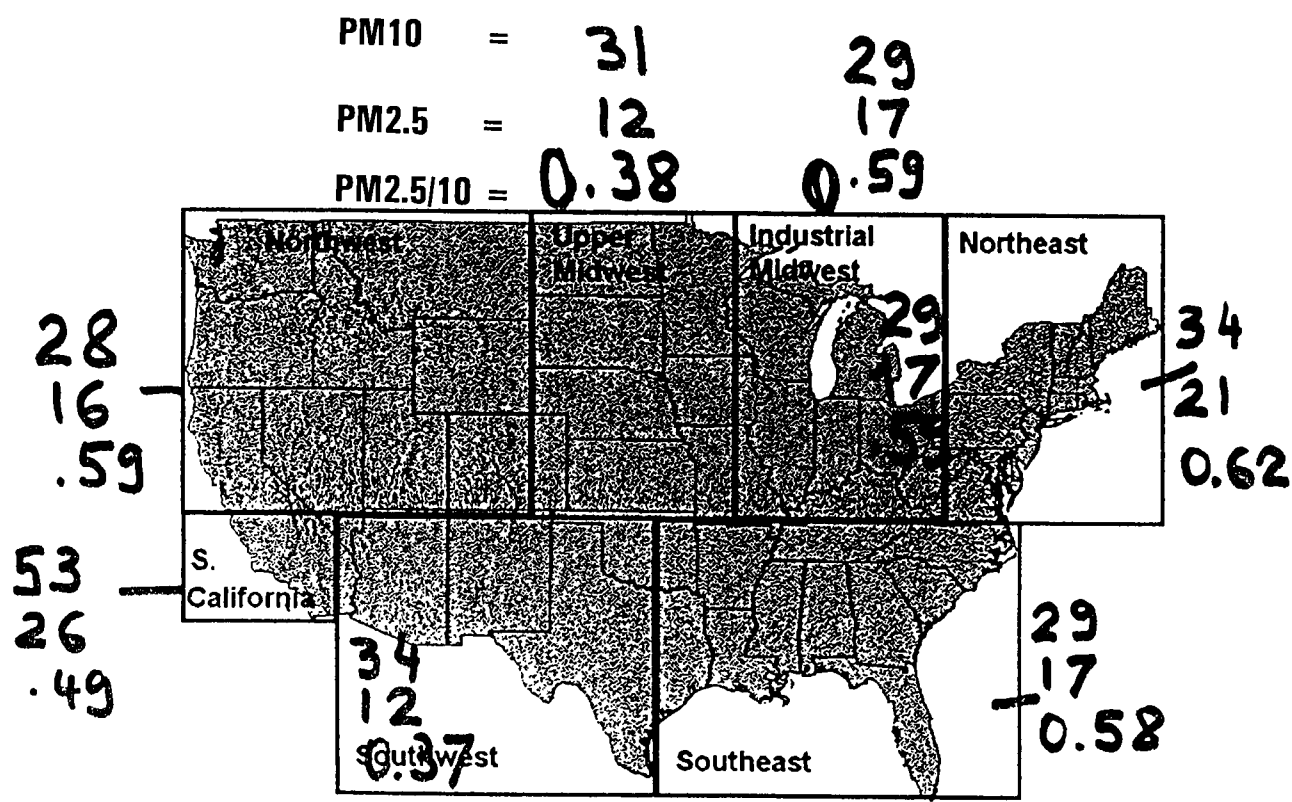


Figure 6-28 Aerosol regions of the conterminous US.

#### 6.4.1 Regional Aerosol Pattern in the Northeast

The Northeast aerosol region covers the New England states, including eastern Pennsylvania and eastern Virginia to the south (Figure 6-29a). In the Northeast, terrain features that significantly influence regional ventilation occur over the mountainous upstate New York, Vermont and New Hampshire. Throughout the year, the Northeast is influenced by Canadian as well as Gulf airmasses. The region includes the Boston-New York megalopolis, as well as other urban-industrial centers. It is known that the Northeast is influenced by both local sources, as well as long range transport of fine particle haze from other regions.

Data from a two year fine particle network in the Northeast (Bennett et al., 1994) yielded a geometric mean concentration of  $PM_{2.5}$  of 12.9 and particulate sulfur ( $1.4 \mu g/m^3$ ),

equivalent to  $4.2 \mu\text{g}/\text{m}^3$  of sulfate), which is somewhat lower than other comparable rural data.

#### **6.4.1.1 Non-urban size and chemical composition in the Northeast**

The summary of the non-urban aerosol chemical composition in the Northeast is presented in Figure 6-29c. The region has 14 monitoring sites, 7 of which are part of NESCAUM in the New England states.

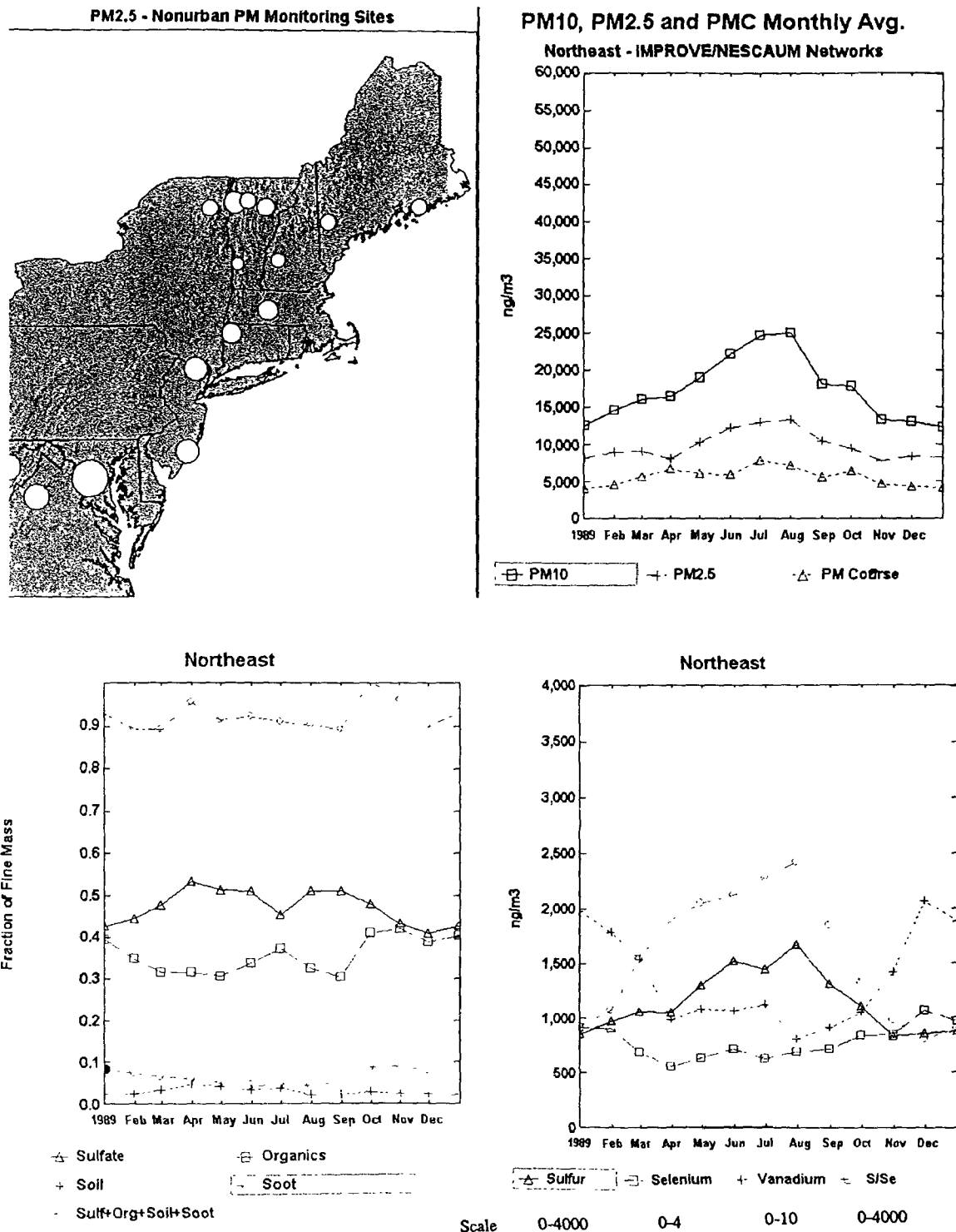
The  $\text{PM}_{10}$  concentration exhibits a factor of two seasonal amplitude between  $12 \mu\text{g}/\text{m}^3$  in the winter, and  $25 \mu\text{g}/\text{m}^3$  in June and July (Figure 6-29b). About 60% of  $\text{PM}_{10}$  is contributed by fine particles throughout the year, and also contribute to the summer-peaked seasonality.

Sulfates are the most important contributors of the fine particle mass in the Northeast, particularly in the summer season when they account for half of the fine mass. The organics account for 30 to 40%, with the higher fractions occurring in the fall and winter, September through January. In fact, during the late fall the sulfate and organic contributions are comparable at 40%. Fine particle soil is remarkably unimportant throughout the year (<5%). Soot on the other hand, is more significant particularly during the fall when it contributes about 10% of the fine mass. The sum of the above four non-urban fine particle aerosol components, account for over 90% of the measured fine particle mass throughout the year. This indicates that nitrates, trace metals and sea salt are of minor importance in the northeastern U.S. fine particle chemical mass balance.

The seasonality of both selenium and vanadium indicates a winter peak (Figure 6-29d). In particular, the vanadium concentration increases by factor of two for December and January compared to the summer values. Also, the V concentration is higher than over any other region indicating the strongest contribution of fuel oil emissions. The S/Se ratio is strongly seasonal with the winter value of 1,000 and the summer peak of 2,000 to 2,500.

#### **6.4.1.2 Urban aerosols in the Northeast**

The Northeast region shows a substantial (39%) decline in  $\text{PM}_{10}$  concentration, from  $36 \mu\text{g}/\text{m}^3$  in 1985 to  $22 \mu\text{g}/\text{m}^3$  in 1993 (Figure 6-30b). The standard deviation among the



**Figure 6-29.** IMPROVE/NESCAUM concentration data for the Northeast.  
 (a) Monitoring locations. (b) PM<sub>10</sub>, PM<sub>2.5</sub>, and PM<sub>C</sub>. (c) Chemical fraction of sulfate, soil, organics, and soot. (d) Tracer concentrations.

1 monitoring stations for any given year is about 30%. The map of the Northeast shows the  
2 magnitude of PM<sub>10</sub> concentrations in proportion of circle radius. It is evident, that the  
3 highest AIRS PM<sub>10</sub> concentrations generally occur in urban centers (Figure 6-30a).

4 The seasonality of the Northeast PM<sub>10</sub> concentration (Figure 6-30d) is a modest 20%,  
5 ranging from 25 to 31  $\mu\text{g}/\text{m}^3$ . There is a summer peak in July, and a rather uniform  
6 concentration between September and May showing only a slight winter peak.

7 The PM<sub>2.5</sub>-PM<sub>10</sub> relationship in the scatter charts (Figure 6-30c) show that on the  
8 average 62% of PM<sub>10</sub> is contributed by fine particles. During high levels of PM<sub>10</sub>, fine  
9 particles dominate some of the months, while coarse particles during other months. It is  
10 likely that urban and rural sampling locations exhibit different PM<sub>2.5</sub>-PM<sub>10</sub> relationship.

11 In general, the regional scale emissions are not expected to vary significantly from one  
12 day to another. However, both meteorological transport, i.e. dilution, as well as aerosol  
13 formation and removal processes are important modulators of daily aerosol concentration.  
14 Daily concentration of particulate matter exhibits strong fluctuation from one day to another,  
15 mainly due to the role of the meteorological transport variability. The AIRS PM<sub>10</sub> database  
16 reports the concentrations every sixth day, synchronously over the entire country. The  
17 sample duration is one day which, over the long run provides the concentration distribution  
18 function of daily samples. For determination of the effects (human health, visibility, acid  
19 deposition) the concentration has to be known at the specific location where the sensitive  
20 receptors reside. Also the concentrations have to be known at a short, e.g. daily time scale,  
21 as well as over the long-term.

22 In order to characterize the one day-scale temporal variation over a given region, the  
23 entire available data aggregated over the entire region for each monitoring day are plotted as  
24 time series. It is recognized that during the other five non-monitored days, the  
25 concentrations may be different from the reported value. The six day sample increment  
26 ensures that both weekday and weekend data are properly taken into account. The physical  
27 interpretation of regionally averaged daily concentration is a measure of the regional scale  
28 meteorological ventilation. High regionally averaged concentrations indicate poor  
29 ventilation, i.e. combination of low wind speeds and low mixing heights and the absence of  
30 fast aerosol removal rates, such as cloud scavenging and precipitation. Low regional  
31 concentrations, on the other hand, represent either strong horizontal transport, deep mixing



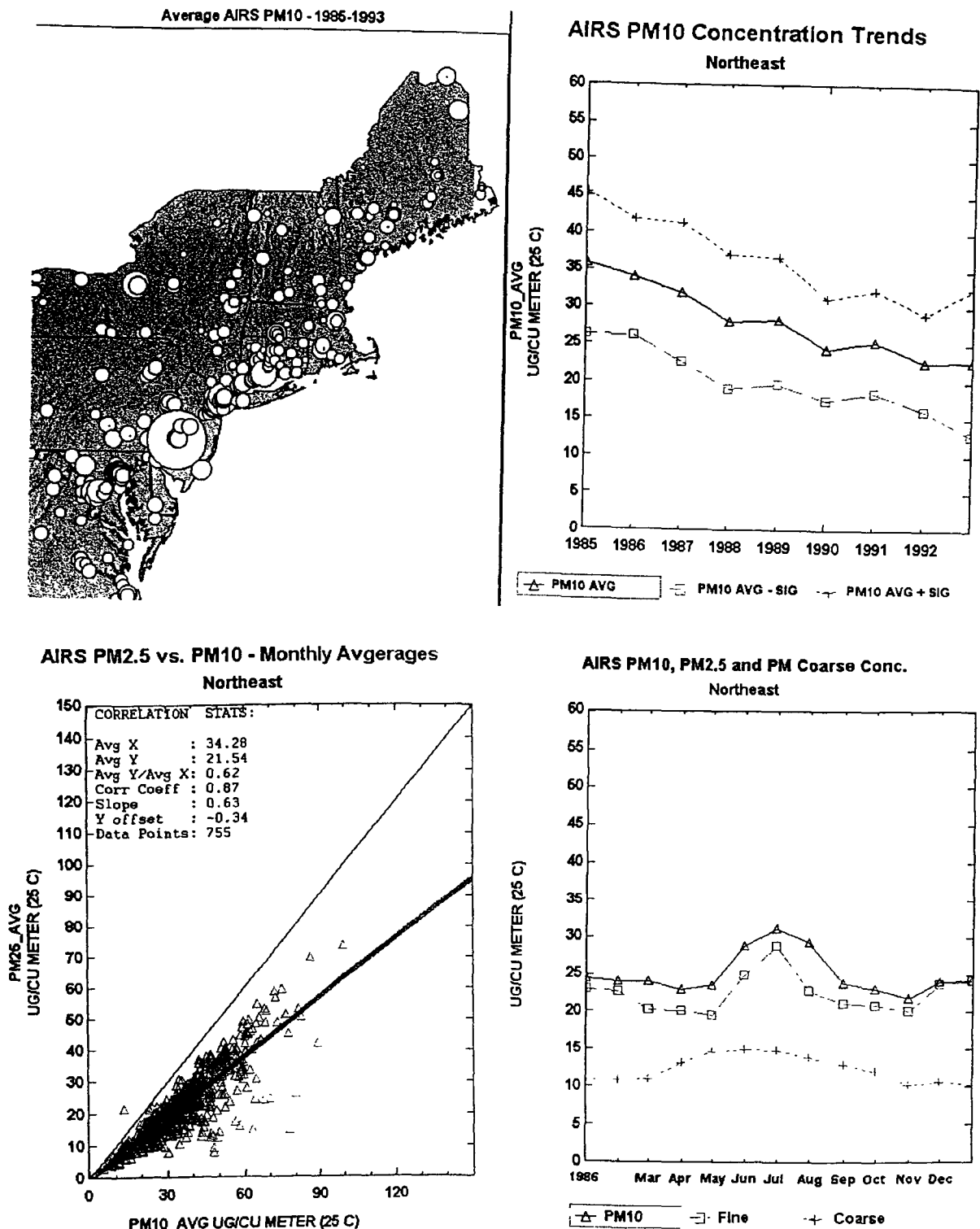


Figure 6-30. AIRS concentration data for the Northeast. (a) Monitoring locations. (b) Regional  $PM_{10}$  concentration trends. (c)  $PM_{10}$ ,  $PM_{2.5}$  relationship. (d)  $PM_{10}$ ,  $PM_{2.5}$ , and  $PM_{Coarse}$  seasonal pattern.

heights, or high regional removal rates. Advection of high aerosol content air masses from neighboring regions may also be a cause of elevated concentration in a given region.

The daily variation of the regional averaged urban  $PM_{10}$  concentration for the Northeast is shown in Figure 6-31. As a guide to the eye the single day concentration data for every sixth day are connected by a line between the data points, although five in-between days are not monitored. The lowest regionally averaged daily urban  $PM_{10}$  is about  $10 \mu g/m^3$ , while the highest is about  $55 \mu g/m^3$ , with a regional average of  $25 \mu g/m^3$ . The highest concentrations ( $> 40 \mu g/m^3$ ) occur primarily in the summer season. The time series also indicate that the high concentration episodes do not persist over multiple six day periods. This is consistent with the notion that the regional ventilation that is caused by synoptic scale air mass changes, which typically occur every four to seven days over eastern US. The daily time series also convey the fact that day to day variation in  $PM_{10}$  is higher than the seasonal amplitude. In fact, visual inspection of Figure 6-31 the concentration seasonality is barely discernible. It can be stated, therefore, that the  $PM_{10}$  concentration in the Northeast is highly episodic, i.e. the temporal concentration variation is both substantial and irregular. The excess urban  $PM_{10}$  (AIRS-IMPROVE) is shown in Figure 6-32.

## **6.4.2 Regional Aerosol Pattern in the Southeast**

The Southeast rectangle stretches from North Carolina to eastern Texas (Figure 6-33). From the point view of regional ventilation the Southeast terrain is flat, with the exception of mildly rolling the southern Appalachian Mountains. The region is known for increasing population over the past decades, high summertime humidity, and poor regional ventilation, due to stagnating high pressure systems.

### **6.4.2.1 Non-urban Size and Chemical Composition in the Southeast**

The non-urban  $PM_{10}$  concentration in the Southeast (Figure 6-33b) is roughly comparable to the Northeast, exhibiting about factor of two seasonal concentration amplitude between  $12 \mu g/m^3$  in the winter, and  $25 \mu g/m^3$  in the summer. An anomalous high  $PM_{10}$  concentration is recorded for July which is contributed exclusively by excess coarse particle concentrations of about  $10 \mu g/m^3$ . With exception of July, the fine particle mass accounts

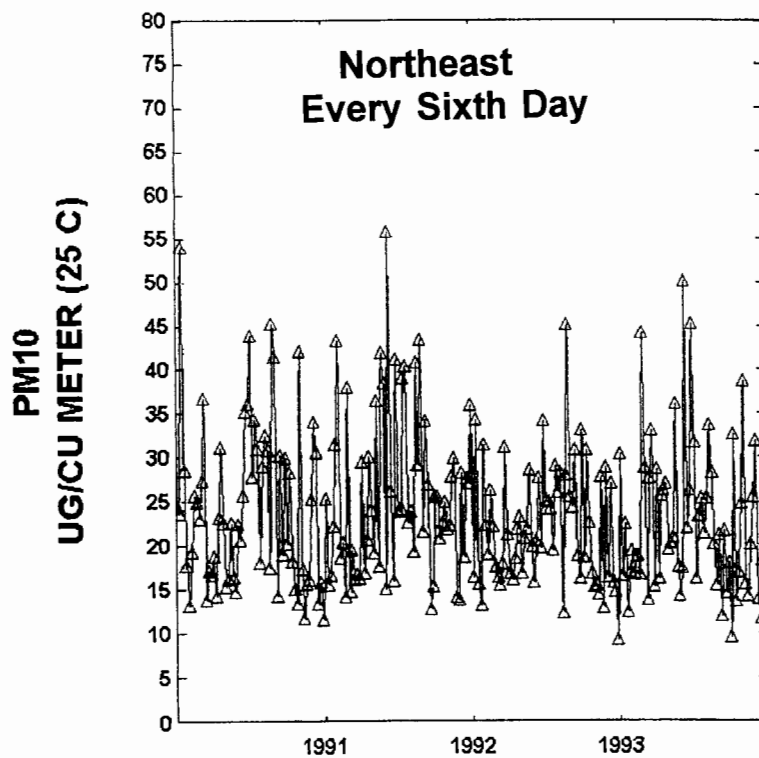


Figure 6-31. Short term variation of  $PM_{10}$  average for the Northeast. Data are reported every sixth day.

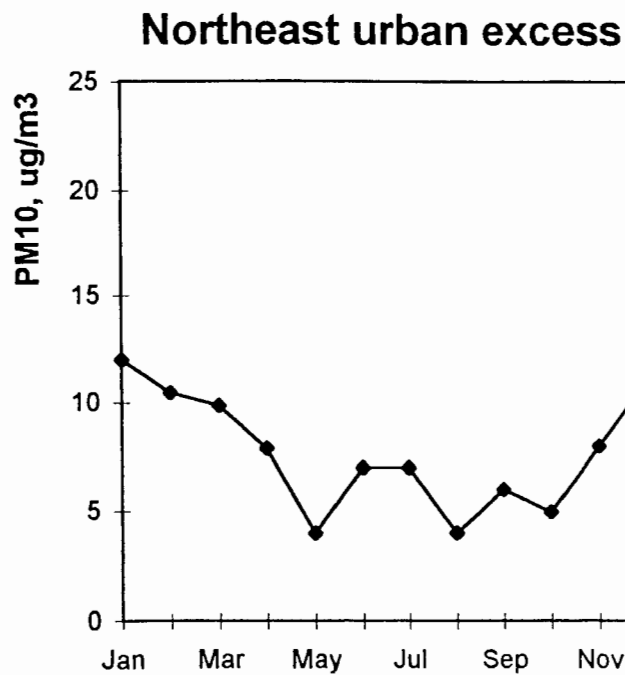


Figure 6-32. Urban excess concentration (AIRS minus IMPROVE) for the Northeast.

1 for about 70% of the non-urban  $PM_{10}$ , leaving the coarse mass of 30% or less throughout the  
2 year (Figure 6-33b).

3 The most prominent aerosol species in the Southeast are sulfates contributing 40 to  
4 50% of the fine mass (Figures 6-33c). The anomalous sulfate fraction (35%) coincides with  
5 the high (20%) soil contribution during July. During other months, soil contribution is  
6 <5% of the fine mass. The relative role of the organics in the non-urban Southeast is most  
7 pronounced during the winter (40%), but declines to 25% during the summer months. The  
8 soot contribution varies between 2% in the summer to 6% in the winter months.

9 The trace element concentrations of selenium and vanadium (Figure 6-33d) are  
10 constant throughout the year, implying that the combined role of emissions and dilution is  
11 seasonally invariant. The concentration of sulfur, on other hand shows a definite summer  
12 peak, that is 2 to 3 times higher than the winter concentrations. Consequently, the S/Se ratio  
13 is strongly seasonal. In fact, the warm season S/Se ratio of 2,500 is higher than over any  
14 other region of the country. If Se-bearing coal combustion is the dominant source of sulfur  
15 in the Southeast, than the high S/Se ratio implies that the sulfate production per coal  
16 production in the summer is 2.5 times that in the winter.

#### 18 **6.4.2.2 Urban Aerosols in the Southeast**

19 There is evidence of significant (34%)  $PM_{10}$  decline over the past decade (Figure  
20 6-34b). By 1993, the average  $PM_{10}$  was  $24 \mu g/m^3$ . It is worth noting that this value is  
21 higher than the corresponding 1993 concentration for the Northeast ( $22 \mu g/m^3$ ). It is also  
22 remarkable that the Southeast concentration trends and patterns most closely resemble the  
23 industrial Midwest described below. The unique feature of the Southeast is the uniformity of  
24 the aerosol concentration among the monitoring stations. In fact the 17% station to station  
25 standard deviation is by far the lowest among the aerosol regions (Figure 6-34b).

26 The Southeast is also characterized by high seasonal amplitude of 37%, ranging  
27 between  $22 \mu g/m^3$  in December through February and  $35 \mu g/m^3$  in July through August  
28 (Figure 6-34d). There is no evidence of a winter peak for the southeastern US.

29 The scattergram of  $PM_{2.5}$ - $PM_{10}$  for the Southeast (Figure 6-34c) shows an average of  
30 58% fine particle contribution, with considerable scatter. It should be noted, however, that

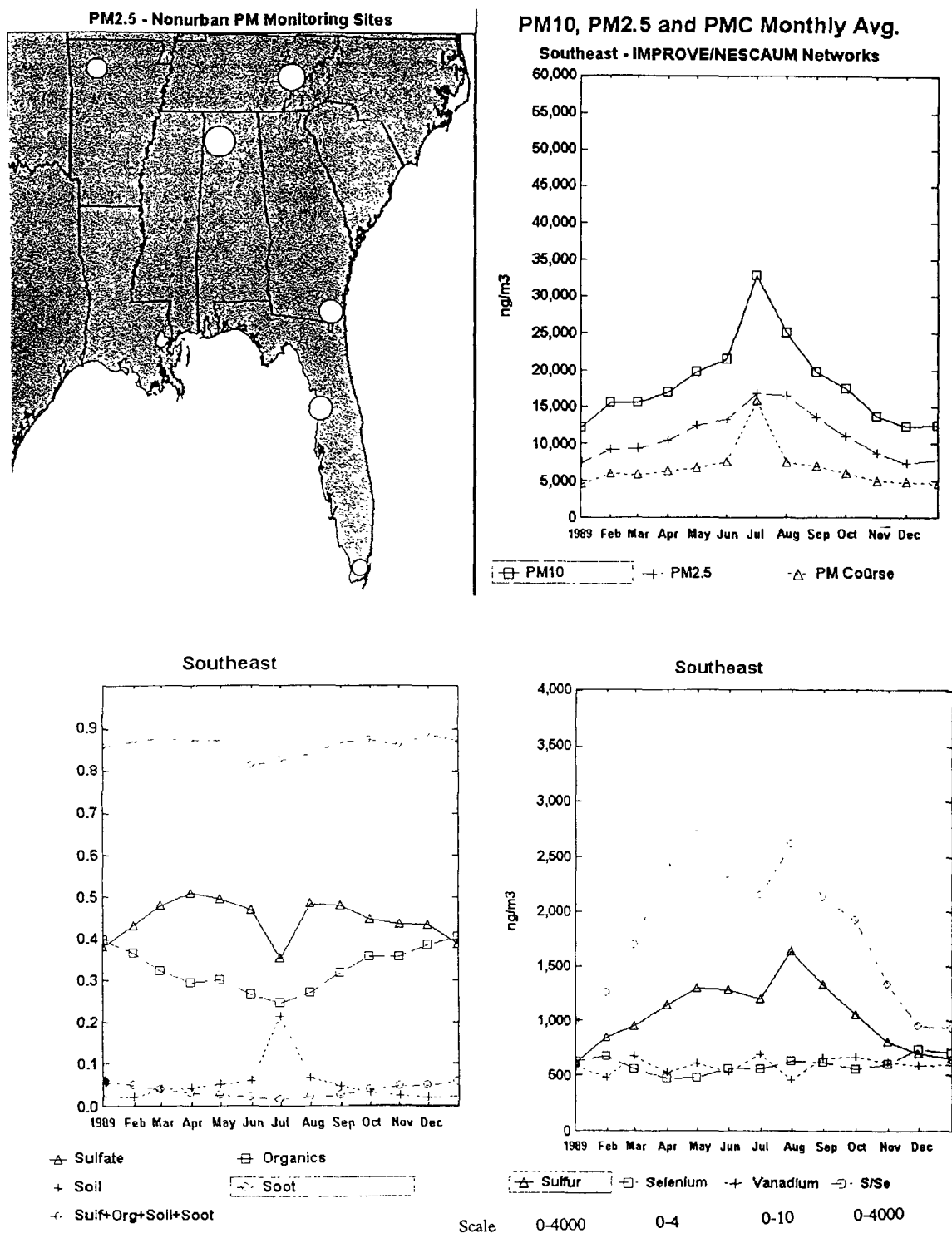
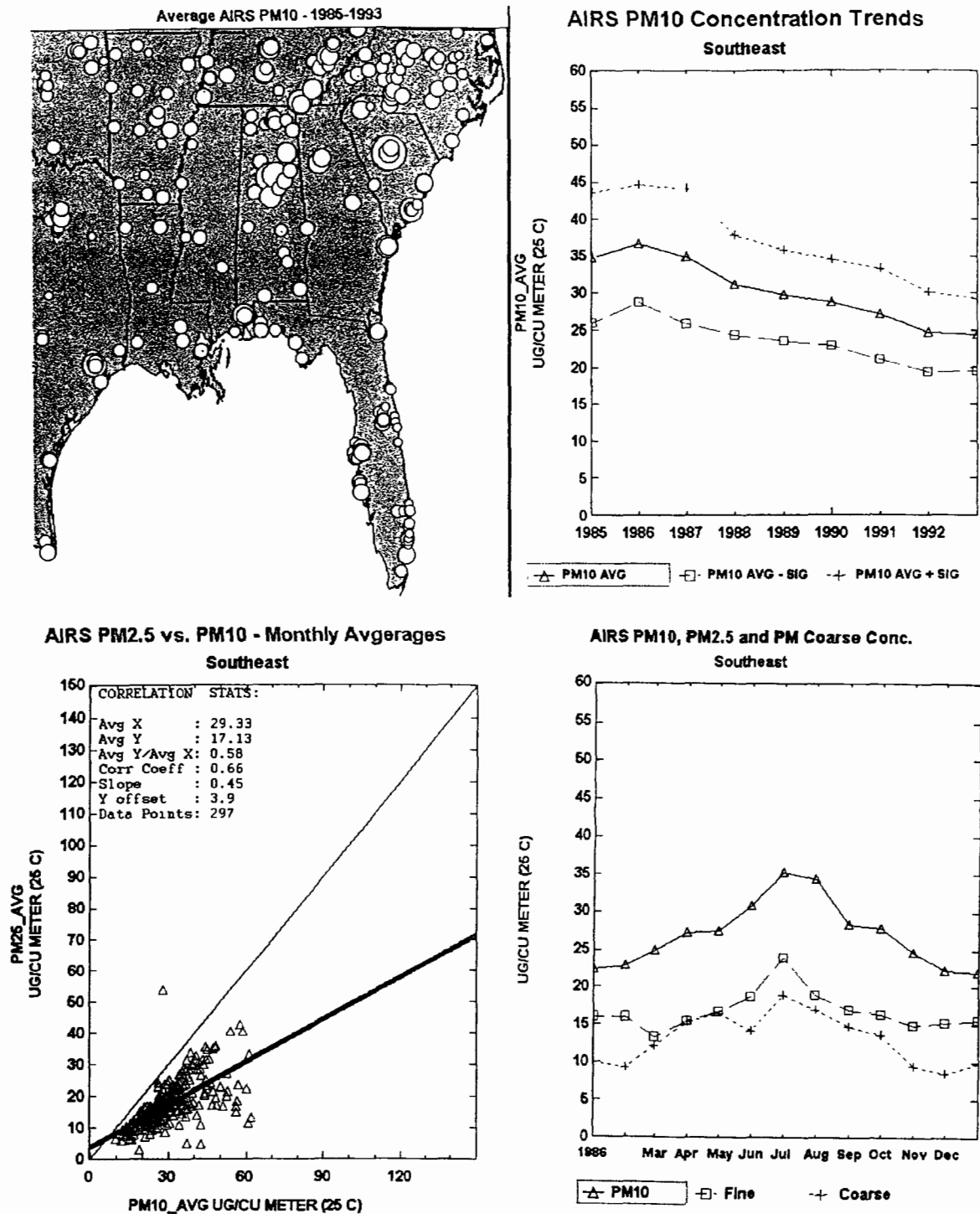


Figure 6-33. IMPROVE/NESCAUM concentration data for the Southeast. (a) Monitoring locations. (b)  $PM_{10}$ ,  $PM_{2.5}$ , and  $PM_{Coarse}$ . (c) Chemical fraction of sulfate, soil, organics, and soot. (d) Tracer concentrations.



**Figure 6-34.** AIRS concentration data for the Southeast. (a) Monitoring locations. (b)  $PM_{10}$ ,  $PM_{2.5}$ , and  $PM_{Coarse}$ . (c) Chemical fraction of sulfate, soil, organics, and soot. (d) Tracer concentrations.

size segregated samples were only available briefly for two monitoring sites which may not be representative for the large southeastern region.

The regionally averaged daily  $PM_{10}$  concentrations over the Southeast (Figure 6-35) shows a clearly discernible seasonality. The concentrations during the winter months are about factor of two lower than during the summer. Overall, the lowest concentrations are about  $14 \mu\text{g}/\text{m}^3$ , and the highest about  $50 \mu\text{g}/\text{m}^3$ , which is about factor of three. However, seasonality of the temporal signal accounts to about half of the variation. Hence, within a given season the sixth day to sixth day variation is only about 50%. It can be concluded that the  $PM_{10}$  concentration over the southeastern United States region is quite uniform in time, although it exhibits a substantial seasonality. It is to be noted that the southeastern United States also exhibits the highest spatial homogeneity, i.e. the average deviation of average concentrations between the stations. A further index of the short-term temporal variation is given in the seasonal maps of concentration standard deviation (Figure 6-34b). The  $PM_{10}$  urban excess (AIRS-IMPROVE) for the southeast region is given in Figure 6-36.

### 6.4.3 Regional Aerosol Pattern in the Industrial Midwest

This aerosol region stretches between Illinois and western Pennsylvania, including Kentucky on the south (Figure 6-37a). The industrial Midwest is covered by flat terrain with the exception of the central Appalachian Mountains in the Virginias. In the winter the region is under the influence of cold Canadian air masses, while during the summer moist airmass transported from the Gulf Coast prevail. This region includes the Ohio and Mississippi River Valleys that are known for high sulfur emission densities. The region also includes major metropolitan areas.

#### 6.4.3.1 Non-urban Size and Chemical Composition in the Industrial Midwest

The seasonal pattern of the non-urban aerosol in the Industrial Midwest is shown in Figure 6-37b. It is worth noting that the regional observations are based on a few monitoring sites and their representativeness is questionable. The  $PM_{10}$  concentrations range between  $10$  and  $22 \mu\text{g}/\text{m}^3$ , comparable to the non-urban levels in other eastern U.S. regions. It is quite remarkable that 70 to 80% of  $PM_{10}$  is contributed by fine particles throughout the year. In fact, the coarse particle concentrations are  $4$  to  $5 \mu\text{g}/\text{m}^3$ , which is lower than over

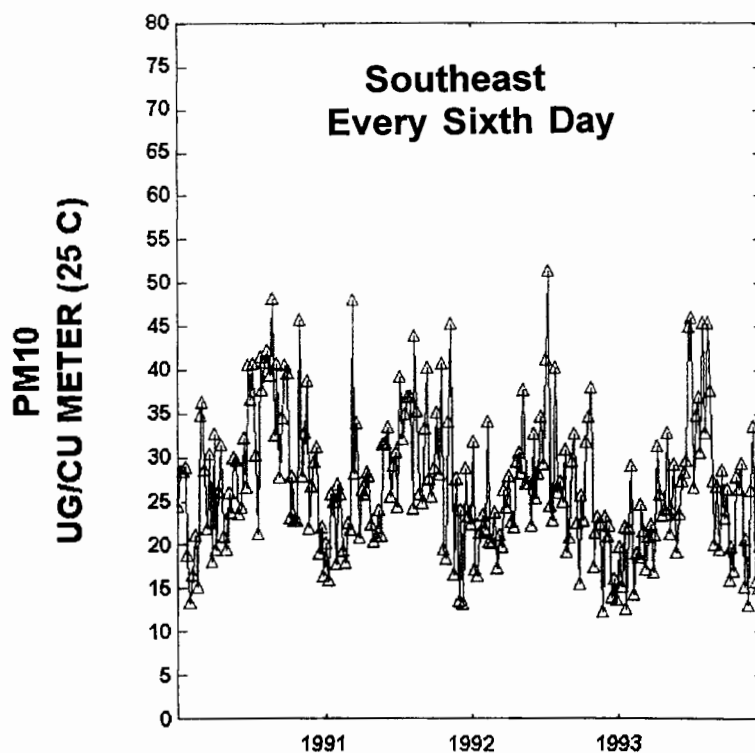


Figure 6-35. Short term variation of  $PM_{10}$  average for the Southeast. Data are reported every sixth day.

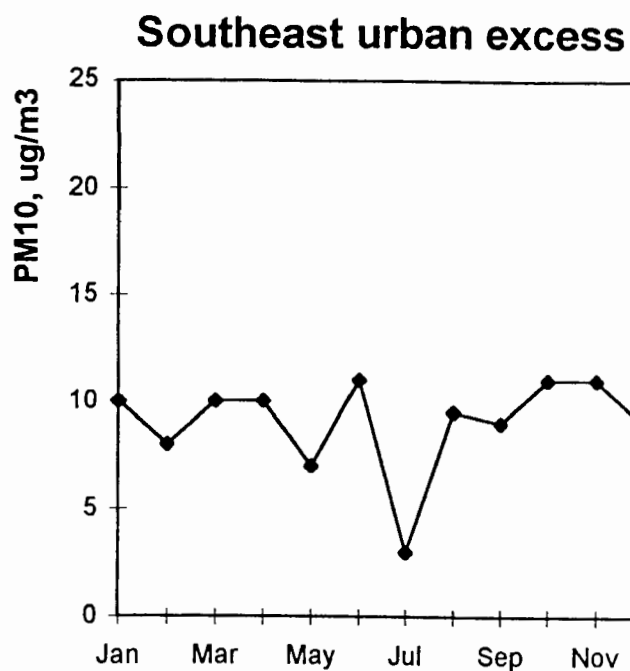
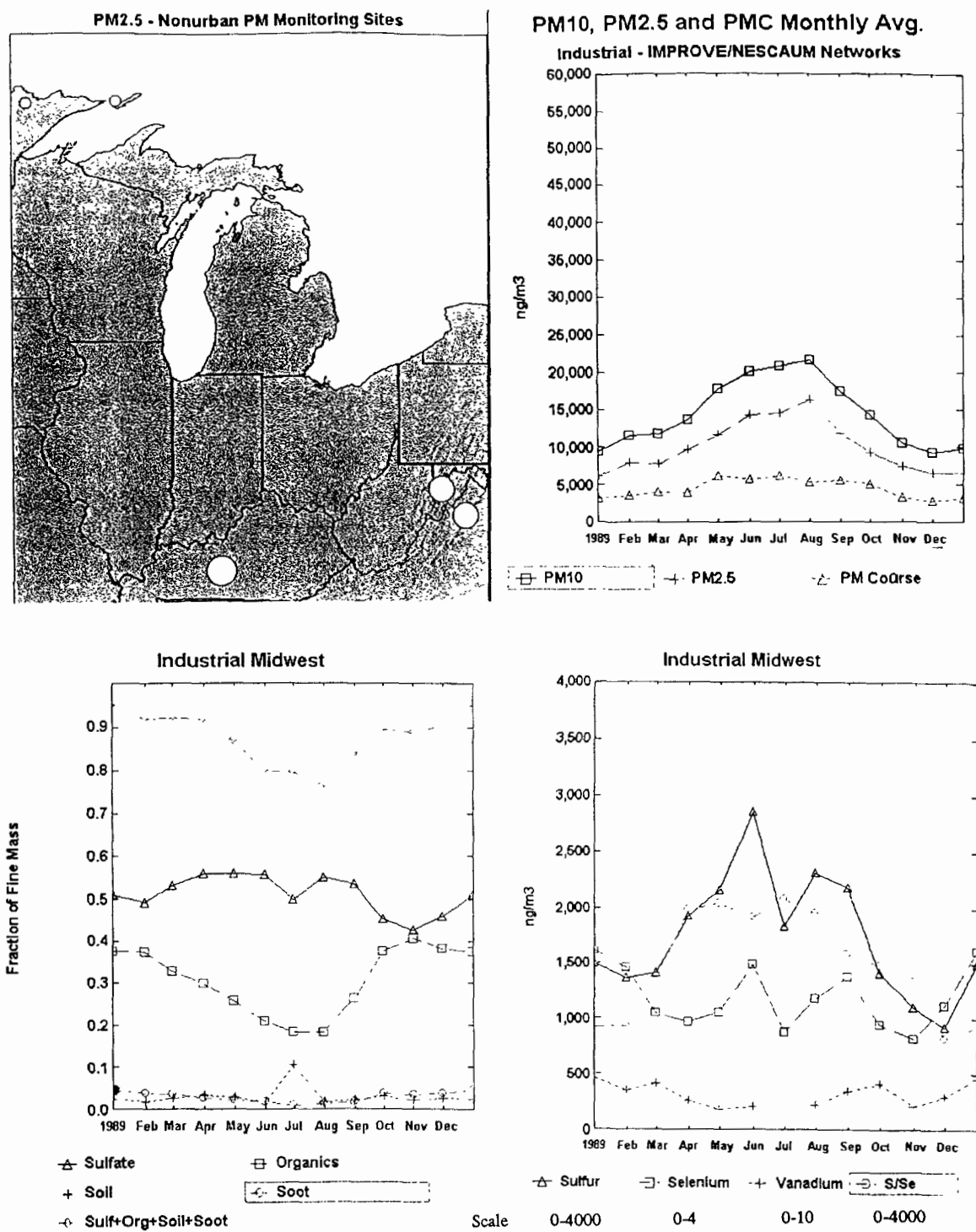


Figure 6-36. Urban excess concentration (AIRS minus IMPROVE) for the Southeast.





**Figure 6-37.** IMPROVE/NESCAUM concentration data for the Industrial Midwest. (a) Monitoring locations. (b) PM<sub>10</sub>, PM<sub>2.5</sub>, and PM Coarse. (c) Chemical fraction of sulfate, soil, organics, and soot. d) Tracer concentrations.

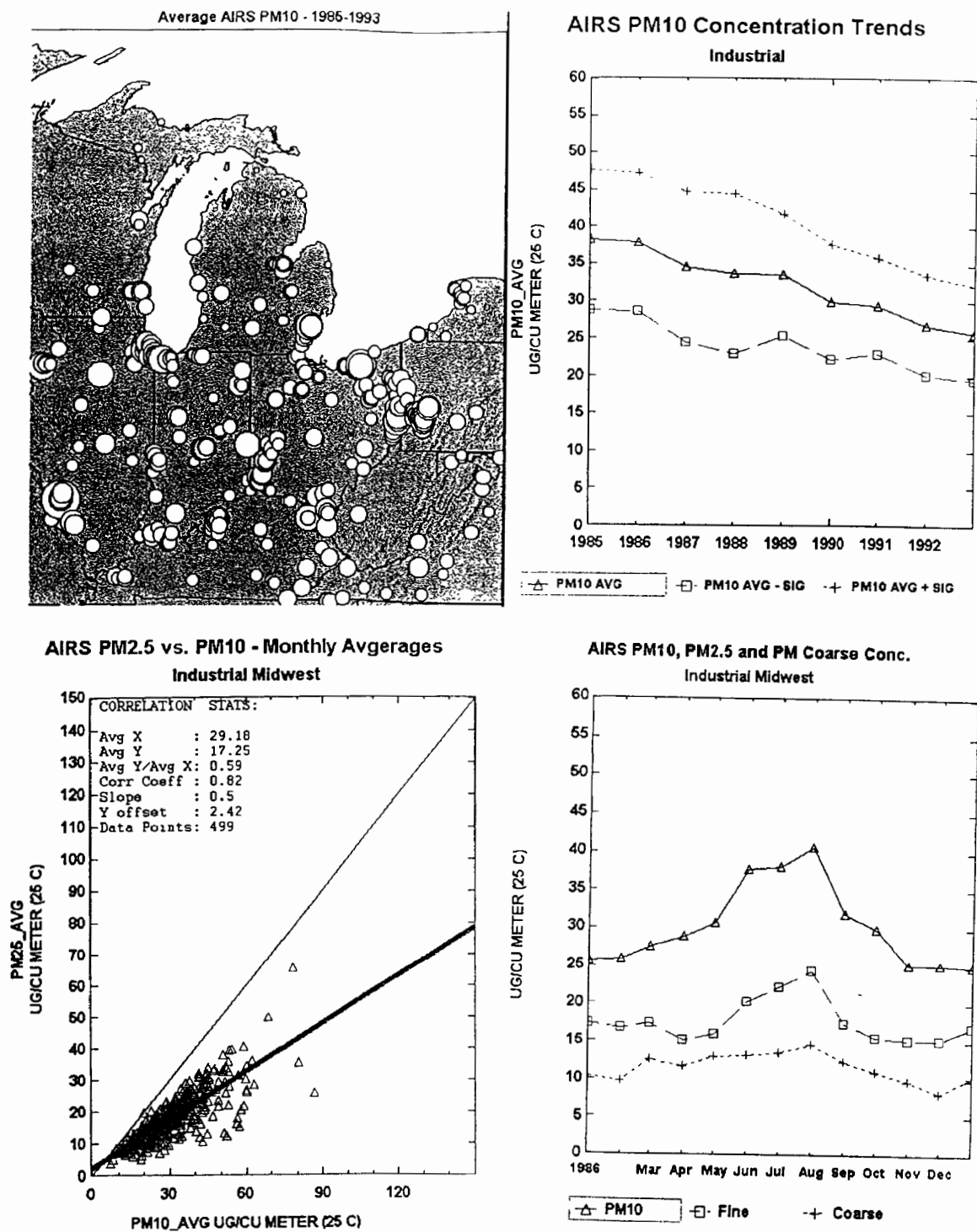
any other region of the US. Hence, the contribution of wind blown dust, fly ash, or other man-induced dust entrainment is not a significant factor in the non-urban areas of the Industrial Midwest.

The chemical mass balance (Figure 6-37c) shows that sulfates are 45 to 55% of the fine mass which is higher than the sulfate fractions in other regions. Organics exhibit a variable contribution that is high (40%) during the cold season (October through February) and remarkably low (20%) in July and August. The strong winter peak for the organic fraction differs markedly from the Northeast where the organics are aseasonal. Another unusual feature of the chemical mass balance is that the sum of sulfate, organics soil and soot is about 75% during the summer and 95% in the winter. It is not known what is the composition of the missing 25% during the summer time.

Chemical tracer data is shown in Figure 6-37d. The chemical tracer for coal combustion, selenium ranges between 1,000 and 1,500 ng/m<sup>3</sup>, which is higher than in any other region. There is a sizeable month to month variation in Se concentration (partly due to a small number of data points) and the seasonality is not appreciable. This means that the combined effects of coal combustion source strength and meteorological dilution is seasonally invariant over the industrial Midwest. The concentration of vanadium, which is a tracer for oil combustion is low throughout the year. The concentration of fine particle sulfur exhibits random monthly variation but indicates a summer peak. The S/Se ratio is a rather smooth seasonal curve ranging between 1,000 in the winter and 2,000 during the summer months. Hence, the sulfate yield is about twice during the summer than during winter months. For comparison both the Northeast and Southeast exhibit higher seasonality (factor of 2.5) in S/Se ratio. A possible explanation for this change in S/Se ratio is that over the industrial Midwest the average age of the aerosol producing emissions is less than over the Northeast or Southeast. Alternatively, the sulfate formation rate may be higher over the Northeast and Southeast.

#### **6.4.3.2 Urban Aerosols in the Industrial Midwest**

The PM<sub>10</sub> concentration trends for the industrial Midwest (Figure 6-38b) show a decline of 34% (from 38 to 25 µg/m<sup>3</sup>) between 1985 and 1993. There is also a 28%



**Figure 6-38.** AIRS concentration data for the Industrial Midwest. (a) Monitoring locations. (b)  $\text{PM}_{10}$ ,  $\text{PM}_{2.5}$ , and  $\text{PM}_{\text{Coarse}}$ . (c) Chemical fraction of sulfate, soil, organics, and soot. (d) Tracer concentrations.

1 deviation among the stations within the region. As in the Northeast, the higher  
2 concentrations occur within urban-industrial areas (Figure 6-38a).

3 The  $PM_{10}$  seasonality (Figure 6-38d) is virtually identical (37% amplitude) to the  
4 seasonality of the Southeast: the lowest concentrations ( $25 \mu\text{g}/\text{m}^3$ ) occur between November  
5 and February, while the highest values are recorded in June through August ( $40 \mu\text{g}/\text{m}^3$ ). It  
6 is quite remarkable that throughout the 1980s of  $PM_{10}$ , the trends and the seasonality of the  
7 midwestern  $PM_{10}$  aerosols is comparable to that of the Southeast. At this time, the only  
8 rationale for separating into a region is the belief that the source types and the aerosol  
9 composition may possibly be different from the Southeast.

10 Fine particles contribute 59% of the  $PM_{10}$  concentration on the average (Figure  
11 6-38c), and high  $PM_{10}$  can occur when either fine or coarse particles dominate. It is notable  
12 that size segregated samples are available primarily from urban-industrial sites over the  
13 industrialized Midwest.

14 Daily concentration over the industrial Midwest (Figure 6-39) varies between 50 and  
15  $75 \mu\text{g}/\text{m}^3$ . The lowest regional concentrations occur during the winter months, while the  
16 highest values (in excess of  $40 \mu\text{g}/\text{m}^3$ ) occur during the summer. It is evident, that  
17 seasonality is an important component of the time series, accounting for about half of the  
18 variance. The elevated concentrations occur only one sixth day observation at the time,  
19 indicating general absence of prolonged episodes that last 12 days or more. The industrial  
20 Midwest also show substantial spatial variability. The urban excess  $PM_{10}$  (AIRS-IMPROVE)  
21 for the industrial midwest is given in Figure 6-40.

#### 22 23 **6.4.4 Regional Aerosol Pattern in the Upper Midwest**

24 The upper Midwest covers the agricultural heartland of the country (Figure 6-40). The  
25 region is void of any terrain features that would influence the regional ventilation. Industrial  
26 emissions and the population density are comparatively low. However, the relatively high  
27  $PM_{10}$  concentrations in this region warrant a more detailed examination. In the winter, the  
28 region is covered by cold Canadian airmasses, while in the summer moist Gulf air alternates  
29 with drier Pacific airmasses.

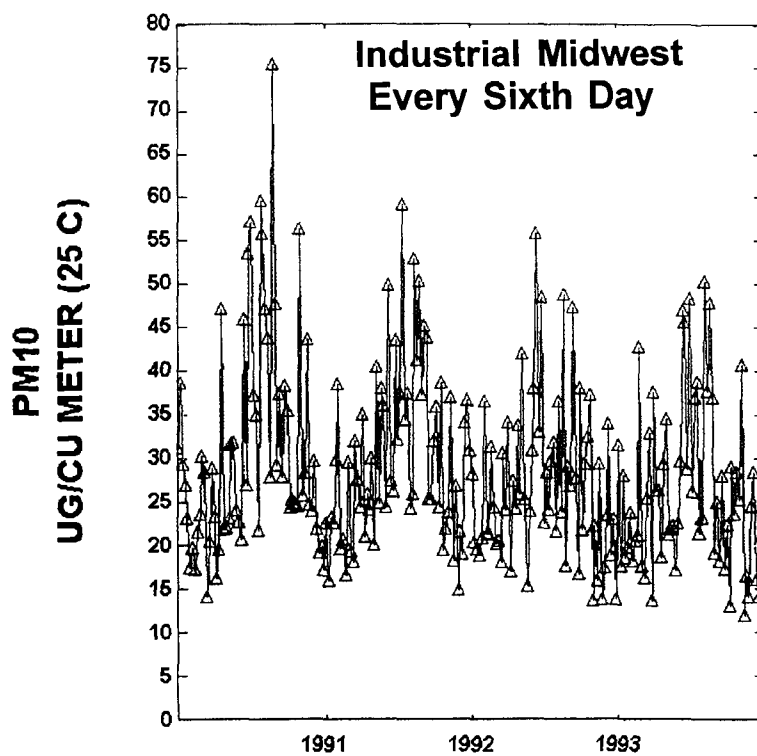


Figure 6-39. Short term variation of PM<sub>10</sub> average for the Industrial Midwest. Data are reported every sixth day.

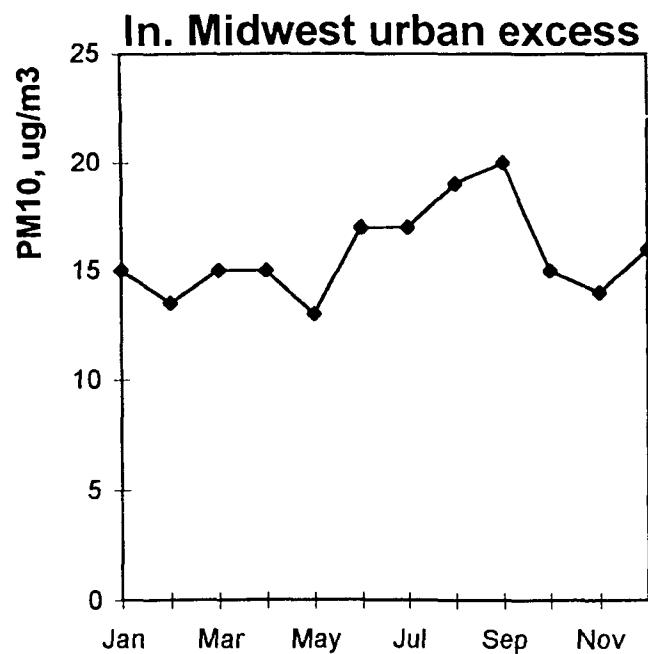


Figure 6-40. Urban excess concentration (AIRS minus IMPROVE) for the Industrial Midwest.

#### 6.4.4.1 Non-urban Size and Chemical Composition in the Upper Midwest

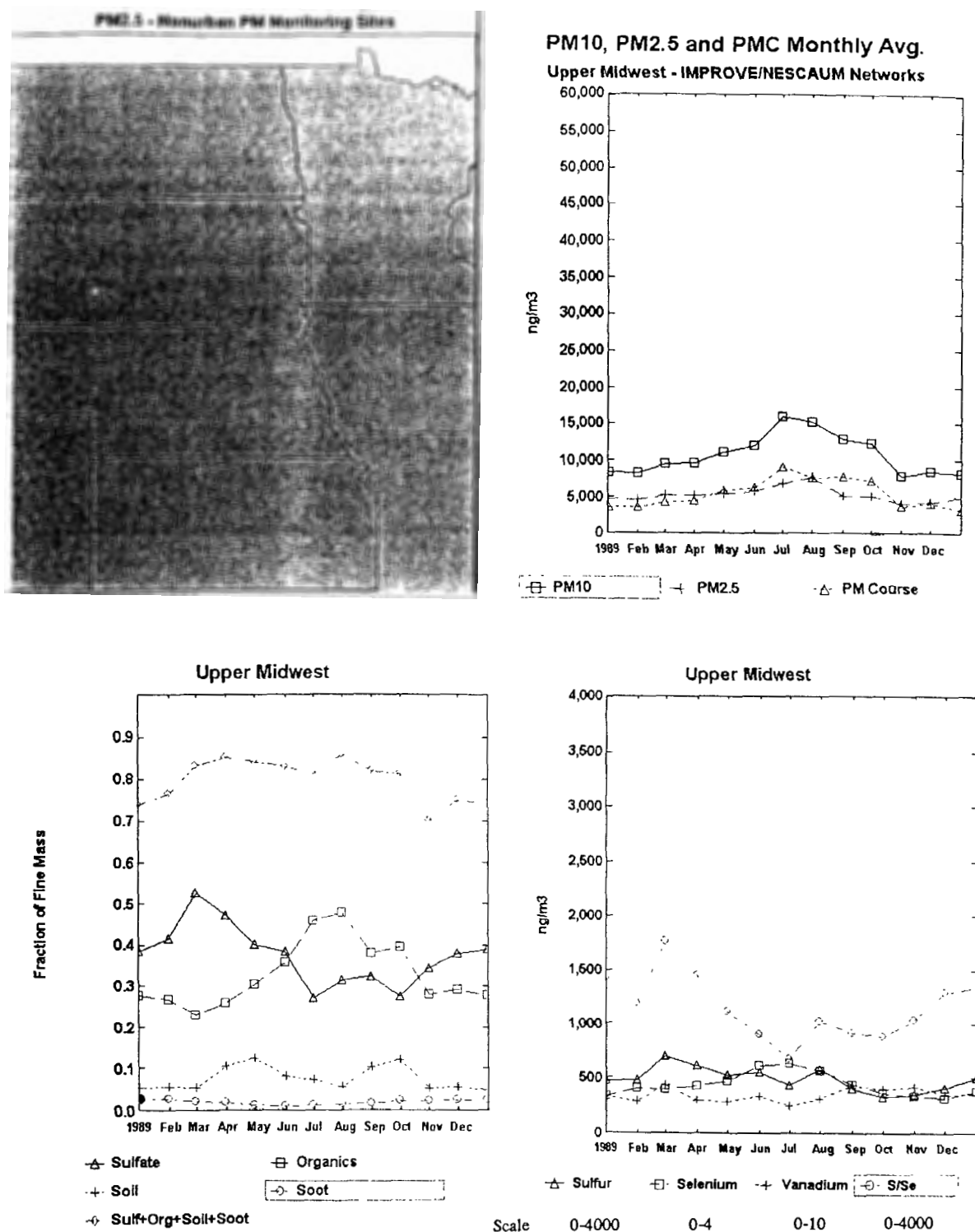
Over the non-urban areas of upper Midwest the  $\text{PM}_{10}$  concentration is about  $8 \mu\text{g}/\text{m}^3$  during November through April winter season, and increases to  $15 \mu\text{g}/\text{m}^3$  during the summer. Fine and coarse particles have a comparable contribution to the  $\text{PM}_{10}$  mass (Figure 6-41b).

The chemical mass balance (Figure 6-41c) indicates that during the March through May spring season sulfates dominate, but during July through October season organics prevail. This is a rather unusual pattern not observed over any other region. The contribution of fine particle soil exceeds 10% in the spring as well as in the fall season.

Chemical tracers are shown in Figure 6-41d. Selenium concentration is low throughout the year (400 to  $600 \text{ ng}/\text{m}^3$ ), but the highest concentrations are observed during the summer. This suggest that either the Se sources or the Se transport into the Upper Midwest from other regions is strongest in the summer. The concentration of the fine particle sulfur is  $<500 \text{ ng}/\text{m}^3$  throughout the year, but somewhat higher during March and April. The spring peak for fine particle sulfur has not been observed in any other region. It is also worth noting that S/Se ratio is the highest during the spring and lowest in July through September. This hints on the possibility that over the Upper Midwest additional sources of fine particle sulfur are present for which Se is not a tracer. Here again, it needs to be pointed out that the above chemical patterns are based on only two monitoring stations.

#### 6.4.4.2 Urban Aerosols in the Upper Midwest

The agricultural upper Midwest (Figure 6-42) shows the smallest decline among the aerosol regions. Over the past decade the region average  $\text{PM}_{10}$  concentration ranged between 25 and  $31 \mu\text{g}/\text{m}^3$ . Some reduction (19%) is evident since 1989. As over the eastern US, the highest concentrations occur in the vicinity of urban areas. Some of the station to station concentration spread arises from low concentrations over western North Dakota. On the average, the deviation among the stations over the region is a moderate 30% (Figure 6-39). The upper Midwest is also unique in that it shows the regionally lowest seasonal amplitude of 19%, with the slightly lower concentrations occurring in December and January. The sparse size segregated data indicate that only 38% of  $\text{PM}_{10}$  is contributed by



**Figure 6-41.** IMPROVE/NESCAUM concentration data for the Upper Midwest. (a) Monitoring locations. (b) PM<sub>10</sub>, PM<sub>2.5</sub>, and PM Coarse. (c) Chemical fraction of sulfate, soil, organics, and soot. (d) Tracer concentrations.

fine particles. This is an indication that wind blown dust from natural or man-induced sources prevails. In this sense, the region is similar to the Southwest.

The daily regionally averaged  $PM_{10}$  concentrations in the upper Midwest (Figure 6-43) range between 15 and 45  $\mu g/m^3$ . The highest values ( $>40 \mu g/m^3$ ) generally occur in the summer season, while the low regional concentrations occur mainly in the cold season, but low values also occur in the summer. It is interesting that the lowest  $PM_{10}$  concentrations over the upper Midwest (15  $\mu g/m^3$ ) are comparable to the Southeast and the industrial Midwest, but differ from these regions by the absence of high concentration events or episodes. In fact, the  $PM_{10}$  “episodes” over the upper Midwest are all in 40 to 45  $\mu g/m^3$  concentration range, compared to 50 to 75  $\mu g/m^3$  in the Midwest. The seasonality is barely discernible from the time series confirming that the day to day variation exceeds the seasonal modulation. The urban excess  $PM_{10}$  (AIRS-IMPROVE) for the upper midwest is given in Figure 6-44.

#### 6.4.5 Regional Aerosol Pattern in the Southwest

The Southwest covers the arid states from western Texas to Arizona (Figure 6-45a). The Southwest is characterized by mountainous terrain features between the southern Rockies and the Colorado Plateau. The industrial activity and agriculture is minor compared to other regions. Major population centers are El Paso, Phoenix, and Tucson. The meteorology of the region is characterized by low annual precipitation, except during the summer monsoon, July through September, when moist air penetrates from the Gulf of Mexico toward the western states, bringing moisture and precipitation.

The geographic pattern Figure 6-45a of hours of blowing dust shows that western Texas and southern California deserts are the dustiest regions of the country. A forty-year trend of dust hours shows that the 1950s had several times the dust occurrence of the 1980s (Patterson et al., 1994). It is likely, that during the severe droughts of the 1930s the dust frequency was even higher.

Wind erosion is linked to relative humidity as well as wind speed, the combined changes in both variables can sometimes trigger dust storms. An example is the dust storm in November, 1991 that caused the severe accident on Interstate 5 in California. Seventeen people died in this 164-car accident with low visibility from dust (Gregory et al., 1994).



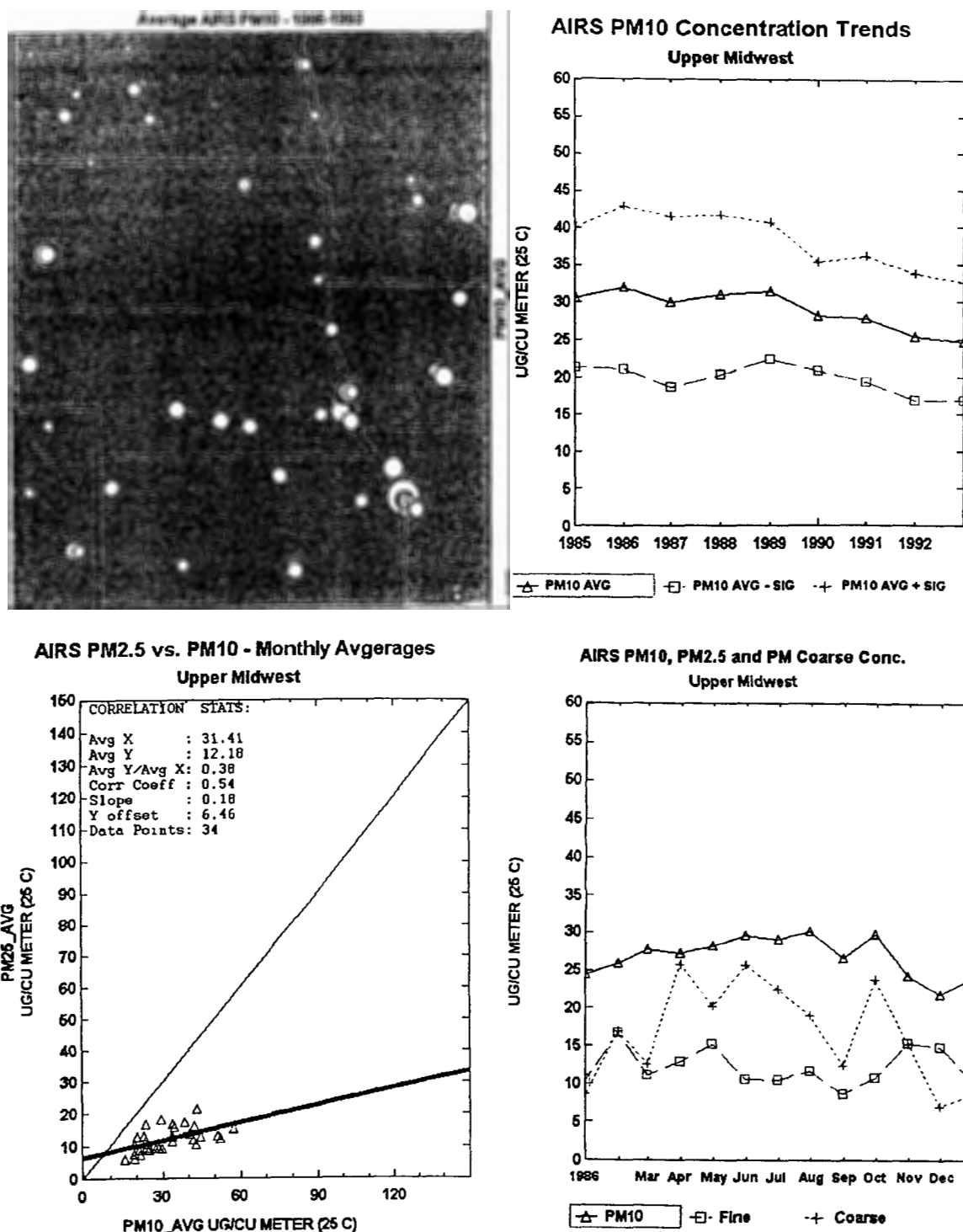


Figure 6-42. AIRS concentration data for the Upper Midwest. (a) Monitoring locations. (b) PM<sub>10</sub>, PM<sub>2.5</sub>, and PM Coarse. (c) Chemical fraction of sulfate, soil, organics, and soot. (d) Tracer concentrations.

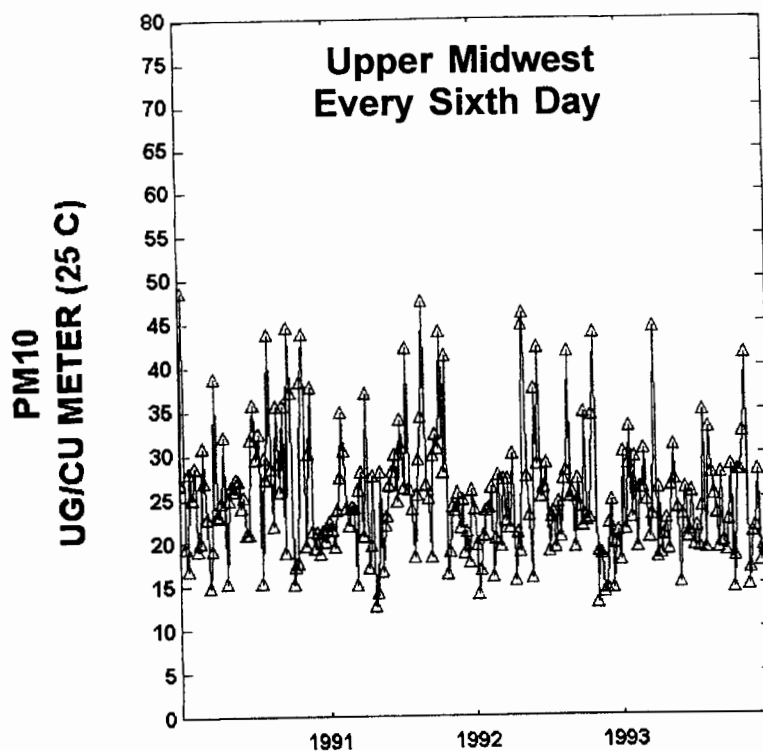


Figure 6-43.

Short term variation of  $PM_{10}$  average for the Upper Midwest. Data are reported every sixth day.

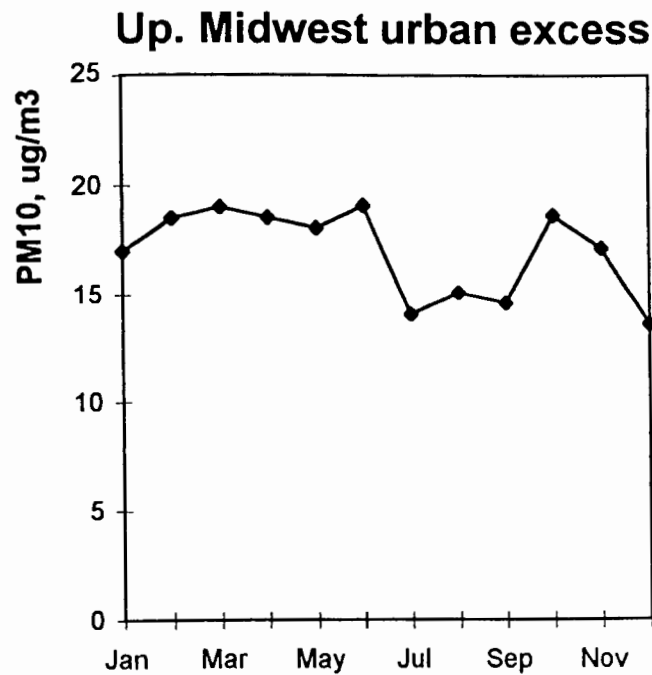


Figure 6-44.

Urban excess concentration (AIRS minus IMPROVE) for the Upper Midwest.

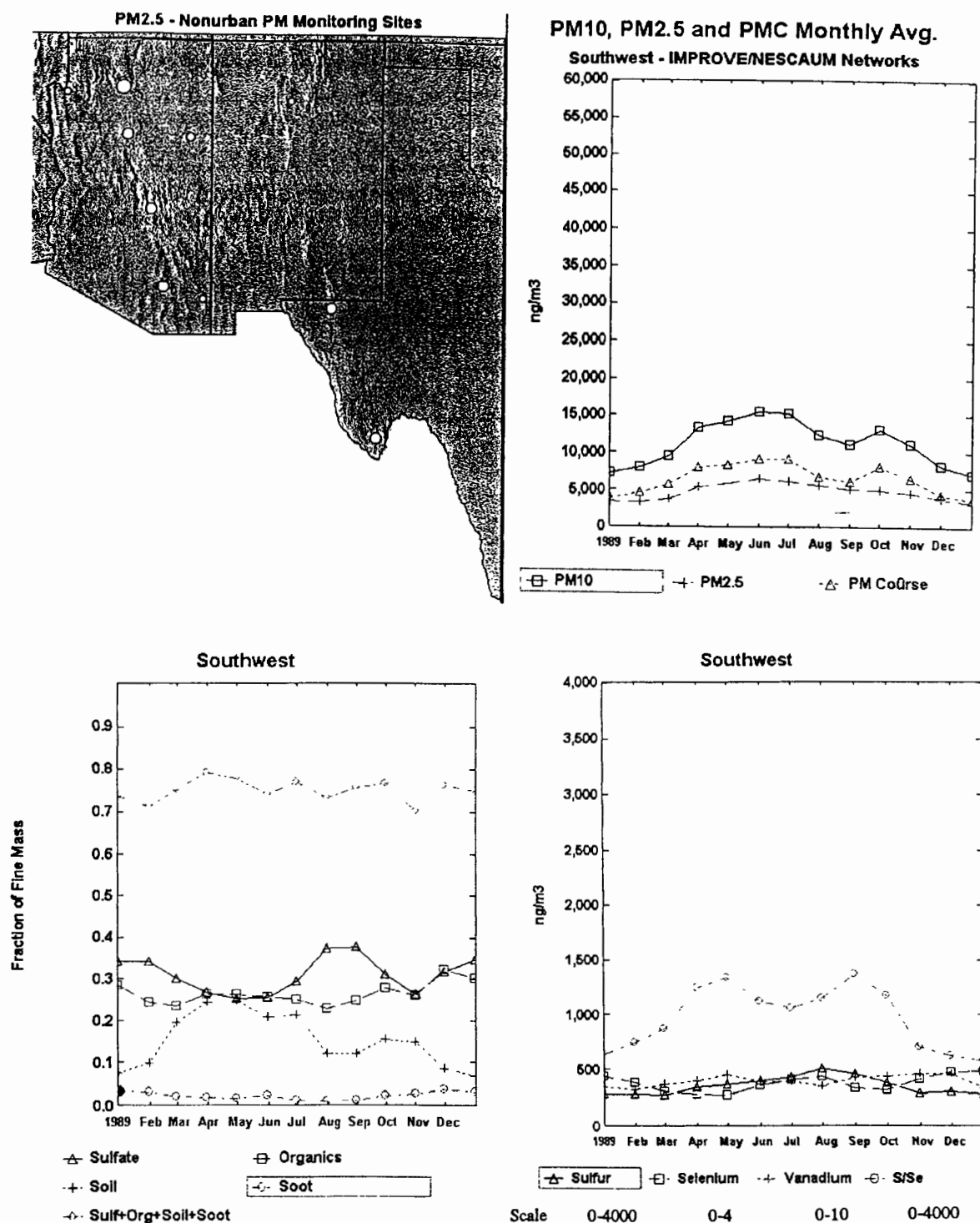


Figure 6-45. IMPROVE/NESCAUM concentration data for the Southwest. (a) Monitoring locations. (b) PM<sub>10</sub>, PM<sub>2.5</sub>, and PMCoarse. (c) Chemical fraction of sulfate, soil, organics, and soot. (d) Tracer concentrations.

1 Gillette and Sinclair, 1990 estimated that dust devils (strongly spiraling updrafts) in  
2 arid regions of southwestern United States have comparable contribution to dust  
3 re-suspension as wind-driven soil erosion.  
4

#### 5 **6.4.5.1 Non-urban Size and Chemical Composition in the Southwest**

6 The PM<sub>10</sub> concentrations at non-urban southwestern sites show a double peak, one  
7 during the late spring (April through July), and another in October. This bimodal seasonality  
8 is imposed by the coarse particle mode. The PM<sub>2.5</sub> mass concentration is unimodal with a  
9 summer peak. Overall, the non-urban PM<sub>10</sub> concentrations are comparatively low (8 to  
10 15 µg/m<sup>3</sup>) and over 60% contributed by coarse particles (Figure 6-45b).

11 The chemical mass balance (Figure 6-45c) shows sulfates to be the main contributors  
12 during the winter (December through March) as well as in late summer (July through  
13 October). However, sulfate and organics contributions are comparable during March through  
14 June as well as during November through December. Fine particle soil plays a prominent  
15 role in the spring fine particle chemical mass balance reaching 25%. However, the role of  
16 fine particle soil dust during December through February dwindles to below 10%.

17 The selenium and vanadium trace elements concentrations (Figure 6-45d) are very low  
18 and rather invariant throughout the year. The fine particle sulfur concentration is low and  
19 exhibits a peak during August, which is the period of the summertime monsoon, when air  
20 masses of Gulf of Mexico penetrate deep into the southwestern US. The S/Se ratio is  
21 comparatively low and bimodal, with peaks in April through May as well as August through  
22 October.  
23

#### 24 **6.4.5.2 Urban Aerosols in the Southwest**

25 The downward PM<sub>10</sub> trend of the Southwest is a remarkable 50% between 1985  
26 (52 µg/m<sup>3</sup>) and 1993 (26 µg/m<sup>3</sup>). The decline was quite steady throughout the period.  
27 Another notable feature of the Southwest is the large concentration spread of 45% among the  
28 monitoring sites (Figure 6-46). Sites with low concentrations (< 20 µg/m<sup>3</sup>) occur adjacent to  
29 high concentration sites (> 50 µg/m<sup>3</sup>).

30 Seasonally, the Southwest PM<sub>10</sub> concentration shows two peaks, one in late spring  
31 April through June, and another during the fall October through November. The

concentration dip in August and September has not been observed for any other region. The late summer concentration drop coincides with the occurrence of the moist monsoonal air flows from the Gulf of Mexico. It is also notable, that the rather high 1993  $\text{PM}_{10}$  concentration of  $26 \mu\text{g}/\text{m}^3$  is only exceeded by the southern California region.

The size segregated aerosol samples from the Southwest clearly show that coarse particles dominate the  $\text{PM}_{10}$  concentration, fine particles contributing only 37%. The scatter chart also reveals that high  $\text{PM}_{10}$  concentration months occur without the presence of fine particles. It is evident, therefore, that in the Southwest natural and man-induced coarse particle dust is the dominant contributor to  $\text{PM}_{10}$  aerosols.

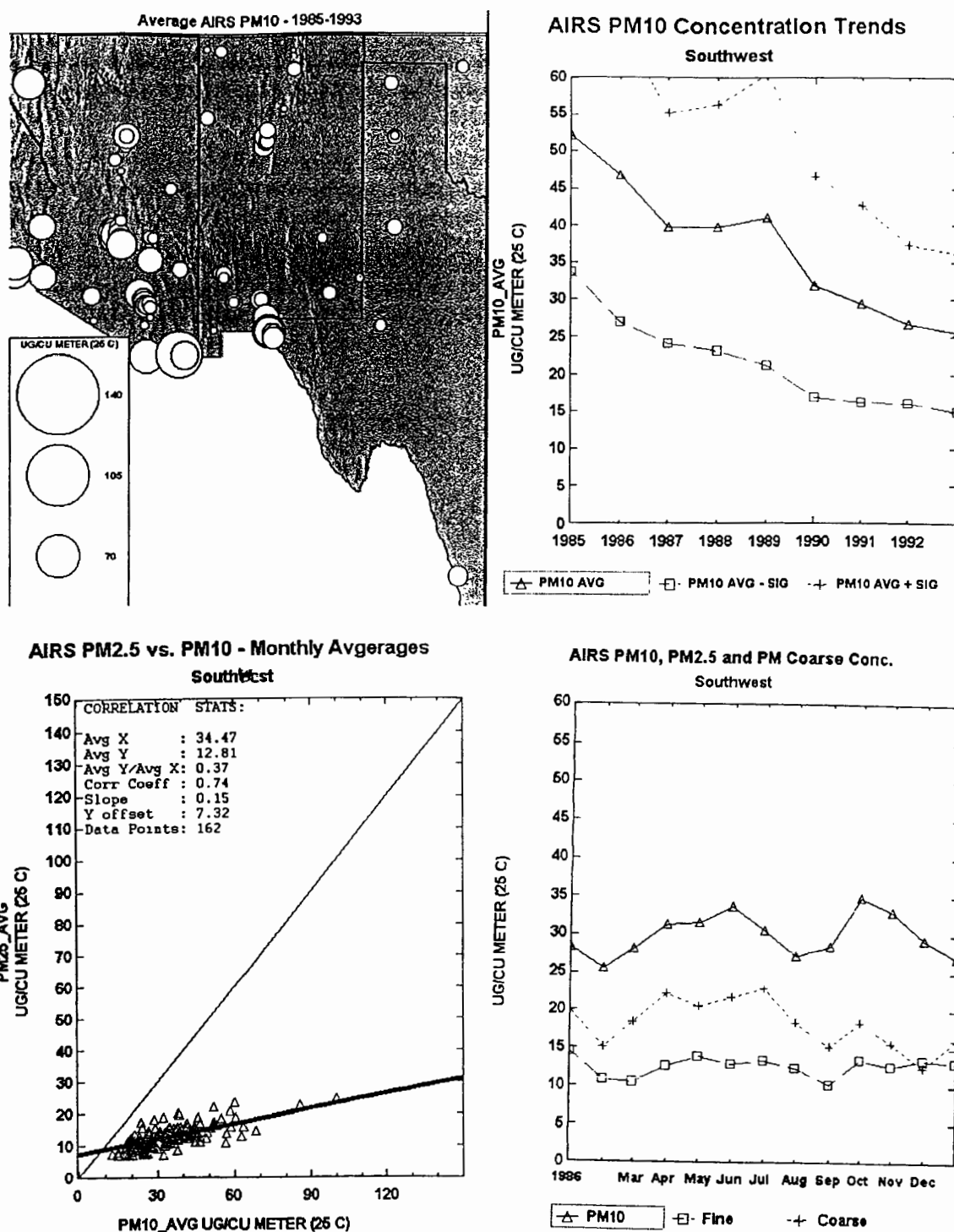
The short term  $\text{PM}_{10}$  concentration over the Southwest (Figure 6-47) exhibits a highly irregular pattern, that ranges between 12 to  $52 \mu\text{g}/\text{m}^3$  regional average for any given day. Both the lowest (10 to  $15 \mu\text{g}/\text{m}^3$ ) as well as the highest values are dispersed throughout the year. The seasonality is virtually indiscernible, being much smaller than the sixth day to sixth day variation. It is worth noting (Figure 6-46b) that the southwestern region has rather low logarithmic standard deviation compared to other regions.

The urban excess  $\text{PM}_{10}$  (AIRS-IMPROVE) for the Southwest is given in Figure 6-48.

#### **6.4.6 Regional Aerosol Pattern in the Northwest**

The Northwest is defined to cover the bulk of the western United States north of the Arizona border (Figure 6-49a). It is covered by mountainous terrain of the Rockies, as well as the Sierra-Cascade mountain ranges. It is clear that the Northwest is actually a collection of many aerosol subregions. The meteorology is highly variable between the Pacific Northwest and the Rocky Mountains with prevailing winds generally from the west. The main feature of the Northwest is pronounced elevation ranges between mountain tops and valleys, and the resulting consequences on emission pattern (confined to the valleys) and limited ventilation. The mountainous Northwest has also industrial population centers, such as Seattle, Portland, Salt Lake City and Denver.

Examining the carbonaceous particles and regional haze in the western and northwestern US, White and Macias, 1989 concluded that in the rural areas the concentrations of particulate carbon are comparable to those of sulfate. Examining particulate nitrate (White and Macias, 1987) showed that the particulate nitrate concentration



**Figure 6-46.** AIRS concentration data for the Southwest. (a) Monitoring locations. (b) PM<sub>10</sub>, PM<sub>2.5</sub>, and PMCoarse. (c) Chemical fraction of sulfate, soil, organics, and soot. (d) Tracer concentrations.

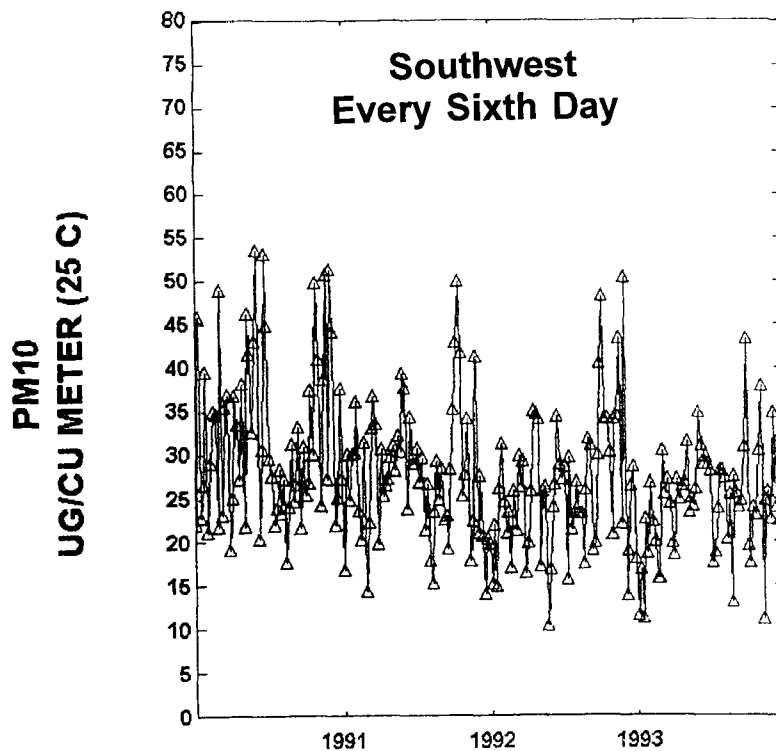


Figure 6-47. Short term variation of  $PM_{10}$  average for the Southwest. Data are reported every sixth day.

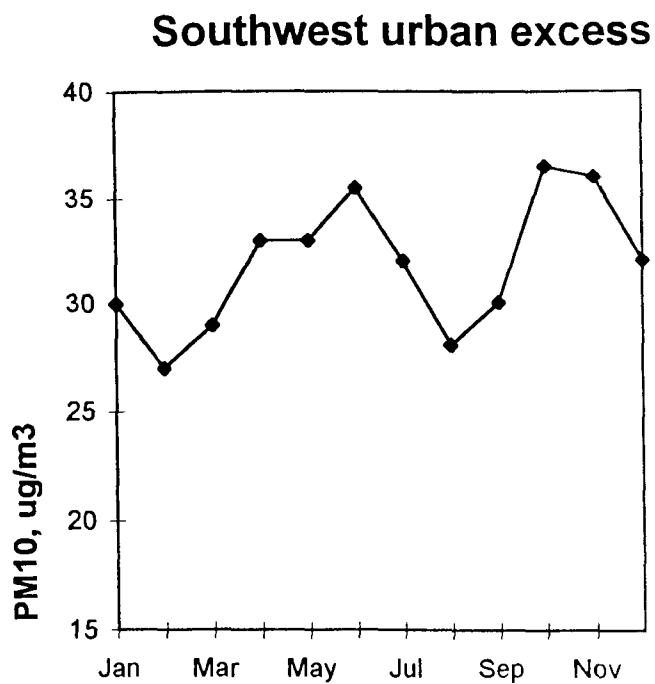
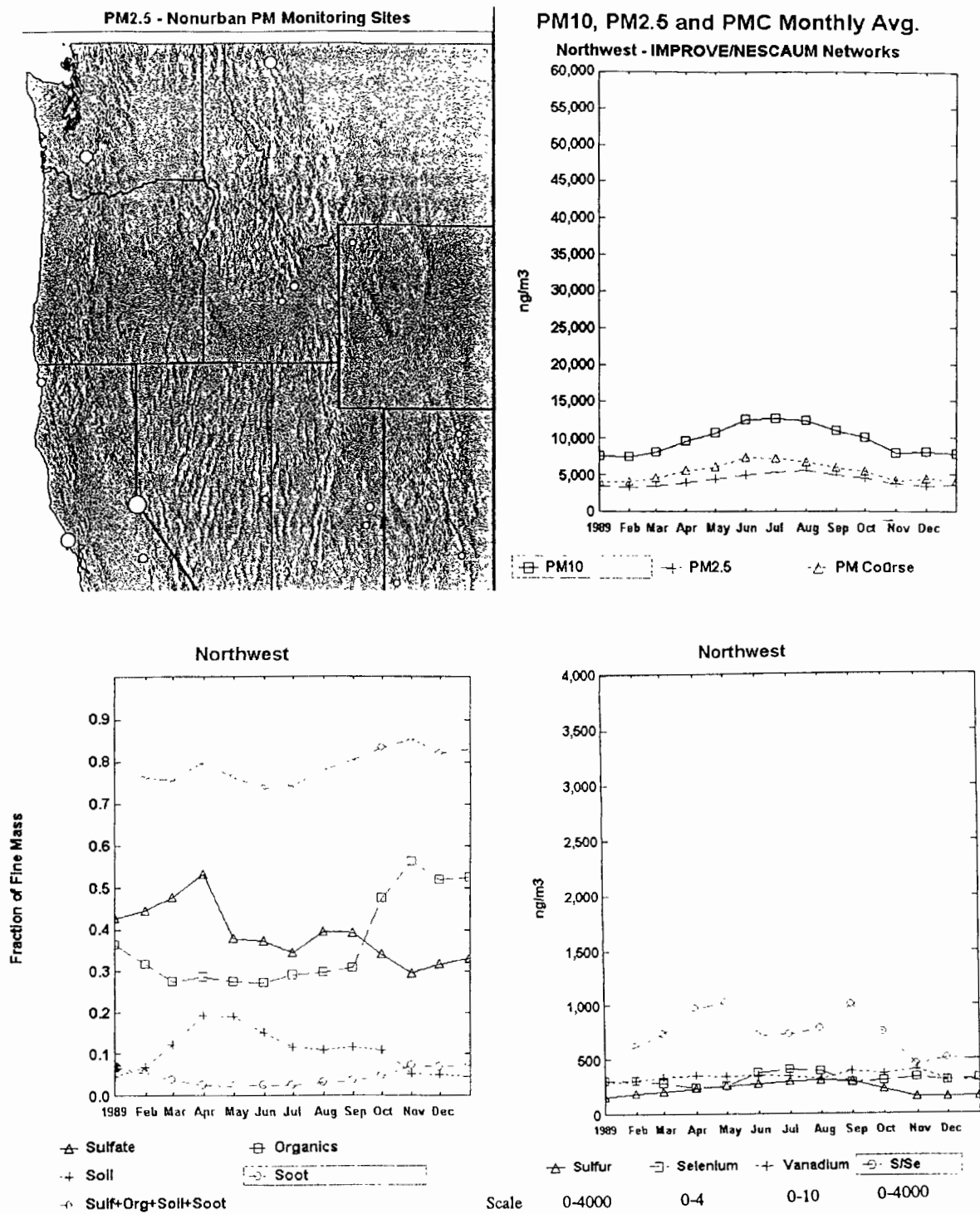


Figure 6-48. Urban excess concentration (AIRS minus IMPROVE) for the Southwest.



**Figure 6-49.** IMPROVE/NESCAUM concentration data for the Northwest.  
 (a) Monitoring locations. (b) PM<sub>10</sub>, PM<sub>2.5</sub>, and PMCoarse.  
 (c) Chemical fraction of sulfate, soil, organics, and soot. (d) Tracer concentrations.



in the northern states, (MT, ID, WY) were substantially higher, both in absolute terms and relative to sulfate concentrations. Aerosol particulate nitrates over rural mountainous West were also episodic, i.e. few samples contributed a large fraction of the fine particle integrated dosage.

#### **6.4.6.1 Non-urban Size and Chemical Composition in the Northwest**

The non-urban PM<sub>10</sub> concentrations show low values ranging between 7 to 14  $\mu\text{g}/\text{m}^3$  in the northwestern US. The seasonality shows a peak in the summer which is contributed by both fine and coarse particles. Coarse particles account for more than half fine mass, particularly during March through June spring season (Figure 6-49b).

The chemical mass balance (Figure 6-49c) shows roughly comparable contributions from sulfates and organics, but their seasonality is phase shifted. Sulfates prevail during the spring season while organics dominate during late fall (October through January). Fine particle soil dust contributes 20% during April and May, but decline well below 10% during the winter months (November through February). Overall, about 80% of the fine mass is accounted for by the sulfates organics, soil and soot.

Both selenium and vanadium concentrations (Figure 6-49d) are low in the Northwest, but there is an indication of a summer peak of Se. The S/Se ratio is between 500 to 1,000, which is the lowest among the regions. It is interesting that this ratio has both spring peak as well as fall peak, similar to the pattern observed for the southwestern United States.

#### **6.4.6.2 Urban Aerosols in the Northwest**

The time trend of aggregated PM<sub>10</sub> concentrations conveys a significant decline of 50% from 1985 to 1993 (from 50 to 25  $\mu\text{g}/\text{m}^3$ ). However, from 1986 to 1993 the decline was only 37%, which is believed to be more representative for the region because of the low station density in the early years. Once again, the average 1993 concentration is 25  $\mu\text{g}/\text{m}^3$  which is comparable to the 1993 concentrations of the eastern U.S. regions. The spread of concentration among the Northwest stations is large, with standard deviation of 45% (Figure 6-50b). This spread in the concentration values is also evident from the various circle sizes of the Northwest map. It is believed but not formally confirmed that low concentrations occur primarily at high elevation sites that are above the daily reach of surface

1 based haze and smoke layers. Inspection of the circles in the northwestern map also reveals  
2 that the highest  $PM_{10}$  concentrations in the Northwest occur at more remote mountainous  
3 valleys, rather than in the center of urban-industrial areas.

4 The seasonality of the northwestern United States has an amplitude of 36% which is  
5 comparable to the strong seasonality of the eastern US. However, the shape of the seasonal  
6 signal is phase shifted to a winter peak. The lowest concentration occurs during March  
7 through May and gradually increases to a peak in December through January, falling sharply  
8 between January and March.

9 The limited  $PM_{2.5}$ - $PM_{10}$  data for the Northwest indicate that on the average 59% of  
10  $PM_{10}$  particles are  $PM_{2.5}$ . The scatter chart also indicates that the extreme  $PM_{10}$   
11 concentrations are contributed mainly by fine particles. Furthermore, the extreme  $PM_{10}$   
12 concentration also occur in the winter season.

13 The daily concentration when averaged over the large and heterogeneous northwestern  
14 region exhibits a remarkably small sixth day to sixth day variation (Figure 6-51).  
15 Furthermore, there is clear seasonality with a strong winter peak. Within a given season, the  
16 regionally averaged concentrations only vary by 20 to 40% from one sixth day to another.  
17 This low temporal variance would indicate homogeneity of aerosol over the region.  
18 However, examination of the logarithmic standard deviation (Figure 6.3.12) shows that the  
19 Northwest is spatially more heterogeneous and has the highest logarithmic standard deviation  
20 among all regions. This apparent discrepancy shows the advantages of aggregations  
21 performed on multiple spatial and temporal scales. Evidently, in the Northwest high  
22 concentration  $PM_{10}$  pockets, in topographically confined airsheds result in strong spatial and  
23 temporal variations. However, the sensory evidence suggests that large scale elevated  $PM_{10}$   
24 concentrations that cover the entire Northwestern region do not exist because high  
25 concentrations are not “synchronized” between the different airsheds. In this sense, the  
26 Northwest differs markedly from the eastern US, where large regional scale airmasses with  
27 elevated  $PM_{10}$  determine the regionally averaged values. The urban excess  $PM_{10}$  (AIRS-  
28 IMPROVE) for the Northwest is given in Figure 6-52.

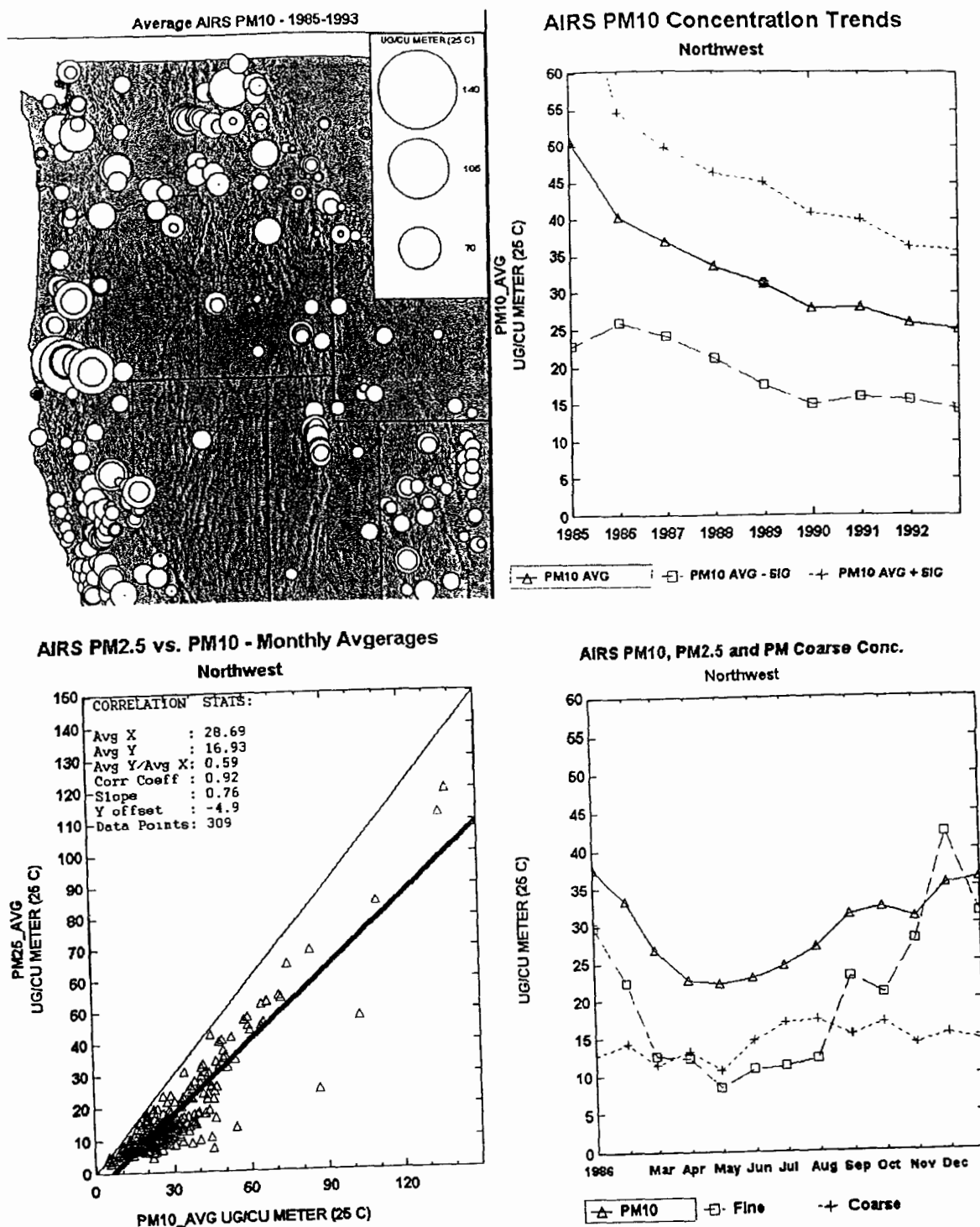


Figure 6-50. AIRS concentration data for the Northwest. (a) Monitoring locations. (b)  $PM_{10}$ ,  $PM_{2.5}$ , and  $PM_{Coarse}$ . (c) Chemical fraction of sulfate, soil, organics, and soot. (d) Tracer concentrations.

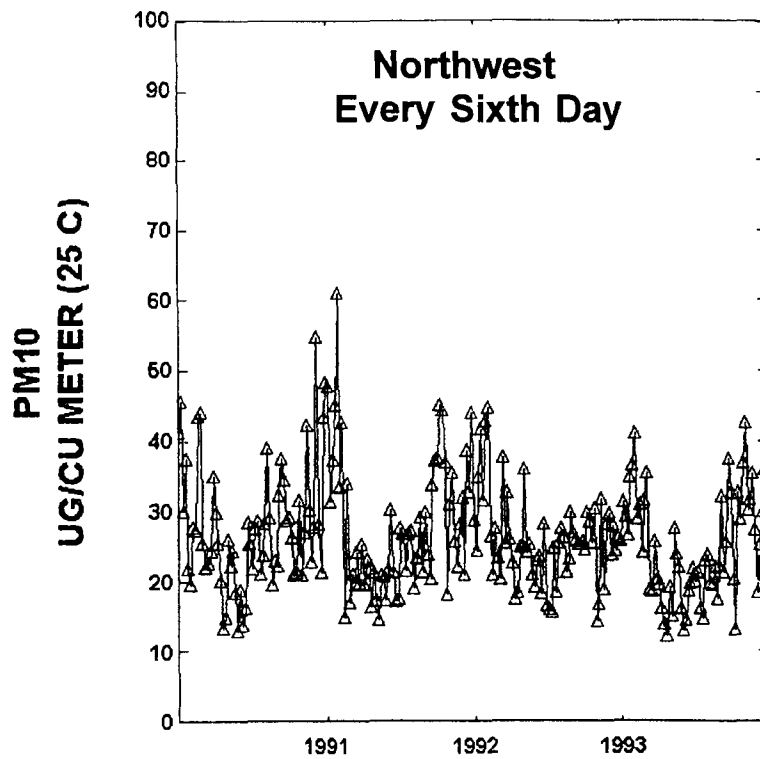


Figure 6-51. Short term variation of  $PM_{10}$  average for the Northwest. Data are reported every sixth day.

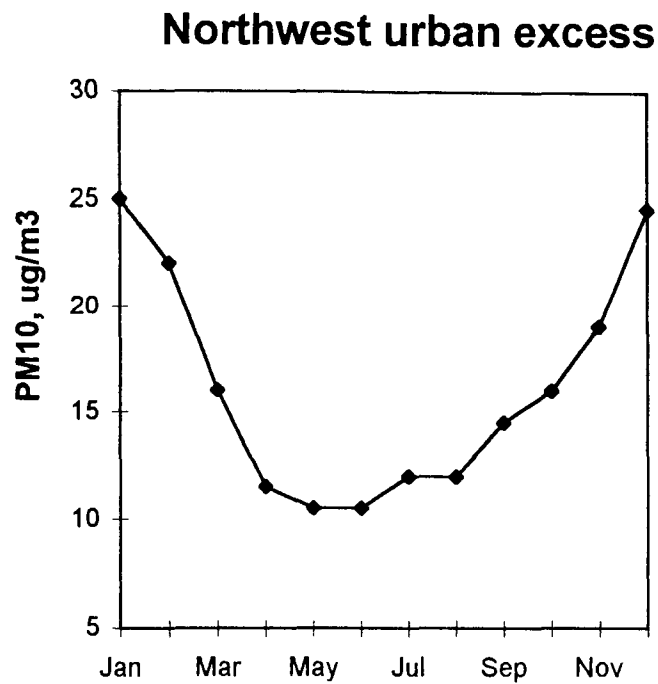


Figure 6-52. Urban excess concentration (AIRS minus IMPROVE) for the Northwest.

## **6.4.7 Regional Aerosol Pattern in the Southern California**

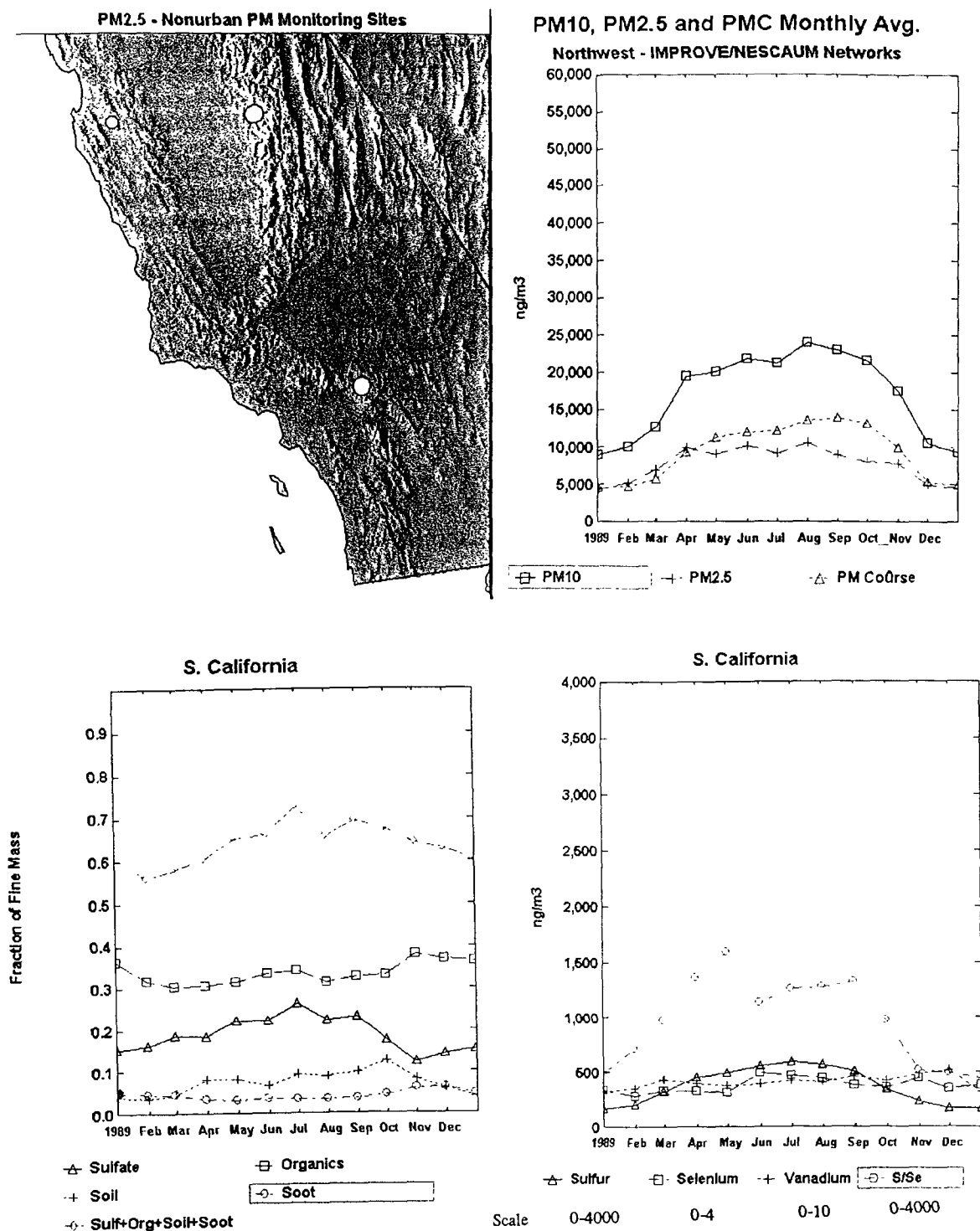
The region covers California, south of San Francisco Bay (Figure 6-53a). It was declared as a separate region primarily because of the known high aerosol concentrations in the Los Angeles and San Joaquin basins. Meteorologically the region is exposed to the air flows from the Pacific that provide the main regional ventilation toward the south and southeast. The precipitation in the region occurs in the winter season, with the summer being hot and dry. The regional ventilation of the San Joaquin Valley is severely restricted by Sierra Mountain ranges. Also, the San Gabriel Mountains constitute an air flow barrier east of the Los Angeles basin. Both basins have high population, as well as industrial and agricultural activities. Hence, human activities are believed to be the main aerosol sources of the region.

### **6.4.7.1 Non-urban Size and Chemical Composition in the Southern California**

The  $PM_{10}$  concentration at the non-urban sites over southern California ranges between  $10 \mu g/m^3$  during December through February, and 20 to  $25 \mu g/m^3$  in April through October. Coarse particles contribute more than 50% of  $PM_{10}$  during the warm season May through October. Both the fine and coarse aerosol fractions are lowest during the winter months (December through March). The summer peak fine particle seasonality at non-urban southern California sites is in marked contrast to the strongly winter peaked urban fine particle concentrations (Figure 6-53b).

The chemical mass balance (Figure 6-53c) of non-urban southern California aerosol is clearly dominated by organics, which contribute 30 to 40% throughout the year. Sulfates account for only 10 to 15% of the fine mass in the winter, and about 20% in the summer months. The sulfate fraction of the non-urban southern California fine mass is the lowest among the regions. Fine particle soil dust is about 10% between April through November and drops to 5% during the winter months. A notable feature of the southern California chemical mass balance is that 45% of the winter, and 35% of the summer fine mass concentration is not accounted by sulfates, organics, soils, and soot. Undoubtedly nitrates are the major contributors to the southern California aerosols.

Both selenium and vanadium (Figure 6-53d) show low values throughout the year without significant seasonality. On the other hand the fine particle sulfur concentration



**Figure 6-53.** IMPROVE/NESCAUM concentration for the Southern California. (a) Monitoring locations. (b) PM<sub>10</sub>, PM<sub>2.5</sub>, and PMCoarse. (c) Chemical fraction of sulfate, soil, organics, and soot. (d) Tracer concentrations.

shows a definite summer peak at 500 ng/m<sup>3</sup>, compared to 200 ng/m<sup>3</sup> during the winter. Consequently, the S/Se ratio increase from 500 in the winter 1,000 to 1,500 in the summer.

#### **6.4.7.2 Urban Aerosols in the Southern California**

The downward concentration trend of southern California between 1985 and 1993 was 41%. However, between 1986 and 1993 the reduction was 27%. By 1993, the southern California annual average PM<sub>10</sub> concentration was reduced to 32 µg/m<sup>3</sup>. However, there is a sizable concentration spread among the stations (40% standard deviation). Inspection of the circle sizes in the map points to uniformly high concentrations in the San Joaquin Valley as well as in the Los Angeles basin. The low concentration sites are located either on the Pacific coast or in the Sierra Mountains. Thus there are clear patterns of basin-wide elevated PM<sub>10</sub> concentrations and lower values in more remote areas (Figure 6-54b).

The seasonality of the PM<sub>10</sub> pattern in southern California is significant at 27%. Furthermore the seasonal pattern is unique that the highest concentrations occur in November, while the lowest in March. However, it is a see saw rather than a sinusoidal pattern.

On the average, about half of southern California PM<sub>10</sub> is contributed by fine particles as shown in PM<sub>2.5</sub>-PM<sub>10</sub> scattergram. Most of the high PM<sub>10</sub> concentration months are dominated by fine particles and tend to occur in the fall. season.

The sixth day average time series for the southern California region (Figure 6-55) shows remarkably high sixth daily variance, between 12 and 75 µg/m<sup>3</sup>. The lowest values tend to occur between January and April, while the highest concentrations (> 50 µg/m<sup>3</sup>) tend to occur during October through December. Concentration excursions factor of two are common between two consecutive six day time periods. However, visual inspection of the sixth daily signal also reveals a substantial seasonality that peaks in the fall September through December and lowest in the spring.

The urban excess PM<sub>10</sub> (AIRS-IMPROVE) for Southern California is given in Figure 6-56.

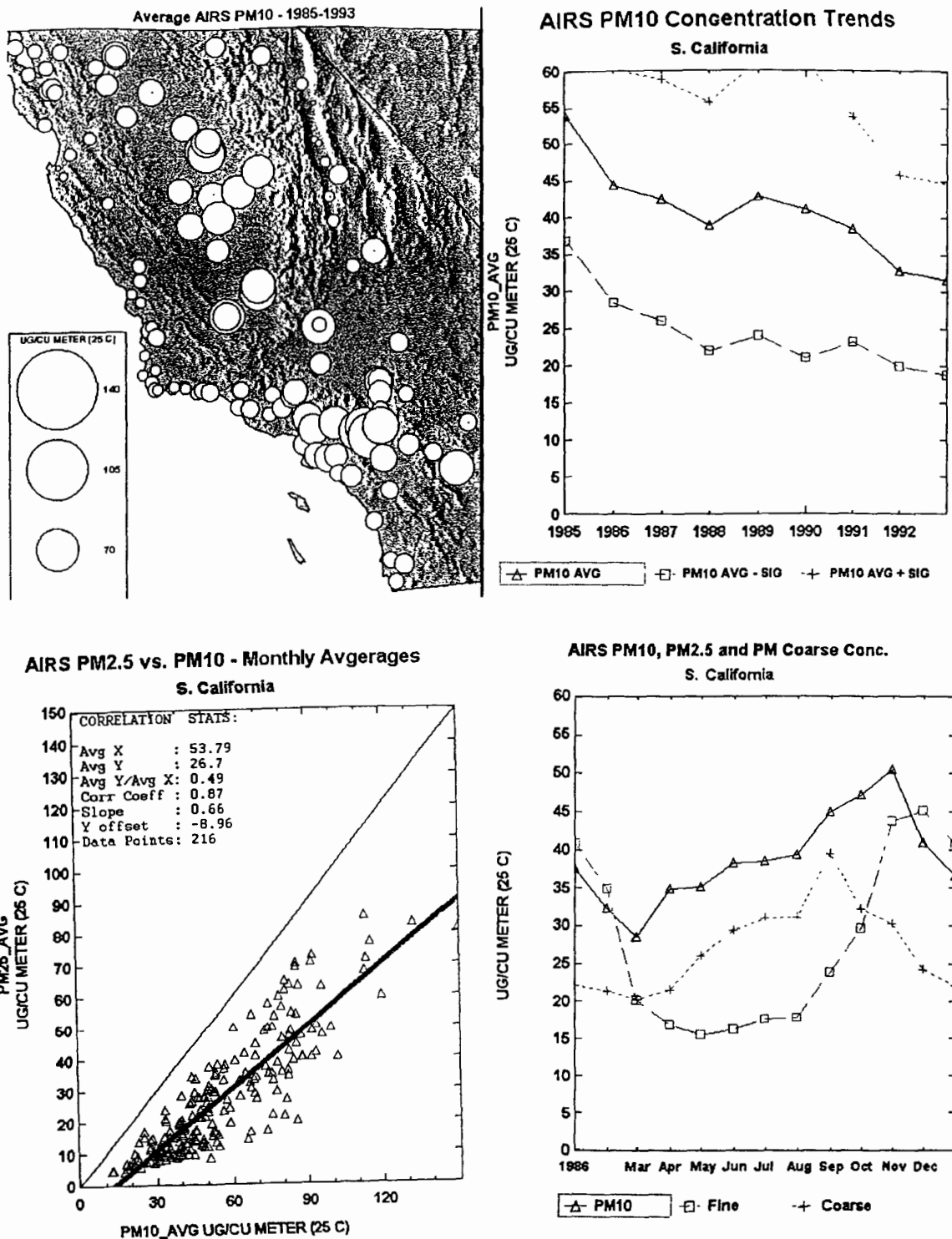
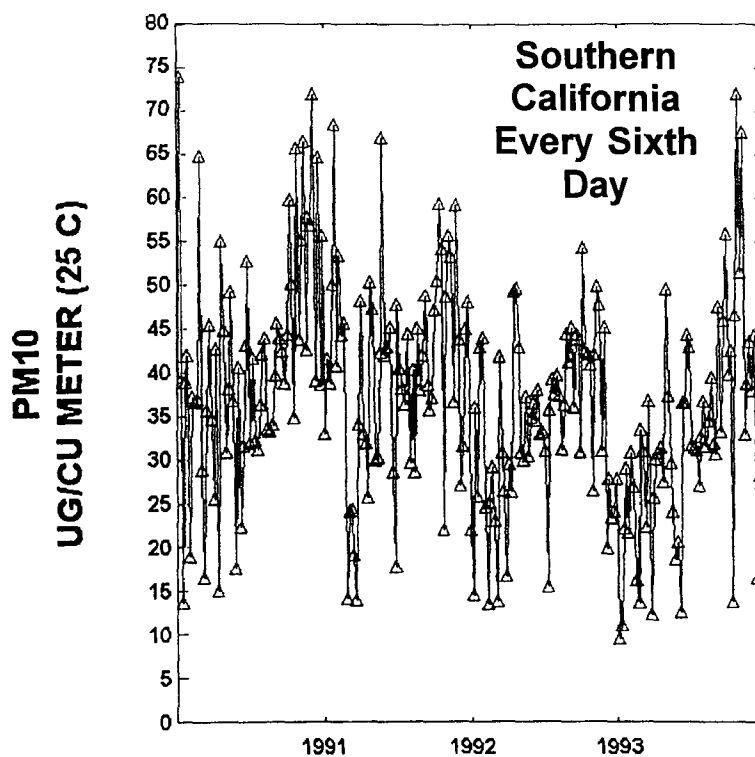
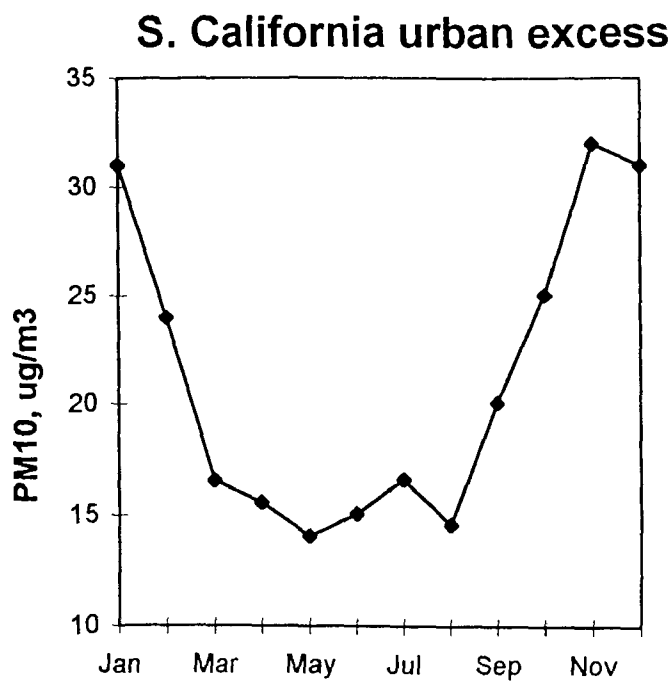


Figure 6-54. AIRS concentration for the Southern California. (a) Monitoring locations. (b) PM<sub>10</sub>, PM<sub>2.5</sub>, and PMCoarse. (c) Chemical fraction of sulfate, soil, organics, and soot. (d) Tracer concentrations.





**Figure 6-55.** Short term variation of  $PM_{10}$  average for the Southern California. Data are reported every sixth day.



**Figure 6-56.** Urban excess concentration (AIRS minus IMPROVE) for the Southern California.

## 6.5 SUB-REGIONAL AEROSOL PATTERNS AND TRENDS

The health and other effects of aerosols are imposed on individuals, and the density of population varies greatly in space. Consequently, the evaluation of effects requires the knowledge of aerosol concentrations over specific locations where sensitive receptors reside. The purpose of this section is to characterize the aerosol pattern at specific sites, small airsheds or sub-regions. The discussions is organized by region and then by monitoring site within a region. Most urban aerosol sampling is confined to  $PM_{10}$  or in some instances to  $PM_{2.5}$  and  $PM_{Coarse}$ . However, detailed chemical composition data are reviewed for several urban areas.

### 6.5.1 Sub-regional Aerosol Pattern in the Northeast

In the northeastern region, the Shenandoah National Park and Washington, DC constitute a natural urban-non-urban pair of size and chemically resolved aerosol data. New York City and Philadelphia are also major metropolitan areas with substantial aerosol data. Whiteface Mountain site distinguishes itself from its background by high elevation.

#### 6.5.1.1 Shenandoah National Park

The  $PM_{10}$  concentration at the Shenandoah National Park IMPROVE site (Figure 6-57a) exhibits a pronounced summer peak ( $27 \mu g/m^3$ ), which is factor of three higher than the low winter value of  $9 \mu g/m^3$ . The strong seasonality is driven by the seasonal modulation of the fine mass which accounts for 70 to 80% of  $PM_{10}$  mass (Figure 6-57a). The coarse particle concentration ranges between 3 to  $6 \mu g/m^3$ , which is small compared to the fine particle mass, particularly in the summer season, when it accounts to < 25% of the  $PM_{10}$ . It is clear that at this remote site, in the vicinity of industrial source regions, fine particles determine the magnitude of  $PM_{10}$ .

The chemical mass balance for the Shenandoah IMPROVE monitoring site (Figure 6-57b) clearly documents the dominance of sulfate aerosols which contributes about 60% of the fine mass during April through September, and about 50% during the winter months. Organics, on the other hand, range from 20% in summer to 30% in the winter months. The contribution of fine particle soil and soot is well below 5%. Throughout the year about 90% of the fine mass is accounted for by these measured substances.

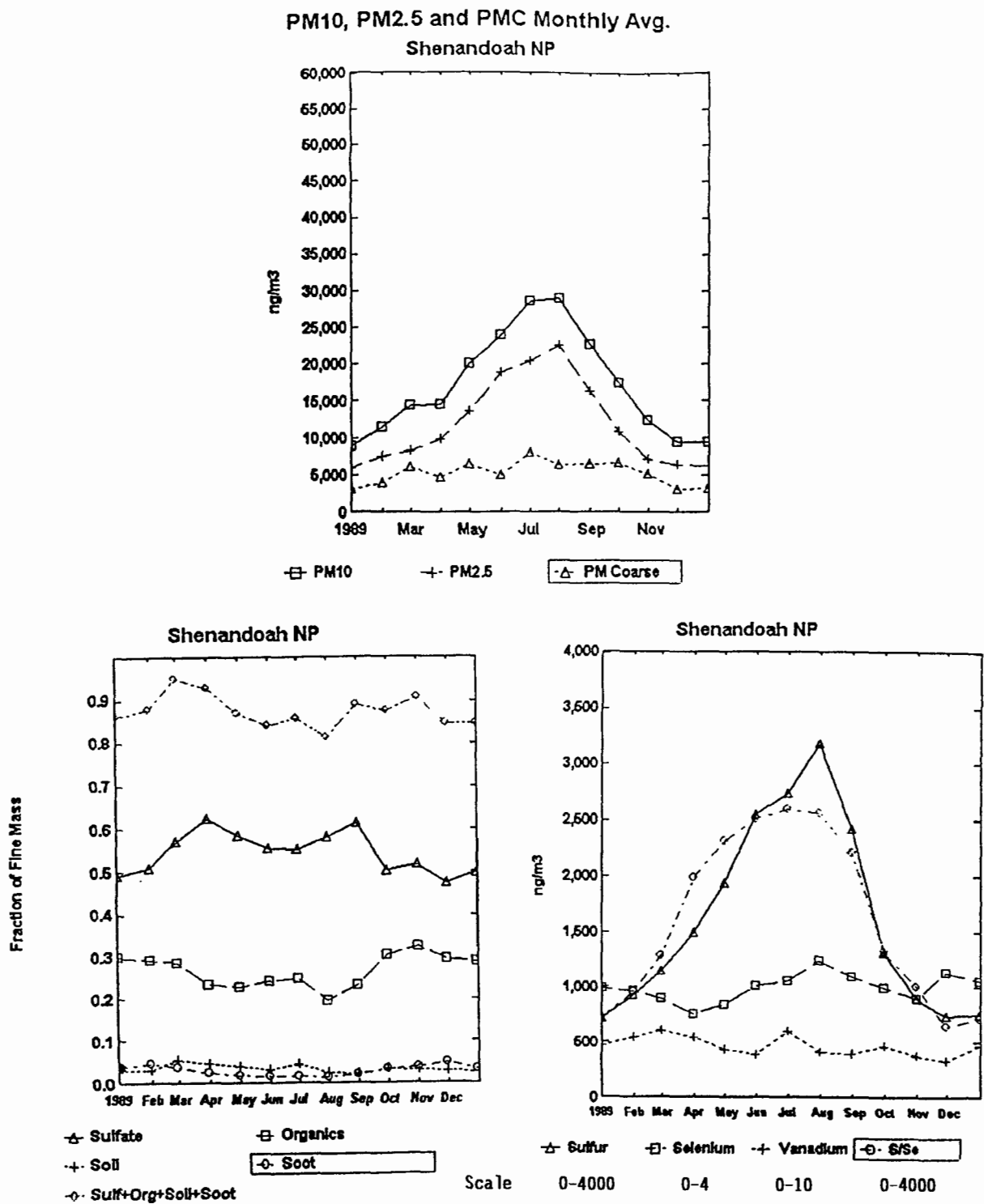


Figure 6-57.

IMPROVE/NESCAUM concentration for Shenandoah National Park. (a) Monitoring locations. (b) PM<sub>10</sub>, PM<sub>2.5</sub>, and PM<sub>C</sub>. (c) Chemical fraction of sulfate, soil, organics, and soot. (d) Tracer concentrations.

Chemical Tracer data is shown in Figure 6-57c. The concentration of coal-tracer selenium shows a mild double peaks, one during December through March, and another in June through September. Vanadium is relatively constant throughout the year. The fine particle sulfur concentration is almost factor of five higher in August (3,300 ng/m<sup>3</sup>) than the December values(700 ng/m<sup>3</sup>). This extreme sulfur seasonality is unique to the Shenandoah site. The S/Se ratio has a remarkably smooth but highly seasonal variation that varies by about factor of four between the winter (700) and summer (2,600) values. If Se-bearing coal combustion was the exclusive source of sulfur at the Shenandoah National Park , then the sulfate yield per emission would be 3 to 4 higher in the summer than in the winter.

An examination of the nature and sources of haze in the Shenandoah Valley/Blue Ridge Mountains area (Ferman et al., 1981) showed that sulfate aerosols were the most important visibility reducing species. Averaging 55% of the fine particle mass, sulfates (and associated water) accounted for 78% of the total light extinction. The second most abundant fine particles, accounting for 29% of the fine mass, was organic carbon. The remaining particle mass and extinction were due to crustal materials.

Using an in-situ rapid response measurement of H<sub>2</sub>SO<sub>4</sub>/(NH<sub>4</sub>)SO<sub>4</sub> aerosol in Shenandoah NP, VA, Weiss et al, 1982, found that the summer sulfate and ammonium ions average 58% of particle mass smaller than 1 mm. The particle composition in terms of NH<sub>4</sub><sup>+</sup>/SO<sub>4</sub><sup>2-</sup> molar ratio ranged from 0.5 to 2.0 with strong diurnal variation. The particles were most acidic at 1500 EDT and least acidic in the period 0600 to 0900 EDT. The water contained in ambient aerosol particles was more strongly associated with sulfate and ammonium ions than with the remainder of fine particle mass.

#### **6.5.1.2 Washington, DC**

The PM<sub>10</sub> concentration at Washington DC (at the top of the National Park Service Headquarters building) is virtually constant over the seasons at 25 to 30 µg/m<sup>3</sup>. Fine particles contribute over 70% of PM<sub>10</sub> throughout the year (Figure 6-58a). The lack of seasonality in the fine particle mass is in sharp contrast to the factor of three seasonal fine mass modulation at the Shenandoah National Park. The coarse particle concentration in Washington, DC is 8 to 10 µg/m<sup>3</sup> throughout the year, exhibiting virtually no seasonality. In

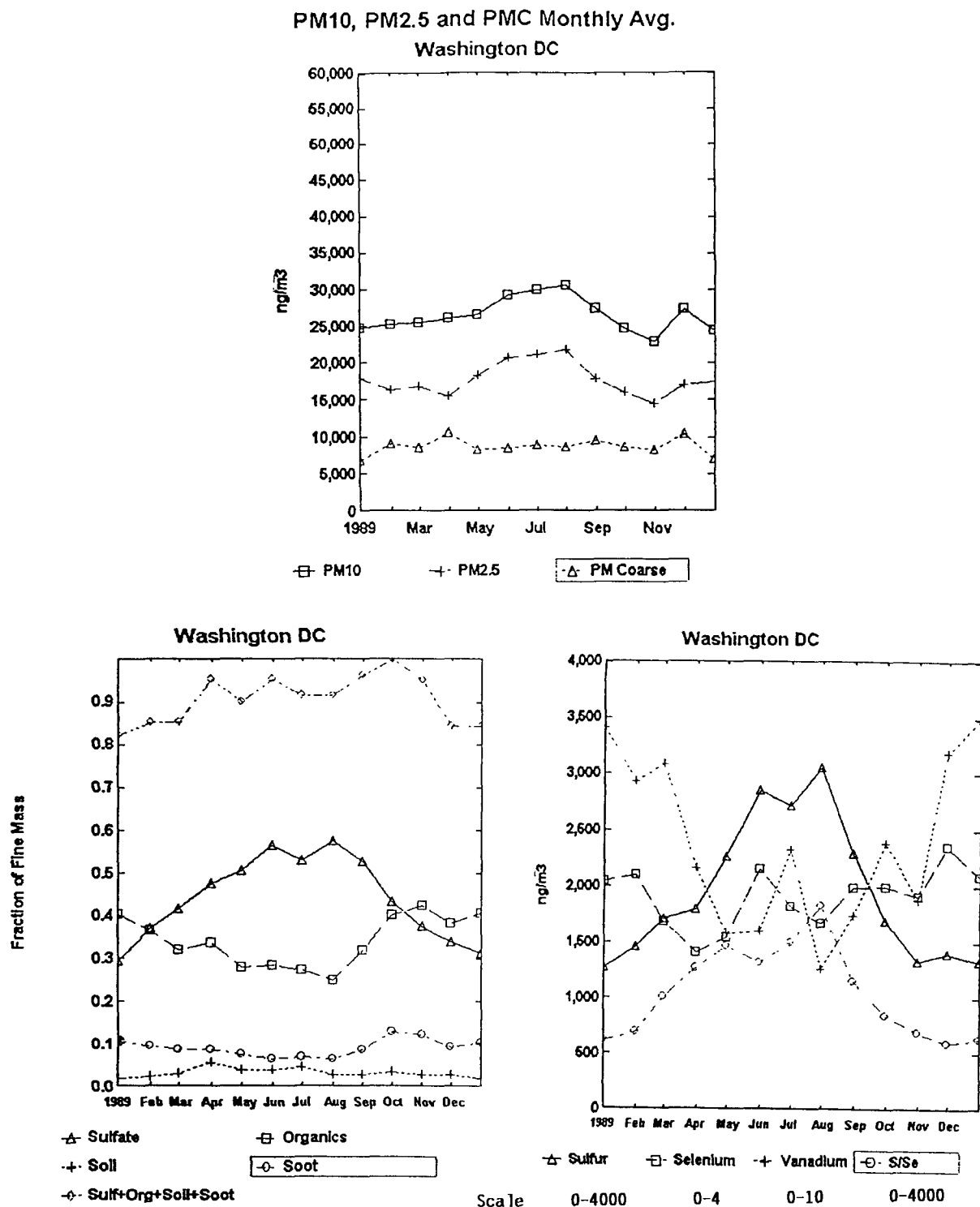
fact, compared to Shenandoah National Park, the excess coarse particle concentration in urban Washington, DC is only  $5 \mu\text{g}/\text{m}^3$  throughout the year.

The chemical mass balance at the urban Washington, DC site (figure 6-58b) is dominated by sulfates during the summer months (50% of fine mass), which declines to 30% in January. Organics, on the other hand, are more important during October through January (40%) but only 30% during May through August. Thus, the relative roles of organics and sulfates at the Washington, DC urban site is fully phase shifted by half a year. Soot is a substantial (9 to 12%) contributor to the fine particle mass, particularly during October through December. Fine particle soil contributes a remarkably low 2 to 5% of the fine particle mass at this urban site. Hence, neither coarse particle, nor fine particle dust is an important factor in Washington, DC.

The chemical tracer species are shown in Figure 6-58c. The coal tracer, selenium concentration ranges between  $1.5$  to  $2.0 \text{ ng}/\text{m}^3$  without appreciable seasonality. The urban Se is also higher than the Se at any of the non-urban site, including the industrialized Midwest. Vanadium, the tracer for fuel oil, varies by factor of two between the high winter values ( $> 8 \text{ ng}/\text{m}^3$ ) and low summer values ( $3 \text{ ng}/\text{m}^3$ ). The pronounced V concentration seasonality is a clear indication of that the emissions from fuel oil and other vanadium sources are seasonal. The fine particle sulfur concentration varies by about factor of two between  $1,400 \text{ ng}/\text{m}^3$  winter concentration, and about  $3,000 \text{ ng}/\text{m}^3$  summer peak. The seasonal modulation of sulfur in Washington, DC is only factor of two compared to the factor of four fine sulfur modulation at Shenandoah National Park. The difference is primarily due to the elevated winter sulfur in Washington, DC. The S/Se ratio is about 0.6 in the winter and about 1.5 in the summer. It differs from Shenandoah by the lower summer S/Se ratios.

#### **6.5.1.3 Comparison of Non-urban (Shenandoah) to Urban (Washington, DC) Aerosols**

The Washington, DC urban site and the companion non-urban Shenandoah monitoring site constitute a rare data pair that allows the quantification of urban-rural differences in fine and coarse particle concentration, and chemical composition. Within Washington, DC, industrial emissions are moderate compared to the industrial midwestern cities. However, both automobile emission density and emissions from winter time heating are expected to be



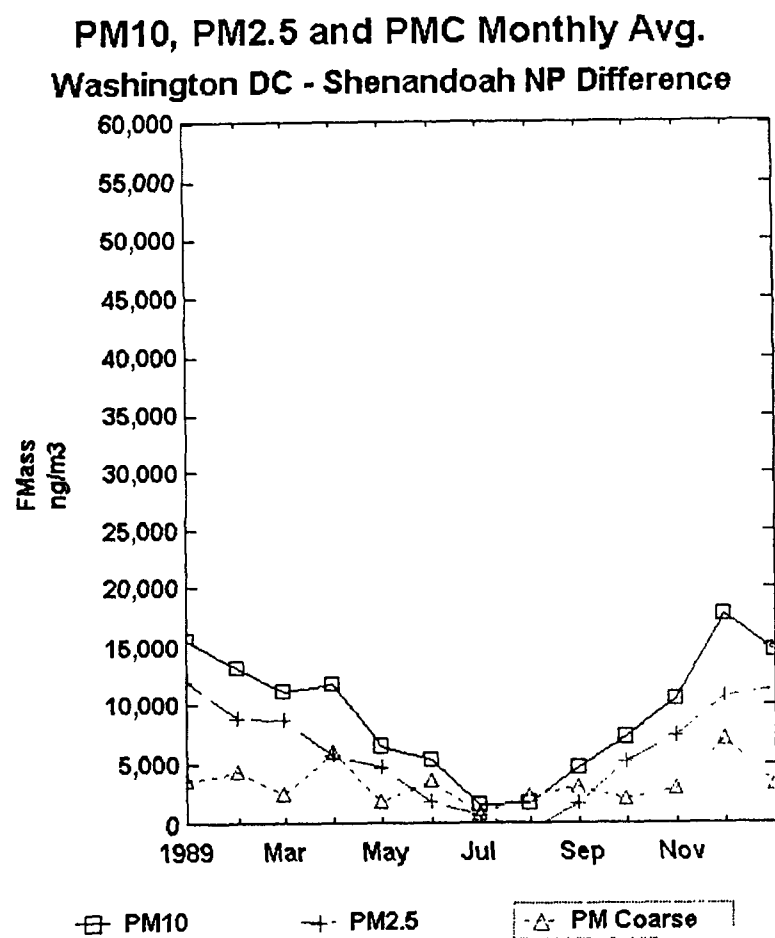
**Figure 6-58.** IMPROVE/NESCAUM concentration for Washington, D.C. (a) Monitoring locations. (b) PM<sub>10</sub>, PM<sub>2.5</sub>, and PM<sub>Coarse</sub>. (c) Chemical fraction of sulfate, soil, organics, and soot. (d) Tracer concentrations.

high. In this section the excess aerosol concentrations in Washington, DC over the Shenandoah site are examined to elucidate the urban influence.

The Washington, DC excess  $\text{PM}_{10}$  concentration (Figure 6-59a) ranges between 15-20  $\mu\text{g}/\text{m}^3$  in the winter, and  $<3 \mu\text{g}/\text{m}^3$  in the summer. Hence, there is almost an order of magnitude higher urban excess during the winter, compared to the summer. The seasonality of the excess  $\text{PM}_{10}$  is driven by the winter peak excess fine particle concentration of 10-12  $\mu\text{g}/\text{m}^3$ . The excess coarse particles hover in the 3 to 6  $\mu\text{g}/\text{m}^3$  range throughout the year. Thus, the urban Washington, DC concentration exceeds its non-urban regional aerosol values during the winter season, and the excess winter time urban aerosol is largely contributed by fine particle mass. This is remarkable, and indicates the diminishing role of coarse particle fly ash, road dust resuspended by automobile or construction, road salt and all other sources of urban coarse particles.

The chemical composition of the excess fine particle concentration over the Shenandoah non-urban background is also shown in Figure 6-59b. Fine particle organics dominate the urban excess chemical mass balance, ranging between 1  $\mu\text{g}/\text{m}^3$  during the summer, and 5.5  $\mu\text{g}/\text{m}^3$  during the winter. The seasonality of excess organics also drives the seasonality of excess fine mass. There is an excess sulfate concentration of 1 to 2  $\mu\text{g}/\text{m}^3$  in Washington, DC, except during July, August, and September. In fact, in August in Washington, DC sulfate concentration is about 0.3  $\mu\text{g}/\text{m}^3$  below the Shenandoah values. The urban excess soot concentration is 1 to 2  $\mu\text{g}/\text{m}^3$  throughout the year. The soil contribution to the fine particle mass is identical to the values of the Shenandoah National Park, yielding virtually no excess fine soil contribution in the urban area. It is worth noting, however, that there is a modest excess coarse concentration of 2 to 5  $\mu\text{g}/\text{m}^3$  in Washington, DC (Figure 6-59). This indicates that soil dust aerosol components that make up the coarse mass are large particles without appreciable mass below 2.5  $\mu\text{m}$ .

The short-term fine mass concentration at Washington, DC and Shenandoah National Park for the year 1992 is shown in Figure 6-60. Although the sampling is conducted Wednesdays and Saturdays for 24-hours, the data points are connected as a guide to the eye. The figure also compares the daily (Wednesdays and Saturdays) fine particle sulfur concentrations at the two monitoring sites. The fine mass concentration time series shows elevated concentrations ( $>30 \mu\text{g}/\text{m}^3$ ) that occur throughout the year. On the other hand,



Washington DC - Shenandoah NP Difference

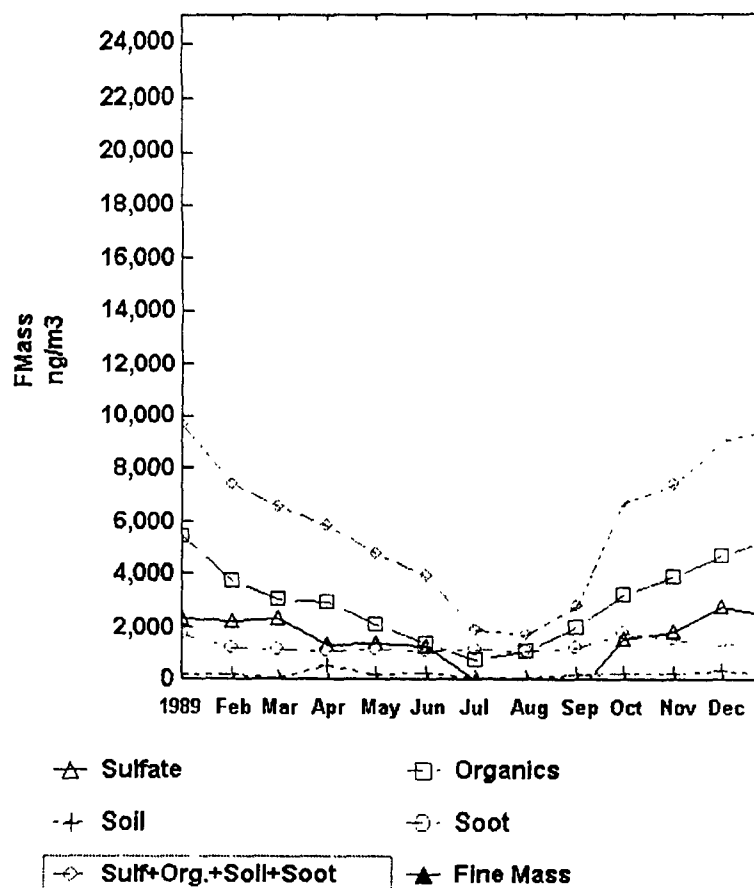


Figure 6-59. Excess aerosol concentration at Washington, D.C. compared to Shenandoah National park. (a) PM<sub>10</sub>, PM<sub>2.5</sub>, and PM<sub>Coarse</sub>. (b) Concentration of sulfate, organics, soil, and soot.



high fine mass levels at Shenandoah are recorded only during the summer season. Particulate sulfur concentration at the urban and non-urban site are comparable and co-vary throughout the year. This indicates that particulate sulfur is part of the regional air mass that at any given day influences both Washington, DC and Shenandoah. Fine particle mass, on the other hand, shows an excess concentration at Washington, DC, particularly during the winter months. Visual inspection of the fine mass daily time series clearly indicates that the concentration change from one daily sample to another can be an order of magnitude different. Consequently, most of the concentration variance is due to random synoptic air mass changes, and to a lesser degree due to periodic seasonal variations. Further concentration variance would exist if hourly data were available.

#### 6.5.1.4 New York City, NY

The New York City metropolitan area is characterized by high population density, moderate industrial activity, and relatively flat terrain. The  $PM_{10}$  concentration over the metropolitan area is shown in Figure 6-61a. The circles in the map show the locations of the monitoring sites and the magnitude of each circle is proportional to the average  $PM_{10}$  concentration at that site using all available data. The observed average concentrations change by about a factor of two to three from one location to another. Higher average concentrations tend to occur near the center of the metropolitan area.

The long-term trend of  $PM_{10}$  averaged over the New York City metropolitan area (Figure 6-61b) shows a decline from about  $35 \mu\text{g}/\text{m}^3$  in 1986 to  $25 \mu\text{g}/\text{m}^3$  in 1992. This  $PM_{10}$  reduction is comparable to the reduction over the entire Northeastern region. The average seasonal pattern over the New York City metropolitan area (Figure 6-61c) is 25 to  $30 \mu\text{g}/\text{m}^3$  throughout the year, but rises to about  $40 \mu\text{g}/\text{m}^3$  in July.

The seasonal pattern at three different individual monitoring sites in the New York City metropolitan area is shown in Figure 6-62. The three sites all show similar seasonality with a summer peak, but with elevated concentrations closer to the city center.

Size segregated aerosol samples in New York City (Figure 6-62e,f) show that at both sites,  $PM_{10}$  concentrations are contributed primarily by fine particles. Furthermore, the seasonality at the Manhattan site shows two peaks, the summer peak and the winter peak. Based on the discussion of the more extensive Washington, DC (Section 6.5.1.2)

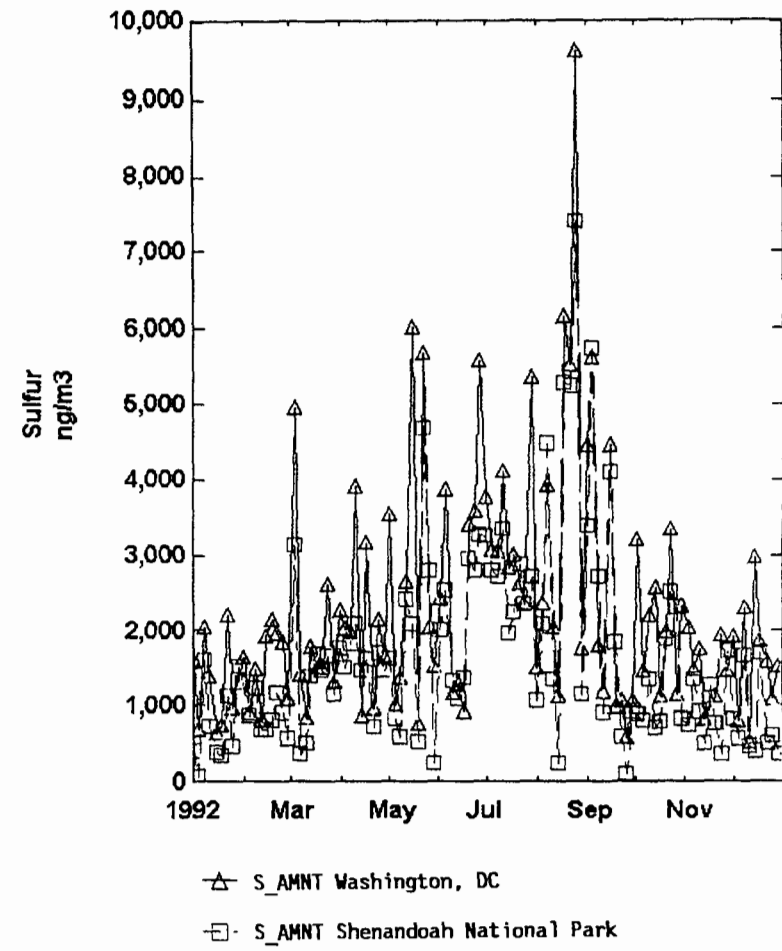
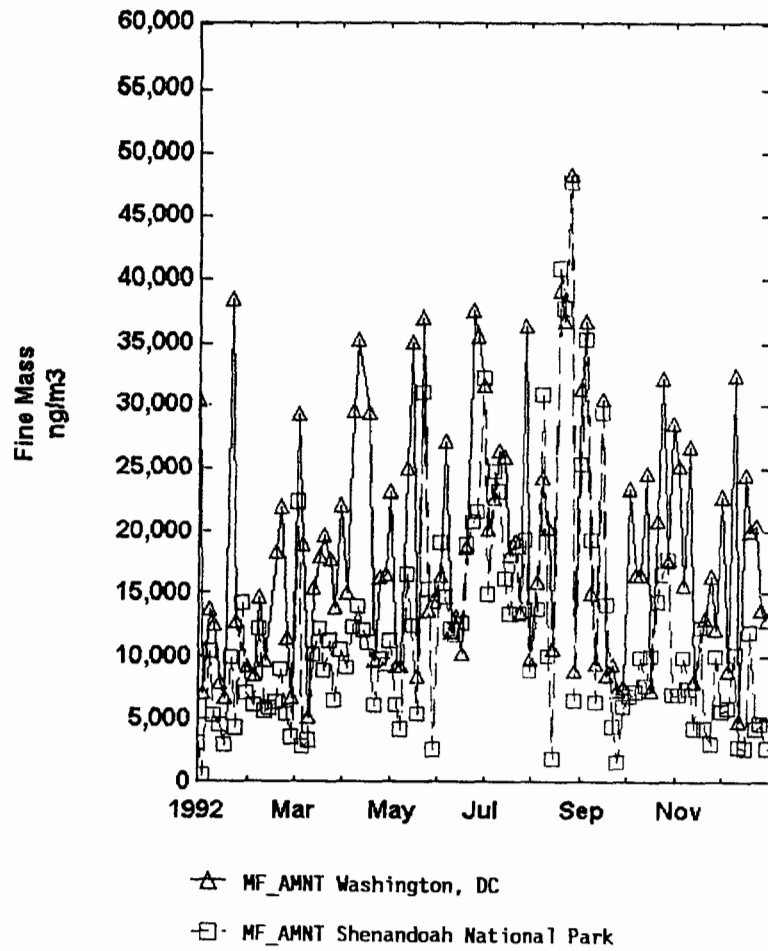
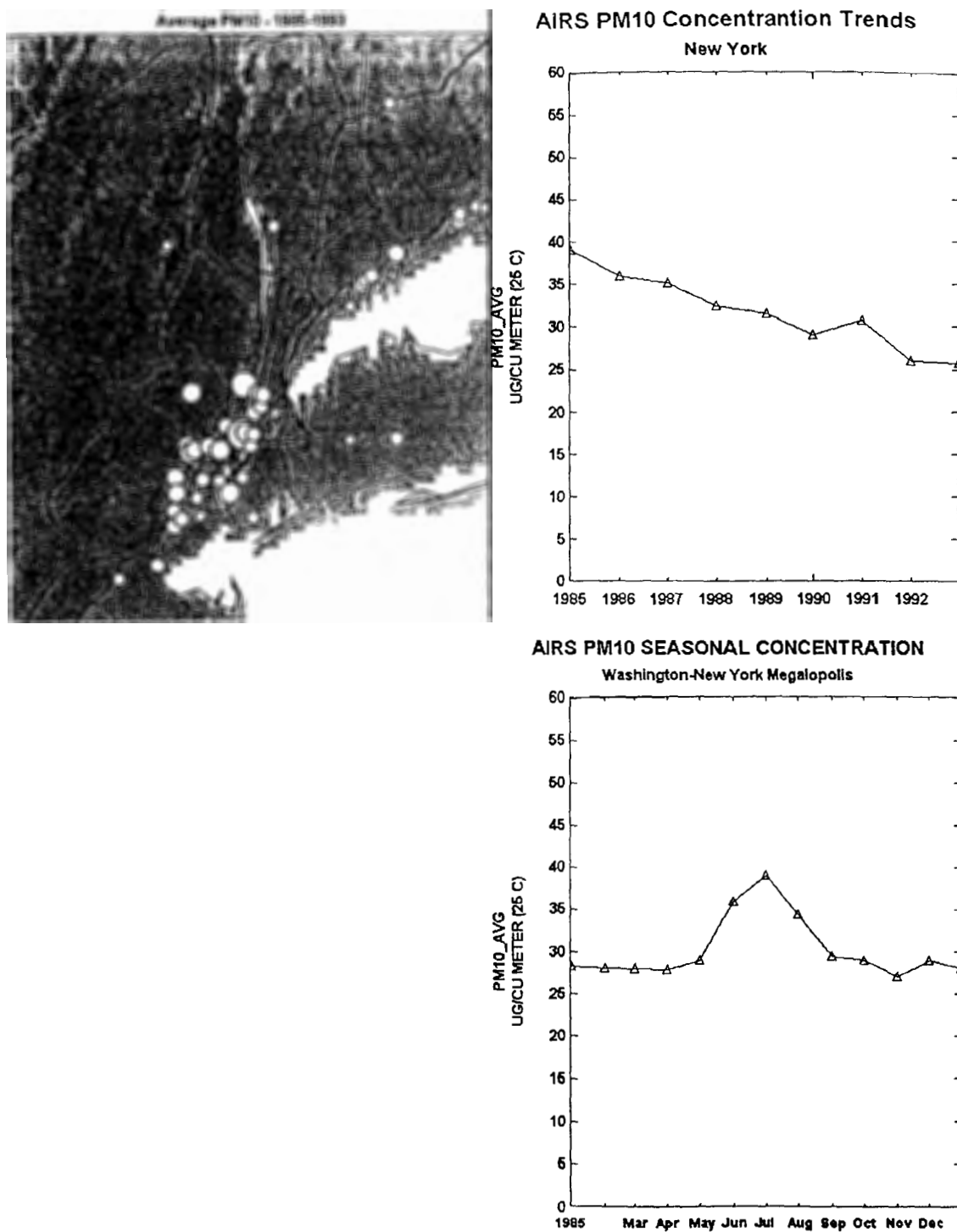


Figure 6-60. Daily concentration of fine mass and fine sulfur at Washington, D.C. and Shenandoah National Park.



**Figure 6-61.** Aerosol concentration map, trend and seasonality in the New York City region.

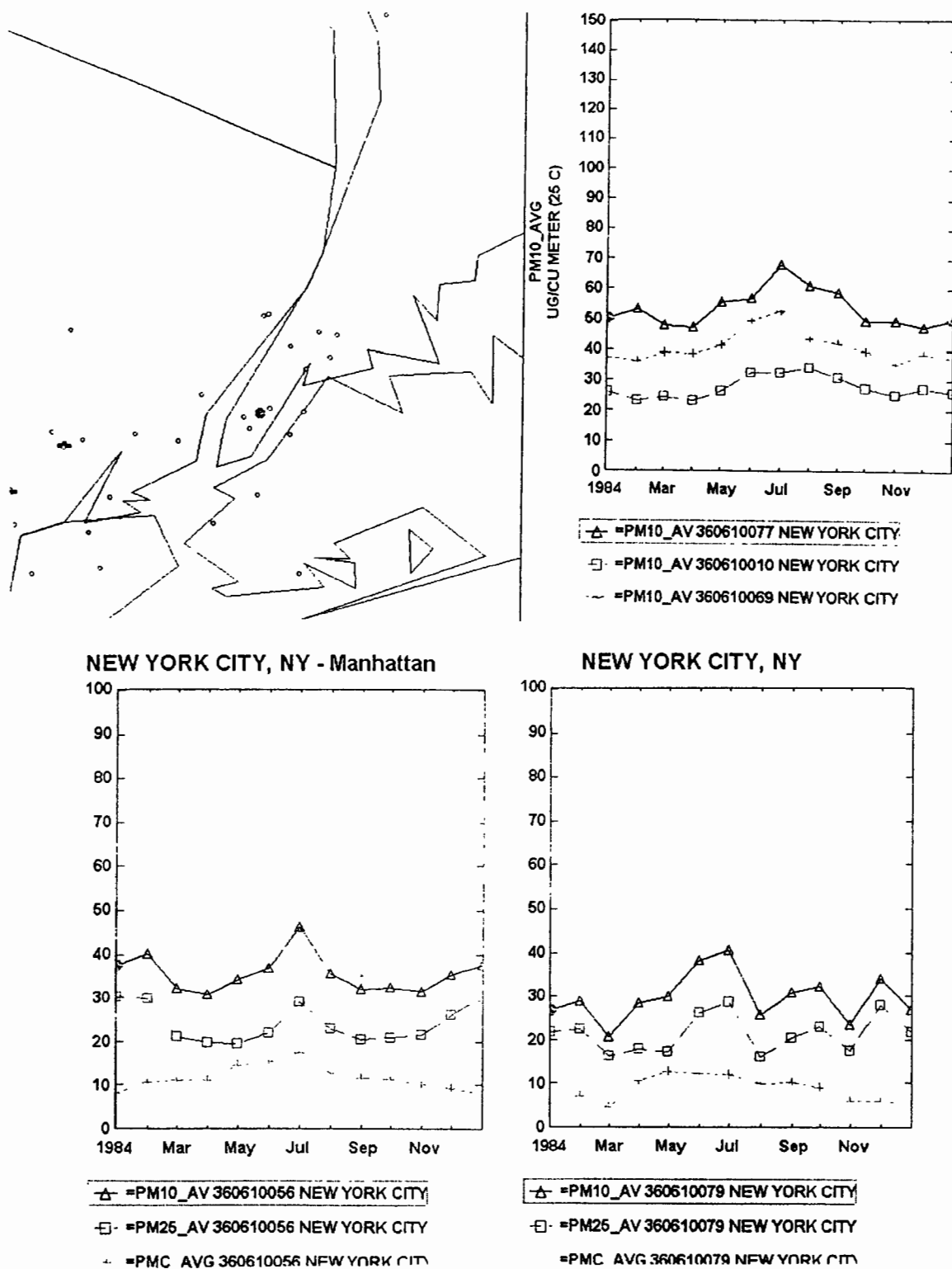


Figure 6-62. Fine, coarse and PM<sub>10</sub> particle concentration near New York City.

1 measurements it can be inferred that the summer peak in the fine mass is mainly due to the  
2 regional haze aerosol, while the winter peak is contributed by the local sources, confined to  
3 the inner metropolitan area.

4 As part of the New York Summer Aerosol study (Leaderer et al., 1978) continuous  
5 size monitoring confirmed the expected bimodal volume distribution with modes between  
6 0.1 to 1.0  $\mu\text{m}$  and over  $>3.0 \mu\text{m}$ . A number of interesting patterns were observed when the  
7 size distribution was averaged by hour of day. The diurnal average total number  
8 concentration showed a pattern which corresponded closely with the normalized diurnal  
9 traffic pattern. Particles  $<0.1 \mu\text{m}$  showed the most marked diurnal variation, following the  
10 total number curve. Moreover, particles in size ranges  $>0.1 \mu\text{m}$  showed little variation in  
11 the diurnal pattern. Analysis of samples processed by the diffusion battery indicated that  
12 approximately  $54\% \pm 18\%$  of the sulfate measured was in the suboptical range (approximately  
13 0.04  $\mu\text{m}$  to 0.3  $\mu\text{m}$ ) with the remainder above 0.3  $\mu\text{m}$ . Little sulfate mass was found in  
14 particles in the nuclei range ( $<0.04 \mu\text{m}$ ). Analysis of impactor samples for sulfates  
15 consistently showed that more than 85% of all water soluble sulfates were  $<2.0 \mu\text{m}$  in size.  
16 Virtually no nitrate was present in the nuclei size range while the suboptical size range  
17 accounted for approximately 30% of the total nitrate. 70% of the total nitrate was found in  
18 the size range  $>0.3 \mu\text{m}$ . Analysis of large stages of Anderson impactor showed that  
19 approximately 50% of particulate nitrate was greater than 5.5  $\mu\text{m}$  in size.

20 Urban and rural particulate sulfur monitoring near New York City in the summer  
21 (Leaderer et al., 1982) indicated that sulfate concentration distributions were regionally  
22 homogeneous and increased with increasing ozone levels and covariant with several other  
23 pollutant and meteorological parameters. Sulfate concentrations correlated strongly with  
24 ammonium and strong acid at all sites. No significant diurnal patterns for sulfate or  
25 ammonium were seen at any site for low and high ozone levels. Strong acid concentrations  
26 were highest at the rural and semi-rural sites, lowest at the urban sites, increased with  
27 increasing ozone levels and exhibited diurnal patterns which matched the ozone diurnal  
28 patterns.

29 Sulfate acidity measurements (Waldman et al., 1991) at Chestnut Ridge, PA (east of  
30 Pittsburgh) suggest that higher acidity occurred in the overnight period (0000 to 0800) in the  
31 late fall, while sulfate had its highest levels in the morning to afternoon period. Size

dependent, mass and composition of New York aerosol for low, medium, and high visibility levels was reported by Patterson and Wagman, 1977. At all levels of visibility, bimodal or multimodal particle size distribution were observed for total mass and for individual components. Decreased visibility corresponded to increased particle mass concentrations especially in the fine particle fraction (ranging in size from about 0.1 to 1.00  $\mu\text{m}$ ). Increases in the proportion of particulate sulfate and to a lesser extent of nitrate, chloride, ammonium, and carbon were also associated with decreased visibility.

Aerosol pattern analysis of a major wintertime (1983) pollution episode in northern New Jersey (Lioy et al., 1985) revealed that the intensity of the episode was the greatest in the area of highest commercial, residential and industrial activities, and that the atmospheric stagnation conditions resulted in the significant accumulation of aerosol mass. The aerosol mass was primarily fine aerosols, and the extractable organic matter compromised about 50% of the particle mass.

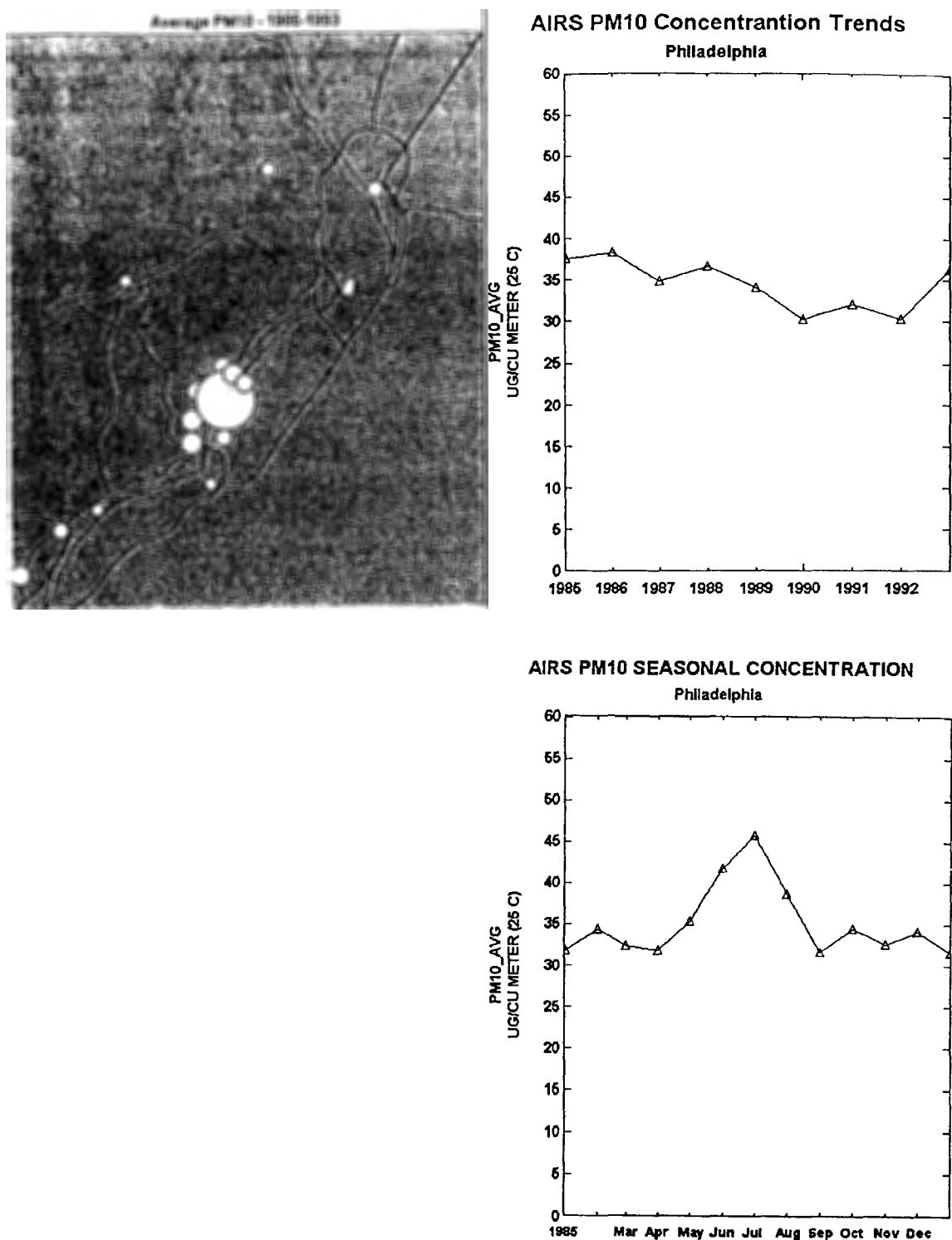
An analysis of the winter aerosol chemistry data in the Northeast (Poirot et al., 1990) found that the winter  $\text{PM}_{2.5}$  apportionment consisted of 48% sulfates, 23 % organic matter, 15% soot, 4% soil, and 10% unexplained.

#### **6.5.1.5 Philadelphia, PA**

The metropolitan area of Philadelphia includes urban-industrial emissions over flat terrain. The map of the area shows relatively uniform  $\text{PM}_{10}$  concentrations throughout the metropolitan area, with the exception of a single site (AIRS #421010149) in the middle of the urban area.

The 1985 to 1992 trend of  $\text{PM}_{10}$  averaged over the metropolitan area is somewhat downward but not significantly. The seasonal concentration of  $\text{PM}_{10}$  (Figure 6-63a) is about 30 to 35  $\mu\text{g}/\text{m}^3$  throughout the year, except during the summer months when it rises above 40  $\mu\text{g}/\text{m}^3$ .

The seasonal average  $\text{PM}_{10}$  concentration for three sites near the center of Philadelphia is shown in Figure 6-64. One of the sites is the high concentration site noted on the metropolitan map. The average  $\text{PM}_{10}$  concentration at that site ranges between 100 to 150  $\mu\text{g}/\text{m}^3$  which is a factor of 2 to 3 higher than the concentration at the neighboring sites. The daily concentration at this anomalous monitoring site (AIRS #421010149) correlates poorly



**Figure 6-63. Aerosol concentration map, trend and seasonality in the Philadelphia region.**

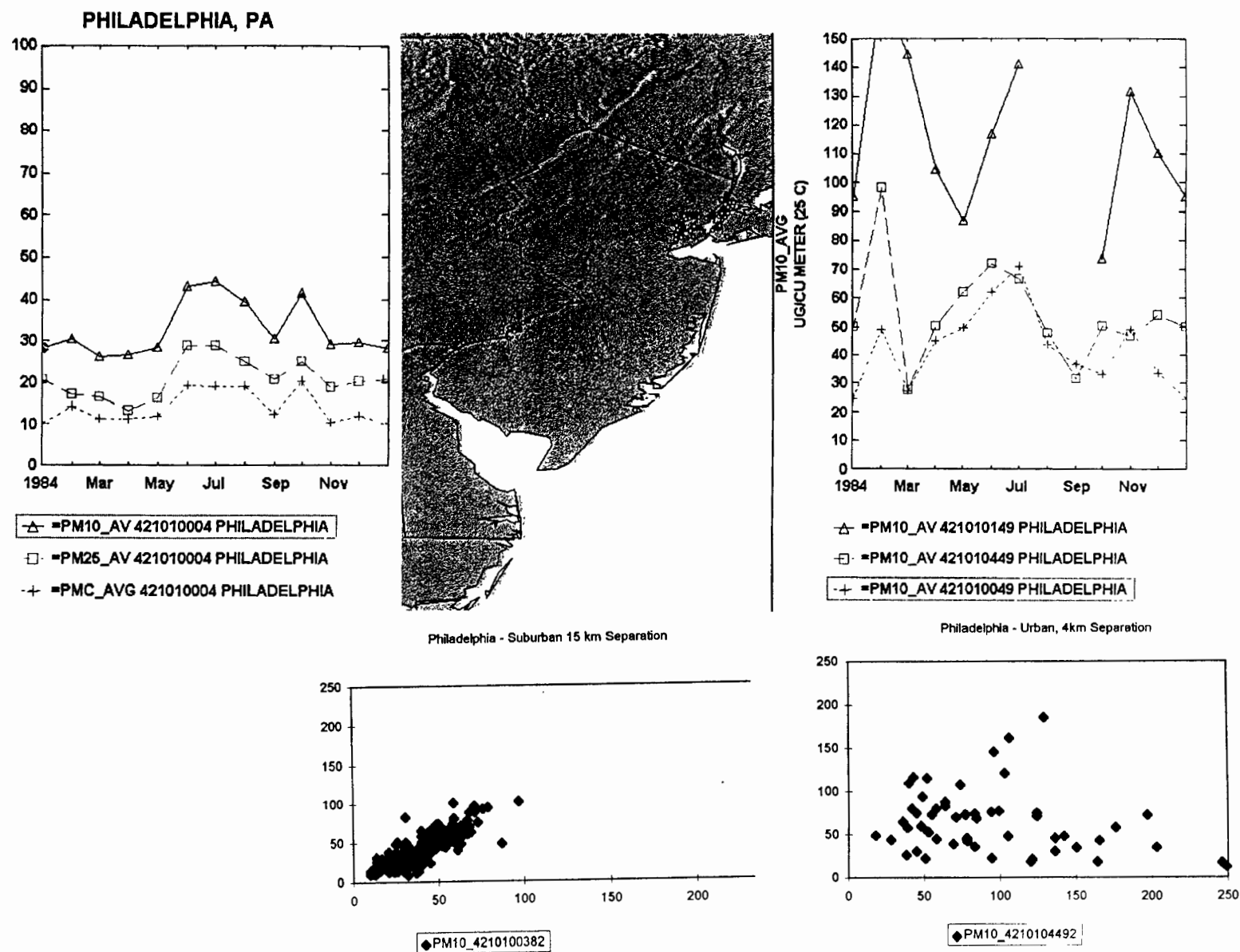


Figure 6-64. Fine, coarse and PM<sub>10</sub> particle concentration near Philadelphia.



1 with an adjacent site (AIRS #4210104492) which is only 4 km apart (Figure 6-64e). This is  
2 an indication that the concentration at the anomalous site is under the influence of strong  
3 local source of  $PM_{10}$ . In contrast, two sites in suburban Philadelphia that are 15 km apart  
4 (Figure 6-64d) show a strong correlation of daily measurements indicating that spatially  
5 uniform regional haze influences the daily values at both sites.

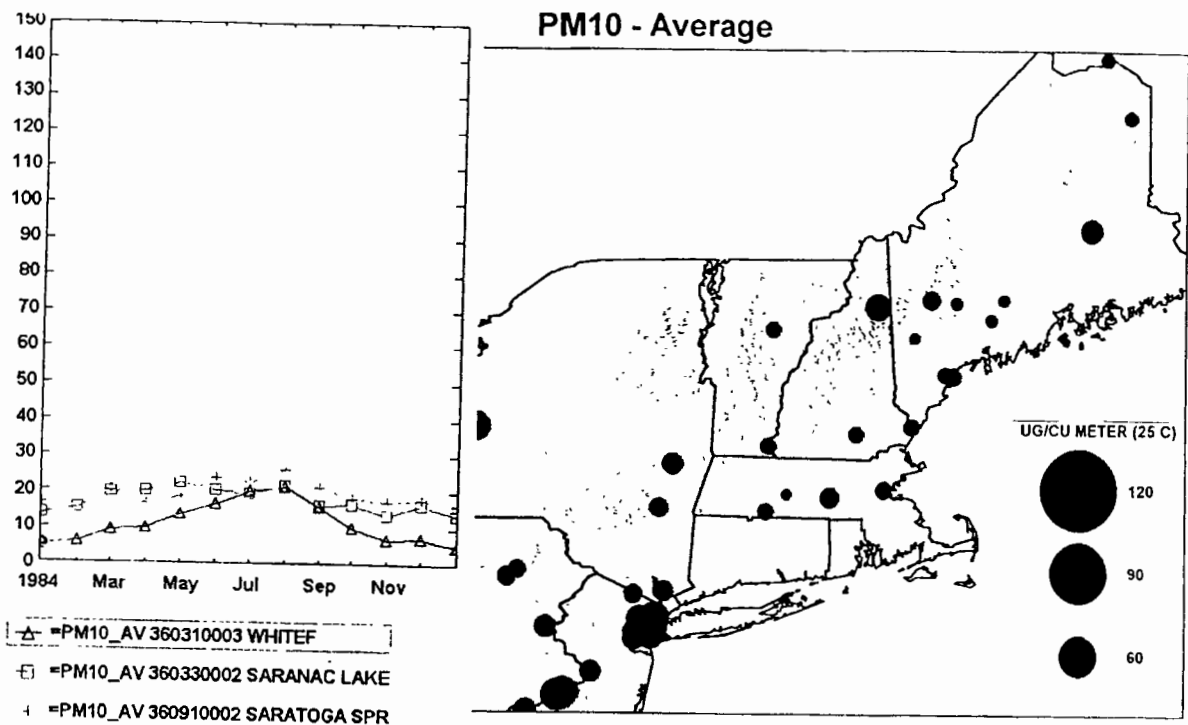
6 Size segregated aerosol samples (Figure 6-64a) at Philadelphia (AIRS #421010004)  
7 show the fine particulate mass is the main contributor of  $PM_{10}$  in this city. It is possible,  
8 however, that at other sampling sites, e.g. the anomalous #4210104492 site, coarse particles  
9 prevail.

10 Outdoor summertime sulfate ( $SO_4^{2-}$ ) concentrations were found to be uniform within  
11 metropolitan Philadelphia (Suh, et al 1995). However, aerosol strong acidity ( $H^+$ )  
12 concentrations were found to vary spatially. Also, the wintertime sulfate pattern was likely  
13 to be more heterogeneous in space and time as discussed for Washington, DC This variation  
14 generally were independent of wind direction, but were related to local factors, such as the  
15  $NH_3$  concentration, population density, and distance from the center of the city.

#### 16 17 **6.5.1.6 Whiteface Mountain, NY**

18 The AIRS sampling location at the Whiteface Mountain in Upstate New York, is a  
19 high mountain top site, elevated from the surrounding terrain. The monitoring site offers the  
20 possibility of comparing mountain tops concentrations to the surrounding lower elevation  
21 sites.

22 The seasonal pattern of  $PM_{10}$  concentration for Whiteface Mountain and the  
23 surrounding low elevation sites, Saranac Lake, and Saratoga Spr. are shown in Figure 6-65.  
24 The concentration at the three sites is virtually identical during June through September.  
25 However, during the winter the mountain top site at Whiteface has a  $PM_{10}$  concentration  
26 which is only one third of the surrounding sites. This indicates that during the winter, the  
27 Whiteface mountain top is above the surface-based aerosol layer, while during the summer  
28 the height of the well mixed aerosol layer rises above the mountain top producing are  
29 resulting in a uniform concentration at all sites. At Whiteface Mountain, NY (Webber et al.,  
30 1985) have found direct microscopic evidence of flyash particles during a summertime (June  
31 23, 1983) sulfate episode.



**Figure 6-65.  $\text{PM}_{10}$  concentration seasonality at Whiteface Mountain and neighboring low elevation sites.**

## 6.5.2 Sub-regional Aerosol Pattern in the Southeast

### 6.5.2.1 Winston-Salem, NC, Florida

Winston-Salem is a small urban area imbedded in the relatively homogeneous region of the Southeast. In fact, the main emphasis of the illustrations below is on the remarkable uniformity of aerosols in that region.

Comparison of three AIRS  $\text{PM}_{10}$  monitoring sites in North Carolina, Winston-Salem, Greensboro, and Raleigh-Durham (Figure 6-66) shows virtually identical concentrations (within 10%), both in absolute magnitudes, and in the seasonality. This is an indication that these sites are exposed to the same regional airmass throughout the year. It also indicates that the excess  $\text{PM}_{10}$  concentrations due to local urban sources are insignificant.

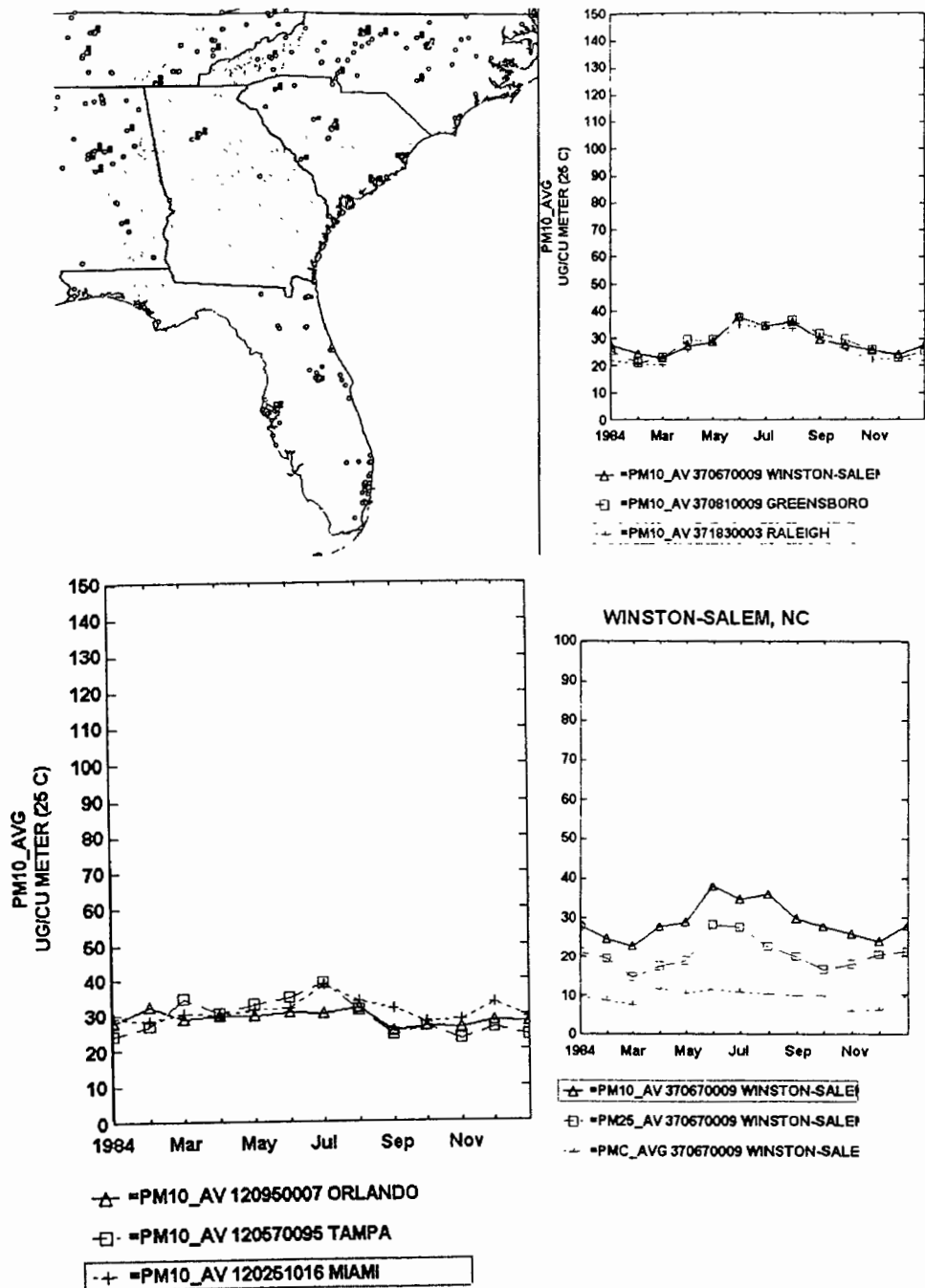


Figure 6-66. Aerosol concentration pattern at North Carolina and Florida sites.

Size segregated monitoring data for Winston-Salem show that fine particles contribute 70 to 80% of the  $PM_{10}$  mass of 25 to 35  $\mu\text{g}/\text{m}^3$ . Coarse particles are seasonally invariant at about 10  $\mu\text{g}/\text{m}^3$  which is typical for eastern US.

The  $PM_{10}$  concentration at monitoring sites in Florida (Orlando, Miami, Tampa) show virtually identical concentrations ranging between 25 to 30  $\mu\text{g}/\text{m}^3$  throughout the year, without appreciable seasonality.

#### 6.5.2.2 Large Southeast Metropolitan Areas

The relative homogeneity of southeastern aerosol concentrations is consistent with the observations at the regional perspective. However, the concentrations in large metropolitan areas such as Atlanta, GA, Birmingham, AL, Mobile, AL, New Orleans, LA, and Houston, TX, Dallas-Fort Worth, TX, show somewhat elevated values. It is evident, however, that these southeastern urban areas do not have high concentration hot spots.

The seasonal  $PM_{10}$  concentration at sites in New Orleans, LA, Mobile and Birmingham, AL show uniformity (20 to 40  $\mu\text{g}/\text{m}^3$ ) with modest seasonality. At sites in Houston, Austin, and San Antonio, TX show similar values, but more spread in concentration.

The size segregated aerosol samples collected in the cities of the Gulf states, Corpus Christi, Fort Worth, Houston, TX and New Orleans, LA all show that fine particle concentrations are relatively low (10 to 20  $\mu\text{g}/\text{m}^3$ ) and are seasonal (Figure 6-67). Coarse particle concentrations, on the other hand, account for more than half of the  $PM_{10}$  mass and their contribution is most pronounced during the summer season.

In Houston, TX Dzubay et al., 1982 found that in summertime fine particle mass contained 58% sulfate and 18 % of carbonaceous material. They also found that the coarse fraction (2.5 to 15  $\mu\text{m}$ ) consisted of 69% crustal matter, 12 % carbon, and 7 % nitrate species.

Characterization of the Atlanta area aerosol (Marshall et al., 1986) show that elemental carbon and particulate sulfur represent, respectively 3.1 to 9.9% and 1.9 to 9.4% of the total suspended particulate mass. The concentration of elemental carbon, sulfur, and TSP exhibit strong seasonal variations, with elemental carbon decreasing from winter to summer, and sulfur and TSP increasing. Elemental carbon appears to be statistically separate

1 from sulfur, indicating that the sources for elemental carbon and particulate sulfur are  
2 distinct.

### 3 4 **6.5.2.3 Great Smoky Mountains**

5 Size segregated fine and coarse aerosol concentrations were measured at the Great  
6 Smoky Mountains National Park in September of 1980 (Stevens et al., 1980). Sulfate and its  
7 associated ions contributed to 61% of the fine particle mass, followed by organics (10%) and  
8 elemental carbon (5%).  
9

## 10 **6.5.3 Sub-regional Aerosol Pattern in the Industrial Midwest**

11 The chemical composition of summertime (July, 1981) fine particles in Detroit (Wolff  
12 et al., 1982) was found as 52% sulfates, 27% organics, 4% elemental carbon, 8% soil dust  
13 Nitrate was found to absent from fine mass. Fine particles, themselves contributed about  
14 64% of the aerosol mass balance.

15 Since the turn of the century, the major cities in the industrial midwestern states had  
16 air pollution problems due to smoke and dust. Pittsburgh, St. Louis, Chicago, and Detroit  
17 were among the formerly notorious air pollution hot spots. The recently acquired PM<sub>10</sub>  
18 database now allows the re-examination of these metropolitan areas in the industrial Midwest  
19 for their concentration pattern in the 1990s.  
20

### 21 **6.5.3.1 Pittsburgh, PA**

22 The average PM<sub>10</sub> concentration over the extended metropolitan area is shown in  
23 Figure 6-68a. The map also includes the industrial cities in the eastern Ohio, Steubenville,  
24 OH, and Weirton, OH, located on the Ohio River. The average PM<sub>10</sub> concentration at the  
25 80 sites shown on the map varies only by about 20% from site to site. Outstanding high  
26 concentration hot spots are also absent. It is thus evident that during the 1985 to 1993  
27 period, the PM<sub>10</sub> concentrations in the Pittsburgh sub-region was spatially rather uniform.

28 The PM<sub>10</sub> concentration trend shows declining values from about 40  $\mu\text{g}/\text{m}^3$  to 30  
29  $\mu\text{g}/\text{m}^3$  (Figure 6-68b) over the 1985 to 1993 period. Figure 6-68b also marks the  
30 concentration standard deviation among the monitoring sites for each year, which is about  
31 15 to 20% and shrinking over time.

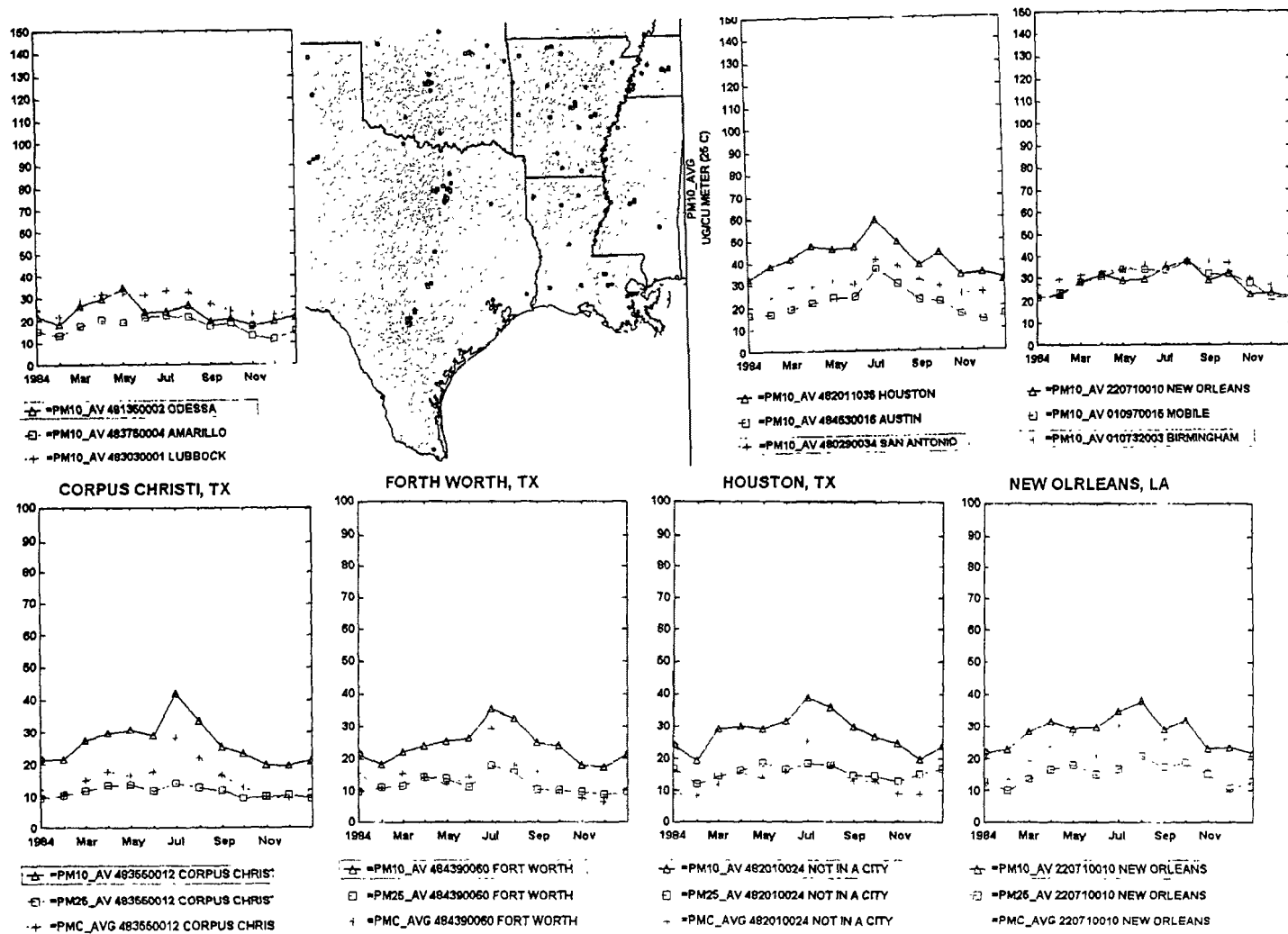


Figure 6-67. Aerosol concentration pattern in Texas and Gulf states.

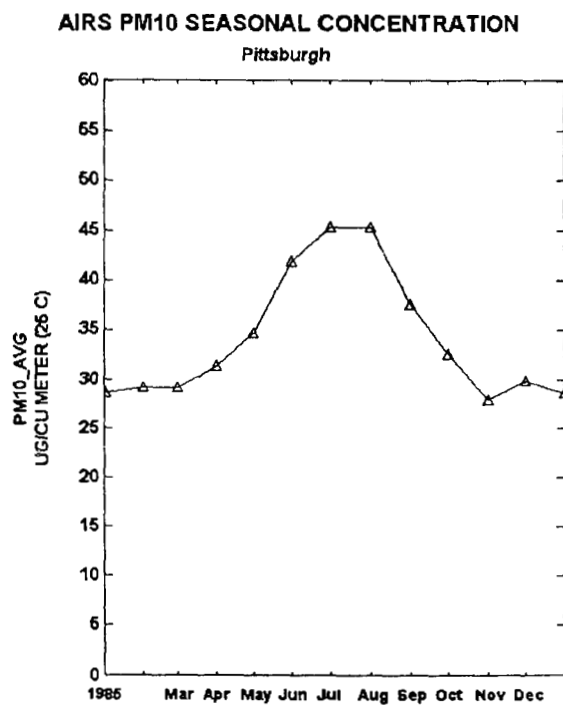
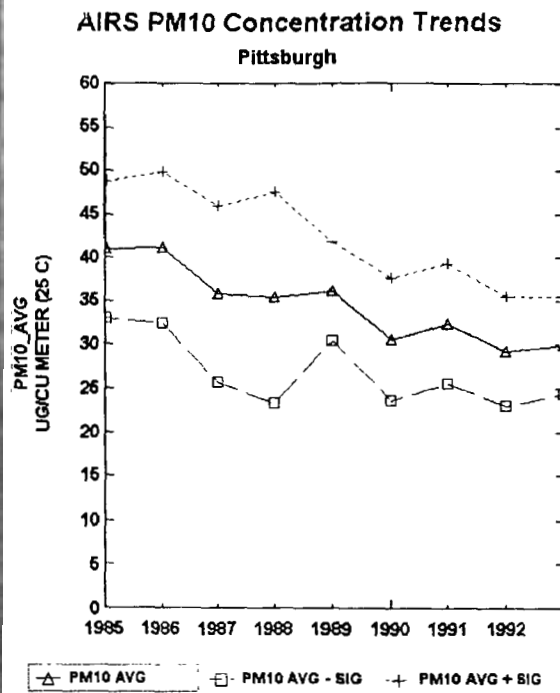


Figure 6-68. Aerosol concentration pattern and trends in the Pittsburgh subregion.

1       The seasonality of the PM<sub>10</sub> pattern (Figure 6-68c) is dominated by a summer peak  
2       (45 µg/m<sup>3</sup>), which is about 50% higher than the winter concentrations (30 µg/m<sup>3</sup>). The  
3       seasonality at sites in Pittsburgh, PA, Weirton, OH, and Steubenville, OH show comparable  
4       values and a seasonal pattern that is slightly above the sub-regional average. Hence, these  
5       formerly highly polluted locations are now virtually identical to their rural background.

6       Size segregated aerosol samples in Pittsburgh, PA and Steubenville, OH (Figure 6-69)  
7       show that fine particles contribute 70 to 80% of the PM<sub>10</sub> mass, and also dictate the summer-  
8       peak seasonality of the PM<sub>10</sub> concentrations. As in other urban monitoring sites in the  
9       eastern US, the coarse particle concentration in Pittsburgh is about 10 µg/m<sup>3</sup> and seasonally  
10      invariant. The size segregated seasonal data for Steubenville, OH exhibit more random  
11      fluctuations as well as discrepancy between the sum of fine and coarse at one hand, and  
12      PM<sub>10</sub> on the other. The discrepancy is attributed to the small number of size segregated  
13      aerosol samples.

14      The remarkable uniformity of fine particles mass and elemental composition from site  
15      to site in the Ohio River Valley was also shown by Shaw and Paur, 1983. Sulfur was the  
16      predominant element in fine particles. Factor analysis of element concentrations indicated  
17      three clusters throughout the year (1) coarse particle crustal elements (2) fine particle sulfur  
18      and selenium (3) fine particle manganese, iron and zinc.

19      The chemical mass balance of Weirton-Steubenville aerosol was examined by  
20      Skidmore et al., 1992. Primary motor vehicle and secondary ammonium sulfate were  
21      dominant contributors to the PM<sub>2.5</sub> aerosol. Steel emissions were also significant  
22      contributors to PM<sub>2.5</sub>. Wood burning and oil combustion were occasionally detected.  
23      Geological material was the major contributor to the coarse aerosol fraction. Primary  
24      geological material, primary motor vehicle exhaust, and secondary sulfate were the major  
25      contributors to PM<sub>10</sub> at all five monitoring sites.

26      The composition of size-fractionated summer aerosol in nearby Charleston, West  
27      Virginia was reported by Lewis and Macias, 1980. Ammonium sulfate was the largest single  
28      chemical component (41%) of the fine aerosol mass. Carbon was also a large component of  
29      both fine and coarse particle mass constituting 16% and 12% respectively. Factor analysis  
30      indicated that four factors were sufficient to satisfactorily represent the variance of



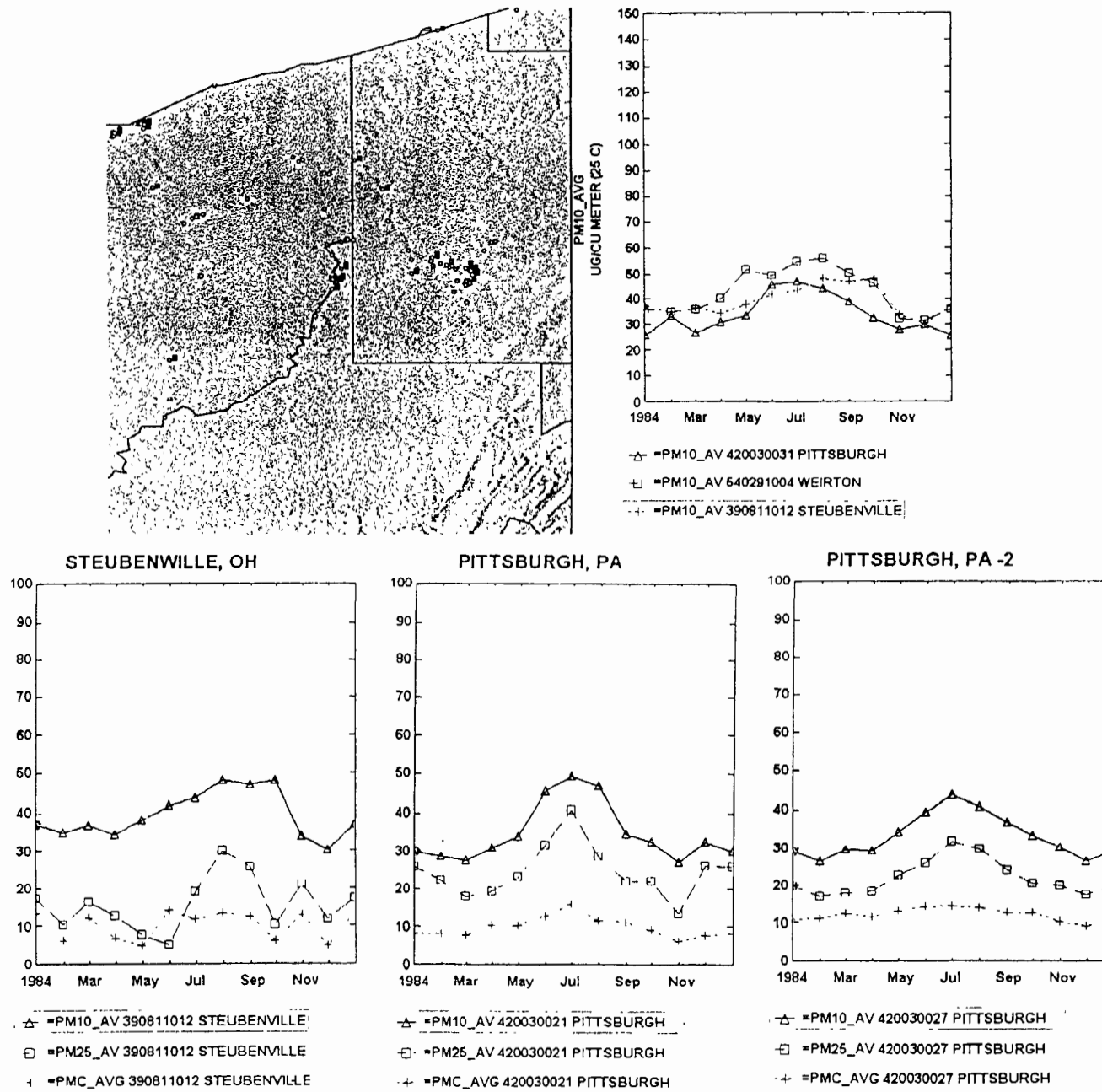


Figure 6-69. Fine, coarse and PM<sub>10</sub> concentration near Pittsburgh.

26 measured parameters. The factors were characteristic of crustal material, ammonium sulfate, automotive emissions, and unidentified anthropogenic sources.

#### 6.5.3.2 St. Louis, MO

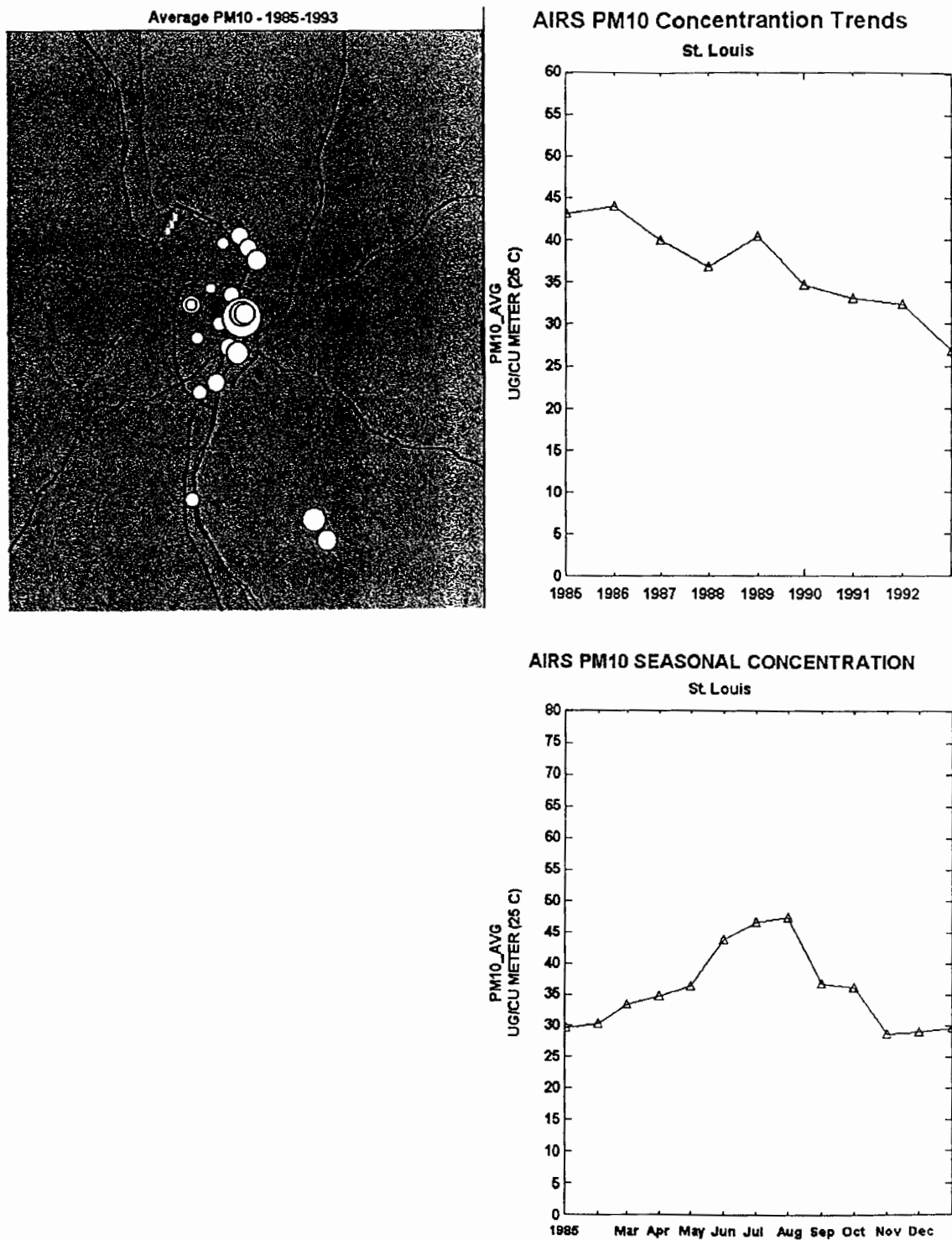
Historically, the St. Louis metropolitan area has been known for high particulate concentrations, particularly on the east side of the Mississippi River. The map of the metropolitan area (Figure 6-70a) shows about factor of 2 to 3 concentration differences among the PM<sub>10</sub> monitoring stations. The monitoring sites east of the river tend to be higher than the western sites of this sub-region.

The average PM<sub>10</sub> in the St. Louis metropolitan area (Figure 6-70b) has been declining from 40 to 45  $\mu\text{g}/\text{m}^3$  to 25 to 30  $\mu\text{g}/\text{m}^3$  by 1993. This decline is comparable to the average reductions over the industrial midwestern region. The seasonality of the sub-regionally averaged concentrations (Figure 6-70c) shows the summer peak with 40 to 50  $\mu\text{g}/\text{m}^3$  which is about 50% higher than the winter averages.

Seasonal comparison of the individual monitoring sites in the area shows that Granite City, IL and East St. Louis, IL have higher PM<sub>10</sub> concentrations throughout the year compared to western St. Louis, MO sites.

Size segregated aerosol samples at three sites west of the Mississippi River (Ferguson, MO, Affton, MO and Clayton, MO) show that fine particles are mostly responsible for PM<sub>10</sub>, including the seasonality (Figure 6-71). Coarse particles contribute 10  $\mu\text{g}/\text{m}^3$  or less throughout the year, although corresponding size segregated aerosol data for more polluted eastside of the Mississippi River are not available.

Monitoring the diurnal and seasonal patterns of particulate sulfur and sulfuric acid in St. Louis (Cobourn and Husar, 1982) noted an afternoon increase in particulate sulfur concentration of about 20%. For the summertime, particulate sulfur concentration was higher than the annual mean by 40%.



**Figure 6-70. Aerosol concentration pattern and trends in the St. Louis subregion.**

### 6.5.3.3 Chicago, IL

Chicago has also been known for industrial dust, smoke, and haze, particularly in East Chicago and Gary, IN. The average  $PM_{10}$  concentrations over the Chicago sub-region (Figure 6-72a) shows that concentrations vary by a factor of two or less throughout the subregion. The downward trend (from 40 to 25  $\mu\text{g}/\text{m}^3$ ) is comparable to the  $PM_{10}$  reductions over the industrial Midwest. The seasonality of  $PM_{10}$  is also typical with the summer peak of 40  $\mu\text{g}/\text{m}^3$  and winter values of 20 to 30  $\mu\text{g}/\text{m}^3$ .

Superposition of seasonal  $PM_{10}$  data at Chicago, IL, East Chicago, IL, and Gary, IN conveys a remarkable spatial uniformity, as well as comparatively low  $PM_{10}$  concentrations in this area that has historically been a smoky and dusty industrial sub-region.

Chemical composition measurements in Chicago (Lee et al., 1993) showed that for concentrations for  $\text{SO}_4^{2-}$  (5.55  $\mu\text{g}/\text{m}^3$ ),  $\text{NH}_4^+$  (2.74  $\mu\text{g}/\text{m}^3$ ),  $\text{NH}_3$  (1.63  $\mu\text{g}/\text{m}^3$ ),  $\text{HNO}_3$  (0.81  $\mu\text{g}/\text{m}^3$ ),  $\text{HNO}_2$  (0.99  $\mu\text{g}/\text{m}^3$ ), for  $\text{SO}_2$  (21.2  $\mu\text{g}/\text{m}^3$ ), for  $\text{NO}_3^-$  (4.21  $\mu\text{g}/\text{m}^3$ ), and for  $\text{H}^+$  (7.7 nmol/ $\text{m}^3$ ). The highest values occurred in the summer, except for  $\text{HNO}_2$  and  $\text{NO}_3^-$  which had the highest values in the winter.

Comparison of atmospheric coarse particles at an urban and non-urban site near Chicago, IL show that the concentration were 50% higher during mid-day than at night. Dry ground samples were 30 % higher than wet ground and 90% higher than frozen ground samples. (Noll et al., 1985).

The analysis of coarse particles in Chicago, IL (Noll et al., 1990) show that the coarse particle mass could be divided into two categories: material that was primarily of crustal origin (Al, Ca, Fe, and Si) and material that was primarily of anthropogenic origin (Cd, Cu, Mn, Ni, Pb, and Zn). The mass of crustal material varied between 15 and 50% of the total coarse mass, while the mass of anthropogenic material was < 1%.

The composition of atmospheric coarse particles at urban (Chicago, IL) and non-urban (Argonne, IL) were reported by Noll et al., 1987. Limestone and silicates were the main source of material at the non urban site. Anthropogenic sources, represented by flyash and coal, were present in the industrial sector sample and rubber tire was present in the commercial sector sample. The mass median diameters (MMD) for different components were as follows: limestone (20 $\mu\text{m}$ , silicates 12 $\mu\text{m}$ , coal, flyash and iron oxide (12 $\mu\text{m}$ ) and rubber tire (25 $\mu\text{m}$ ).

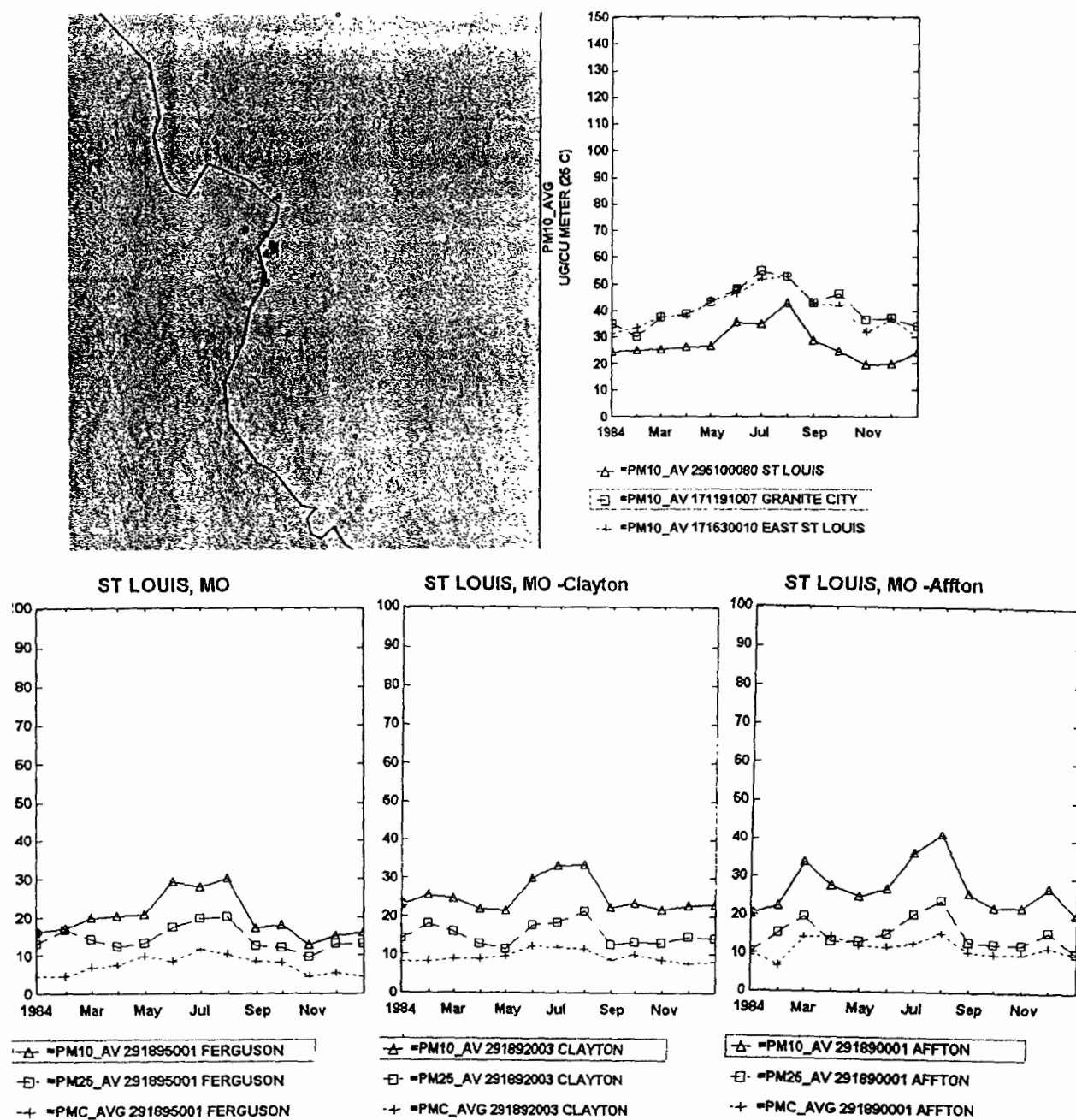


Figure 6-71. Fine, coarse, and PM<sub>10</sub> concentration pattern near St. Louis.

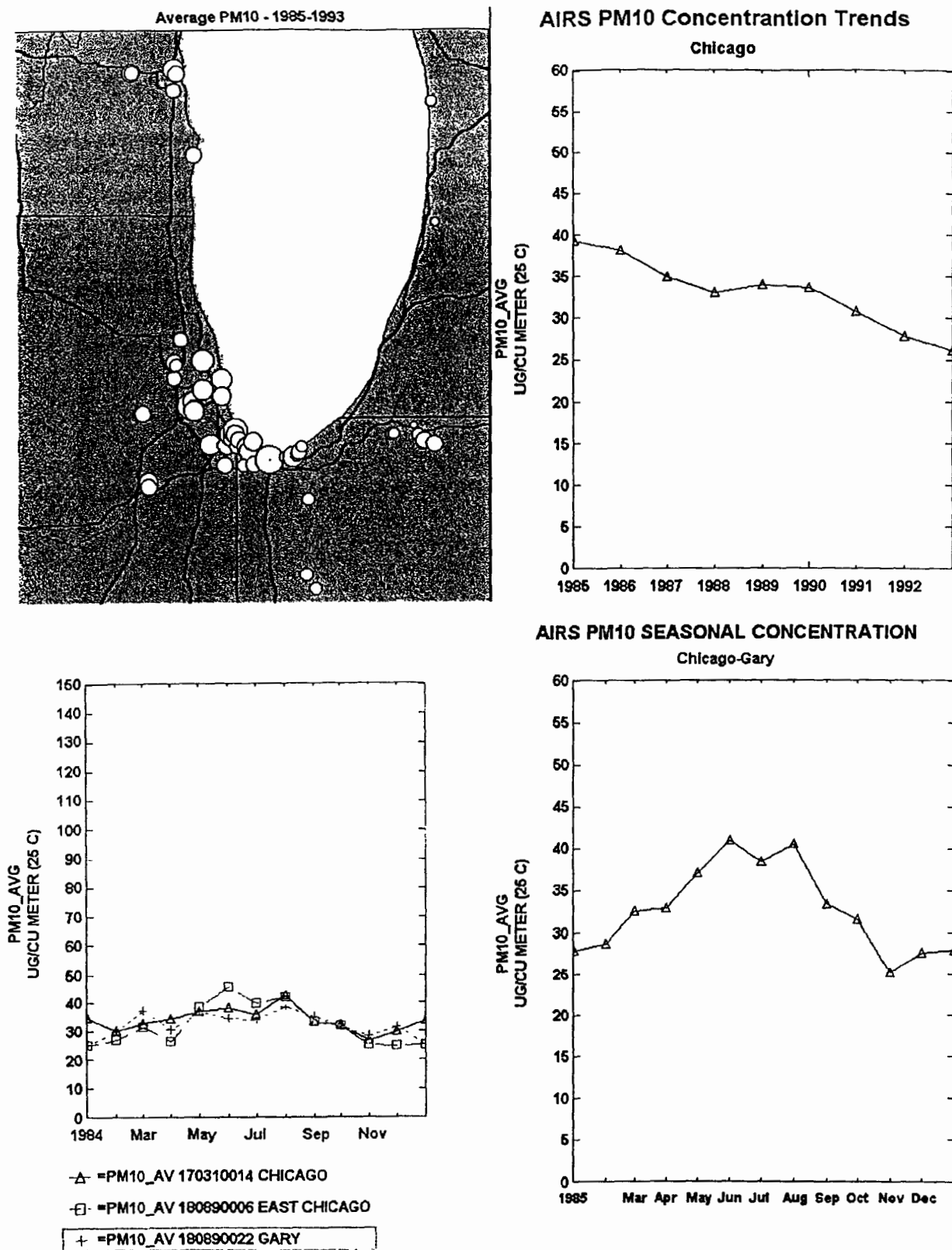


Figure 6-72. Aerosol concentration pattern and trends in the Chicago subregion.

#### 6.5.3.4 Detroit, MI

Detroit is the center of the automotive industry and has been studied by several investigators.

In Detroit, July, 1981 (Wolff and Korsog, 1985) fine mass average was found to be  $42.4 \mu\text{g}/\text{m}^3$ . A major contribution (50%) of sulfate source which appears to be coal combustion was identified. The coarse fraction which averaged as  $25.8 \mu\text{g}/\text{m}^3$  was dominated by crustal material which accounted for about two-thirds of the coarse material. Significant contributions were also identified from motor vehicles (mostly due to reintrained road dust) and iron and steel industry emissions.

The seasonal variations in nitric acid, nitrate, strong aerosol acidity, and ammonia in urban area, Warren, MI was examined by Cadle, 1985. The greatest variations was for ammonia, which was 8.5 times higher in summer than winter. The least variation was for particulate nitrate which had a summer maximum only 1.8 times higher than in spring minimum. It was noted that ammonium nitrate volatilization from filters and impactors can cause large errors in summertime measurements, but the errors are not significant during the winter.

The influence of local and regional sources on the concentration of particulate matter in urban and rural sites near Detroit, MI was investigated by Wolff et al., 1985. Analysis of spatial variations of the various particulate components revealed: (1) at all four sites the  $\text{PM}_{2.5}$  was dominated by regional influences rather than local sources. The site in industrial sector had the largest impact of local sources, but even at this site the local influences appear to be smaller than the regional ones. (2) the regional influences were most pronounced on the sulfate levels which accounted for the largest fraction (40-59%) of the  $\text{PM}_{2.5}$ . (3) organic carbon compounds were the second most abundant  $\text{PM}_{2.5}$  species accounting for 20 to 49% of the mass. Organic carbon seems to be controlled by both local and regional organic carbon influences. Vehicular emissions and possibly secondary reactions appear to affect the organic carbon concentrations (4) elemental carbon appears to be dominated by local emission (5)  $\text{PM}_{\text{Coarse}}$  was dominated by local sources, but at the industrial site unknown non-crustal elements were significant components of coarse mass.

## **6.5.5 Sub-regional Aerosol Pattern in the Southwest**

Southwest is a dusty region and much of the discussion below pertains to coarse particles and soil dust.

The arid southwestern U.S. metropolitan areas (El Paso, TX, Phoenix-Tucson, AZ) has modest industry and national parks (grand Canyon) where the prevention of visibility degradation has been stated as a national goal.

### **6.5.5.1 El Paso, TX**

The  $PM_{10}$  concentration in the El Paso, TX subregion shows that the high and low concentration sites can be found in close vicinity of each other (Figure 6-73a). This is an indication that local sources of  $PM_{10}$  with limited range of impact are important. The  $PM_{10}$  trend since 1985 (Figure 6-73b) shows a remarkable reduction from  $60 \mu\text{g}/\text{m}^3$  to  $30 \mu\text{g}/\text{m}^3$ , although the downward trend is not monotonic. This substantial reduction parallels the factor of two  $PM_{10}$  decline over the entire southwestern region.

The seasonality of  $PM_{10}$  over the El Paso, TX sub-region (Figure 6-73c) is bimodal with peaks in the spring time, March through July, as well as another peak, October through November. This double peak seasonality at El Paso, TX also parallels the seasonality of the entire region. The double peak is further illustrated by superimposed seasonal charts for Tucson, AZ, Albuquerque, NM and El Paso, TX. It is evident, that these three widely spaced sampling sites all show the concentration reduction in August which coincides with the arrival of moist “monsoon” flow from the Gulf of Mexico toward Arizona.

Size segregated aerosol samples for El Paso, TX (AIRS #481410037) shows that coarse particles dominate the  $PM_{10}$  concentrations, accounting for about 70% of the  $PM_{10}$  mass (Figure 6-74a). This is consistent with the important role of coarse particles over the arid Southwest. In comparison, size segregated data for San Antonio, TX (Figure 6-74b) located closer to the Gulf Coast in Texas, shows that fine and coarse mass have comparable contributions, similar to Houston, TX.

### **6.5.5.2 Phoenix and Tucson, AZ**

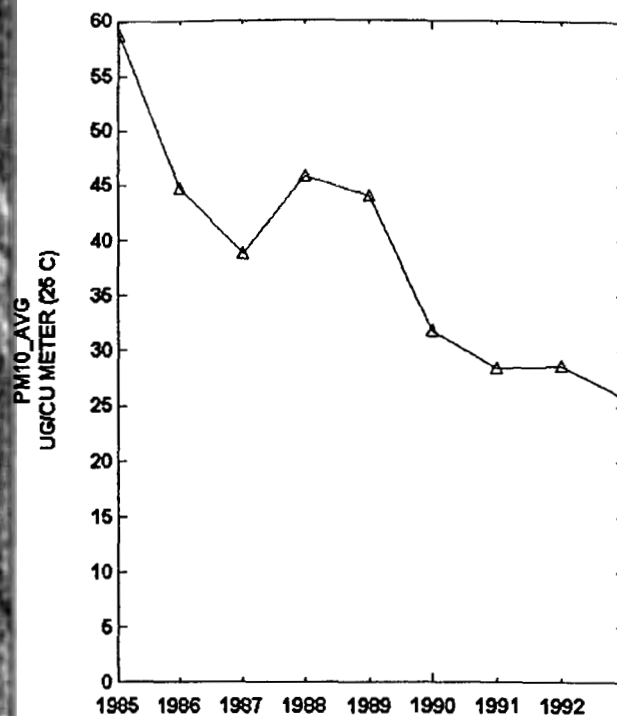
The Phoenix-Tucson sub-region (Figure 6-75a) shows substantial  $PM_{10}$  concentration range. Samplers within Phoenix or Tucson area indicate 2 to 3 times higher concentrations





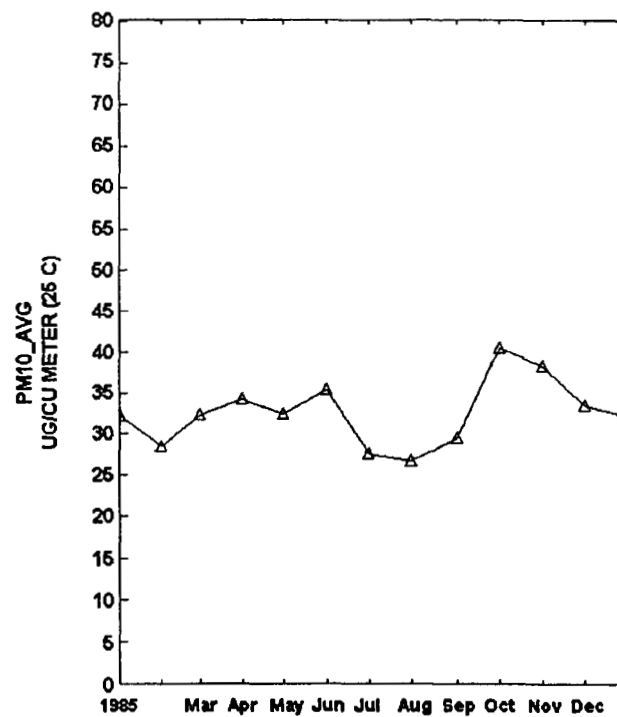
**AIRS PM10 Concentration Trends**

**El Paso**

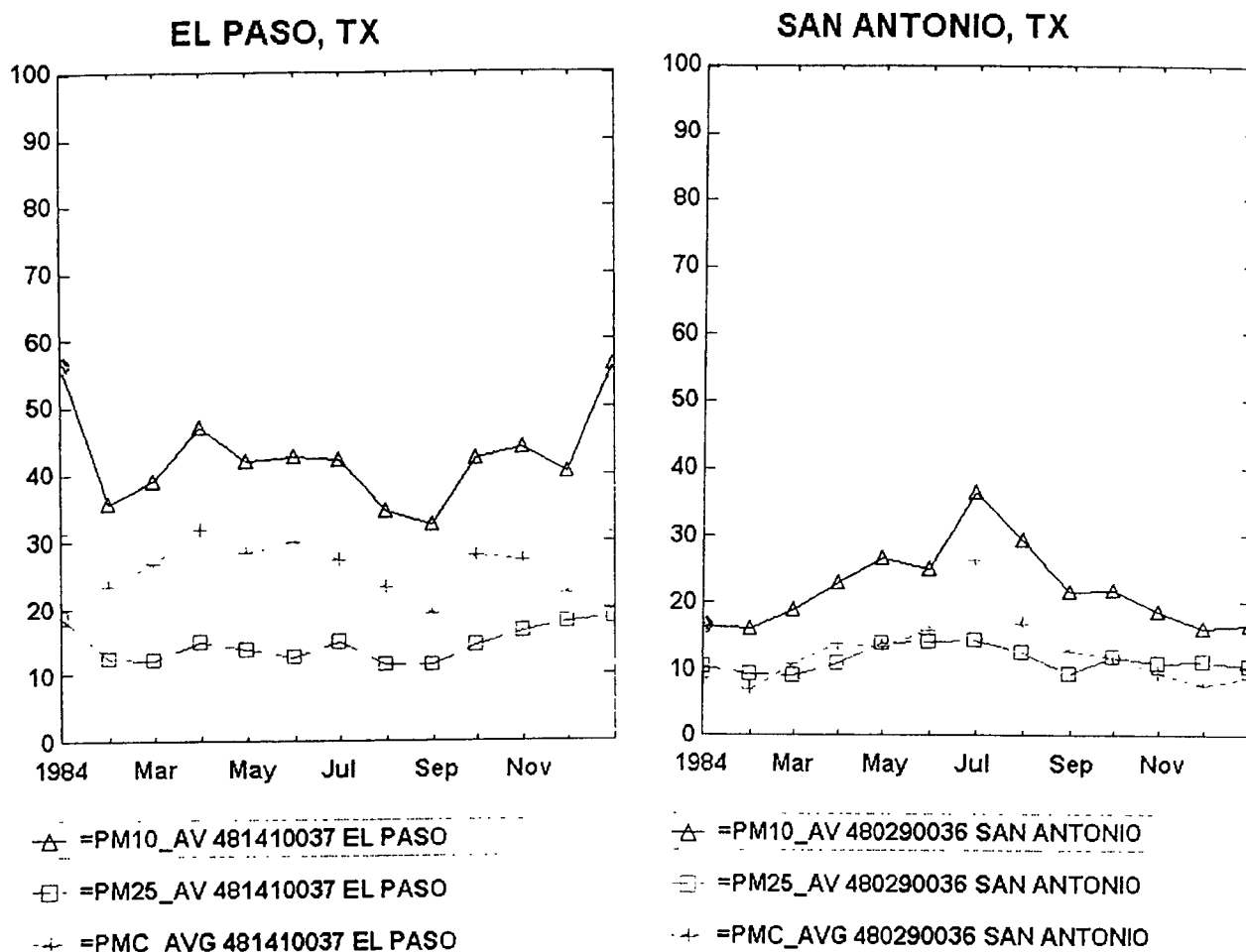


**AIRS PM10 SEASONAL CONCENTRATION**

**El Paso**



**Figure 6-73. Aerosol concentration pattern and trends in the El Paso subregion.**



**Figure 6-74. Fine coarse, and PM<sub>10</sub> concentration pattern near El Paso.**

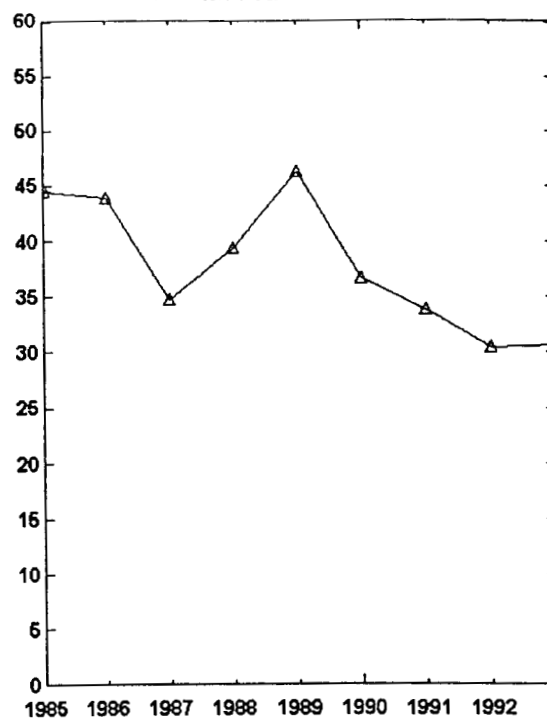
than the more remote sites, particularly the ones in the mountains. There is a general decline of PM<sub>10</sub> level between 1985 and 1993, but it is in the presence of substantial year to year variation (Figure 6-75b). The average PM<sub>10</sub> seasonality of the Phoenix-Tucson sub-region (Figure 6-75c) shows the bimodal spring and fall peak pattern which is characteristic for the entire Southwest region.

The wintertime aerosol chemical pattern in Phoenix was reported by Chow et al., 1990. Solomon and Moyers (1986). They found fine particle crustal species, sulfates, nitrates, and organic and elemental carbon to be at least five times higher in concentration when comparing samples during a haze episode to samples taken during good visibility.



### AIRS PM10 Concentration Trends

Phoenix-Tucson



### AIRS PM10 SEASONAL CONCENTRATION

Phoenix-Tucson

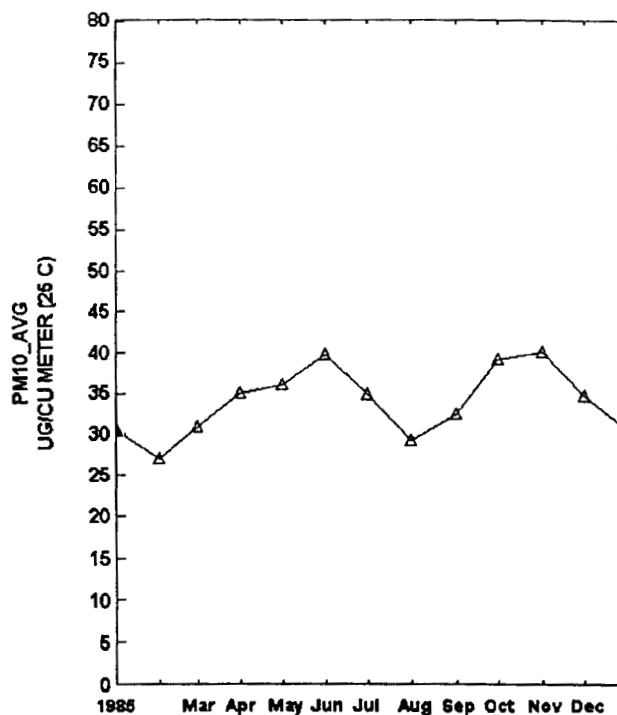


Figure 6-75.

Aerosol concentration pattern and trends in the Phoenix-Tucson subregion.

1 During the Phoenix Urban Haze Pilot Study during the winter 1988 to 1989 (Frazier  
2 C.A.,1989) a definite diurnal cycle in  $PM_{2.5}$  concentrations was observed. The maximum,  
3 generally but not always, occurred at night, which is consistent with the meteorological  
4 observations or poor dispersion and dilution.

5 A chemical characterization of wintertime fine particles in Phoenix, AZ (Solomon and  
6 Moyers, 1986) showed a dominance of organic and nitrate aerosols. The composition of the  
7 Phoenix wintertime haze is most like that of Denver, CO, a city which also experiences  
8 wintertime inversions (Pierson and Russell, 1969; Countess et al., 1980; Groblicki et al.,  
9 1981). In both cities the average measured  $NO_3^-$  concentrations was about 1 to 2 times that  
10 of average  $SO_4^{2-}$  concentration. In addition, the average  $SO_4^{2-}$  concentration measured in  
11 Phoenix was much lower than those observed at other locations throughout the US, but  
12 similar to the regional values observed in the Southwest (Moyers, 1981).

13 Wintertime  $PM_{10}$  and  $PM_{2.5}$  chemical compositions and source contributions in  
14 Tucson, AZ (Chow et al., 1992) show that the major contributors to the highest  $PM_{10}$   
15 concentrations were geological material (> 50%) and primary motor vehicle exhaust  
16 (> 30%) at three urban sampling sites. Secondary ammonium sulfate, secondary ammonium  
17 nitrate, and copper smelter aerosols were found to contribute less than 5% to elevated  $PM_{10}$   
18 concentrations.

19 It is instructive to compare chemical concentrations in Phoenix with wintertime values  
20 in other mountainous, arid communities (Denver (commercial), CO, Reno (commercial),  
21 NV, and Sparks (residential), NV. Organic carbon (OC) at the Phoenix site was twice the  
22 elemental carbon at the Denver and Sparks sites, while the OC/EC ratio was one to one at  
23 Phoenix and Reno sites. Wood burning contribution at Reno site was very low. The  
24 average arsenic concentrations in Phoenix was four times higher than observed in other  
25 cities, which indicates the potential influence of Arizona smelters located within 100 miles of  
26 Phoenix. Average sulfate levels in Phoenix were higher than they were in Denver, which  
27 has less local emissions of  $SO_2$ . Nitrates were major source of visibility reduction in  
28 Denver. In Phoenix, nitrates were significant, but the carbonaceous species appear to have  
29 much larger role in visibility impairment. The average light absorption ( $b_{abs}$  in Phoenix was  
30 nearly a factor of three higher than the averages obtained in Denver.

## 6.5.6 Sub-regional Aerosol Pattern in the Northwest

The mountainous northwestern United States has many aerosol regions with different characteristics. The discussion below will examine South Lake Tahoe, as a case study for mountain-valley difference, Salt Lake City, UT, Denver, CO, Idaho-Montana sites, and several Washington-Oregon sites.

Dresser 1988 investigated the winter  $PM_{10}$  concentrations in a small ski resort town, Telluride, CO and found that the street dirt and sand are major contributors, particularly during the dry post snow period.

Wintertime aerosol characterization and source apportionment was also conducted for San Jose, CA, attributing 45% of the  $PM_{10}$  mass to residential wood combustion (Chow et al., 1995).

In Portland, OR, carbonaceous aerosol was found to account for about 50% of fine aerosol mass (Shah et al., 1984)

### 6.5.6.1 South Lake Tahoe

South Lake Tahoe IMPROVE monitoring site is located in a in a populated area on the south shore of Lake Tahoe. The Bliss State Park IMPROVE monitoring site is to the northwest, elevated (700ft) and removed from the populated areas. The pair of sites illustrates the populate-remote difference in aerosol pattern. The aerosol and visibility at the two lake Tahoe sites were also examined (Molenar et al., 1994)

The concentration of all aerosol components is substantially higher on the south lake shore compared to the more remote site. The seasonality and chemical composition is also substantially different. The excess  $PM_{10}$  concentration at the S. Lake Tahoe site compared to Bliss State Park (Figure 6-76) is about  $5 \mu g/m^3$  during the warm season, May through September, and it climbs to  $28 \mu g/m^3$  excess in January. The factor of five seasonal modulation for valley excess  $PM_{10}$  is likely contributed by winter time emission sources, poor dispersion compared to the summer, as well as fog, that tend to enhance the aerosol formation. Fine and coarse particles contribute roughly equally to excess  $PM_{10}$  mass concentration. However, fine particles contribute about 60% during the fall season and coarse particles prevail (>60%) during the spring. Both fine and coarse particles show a

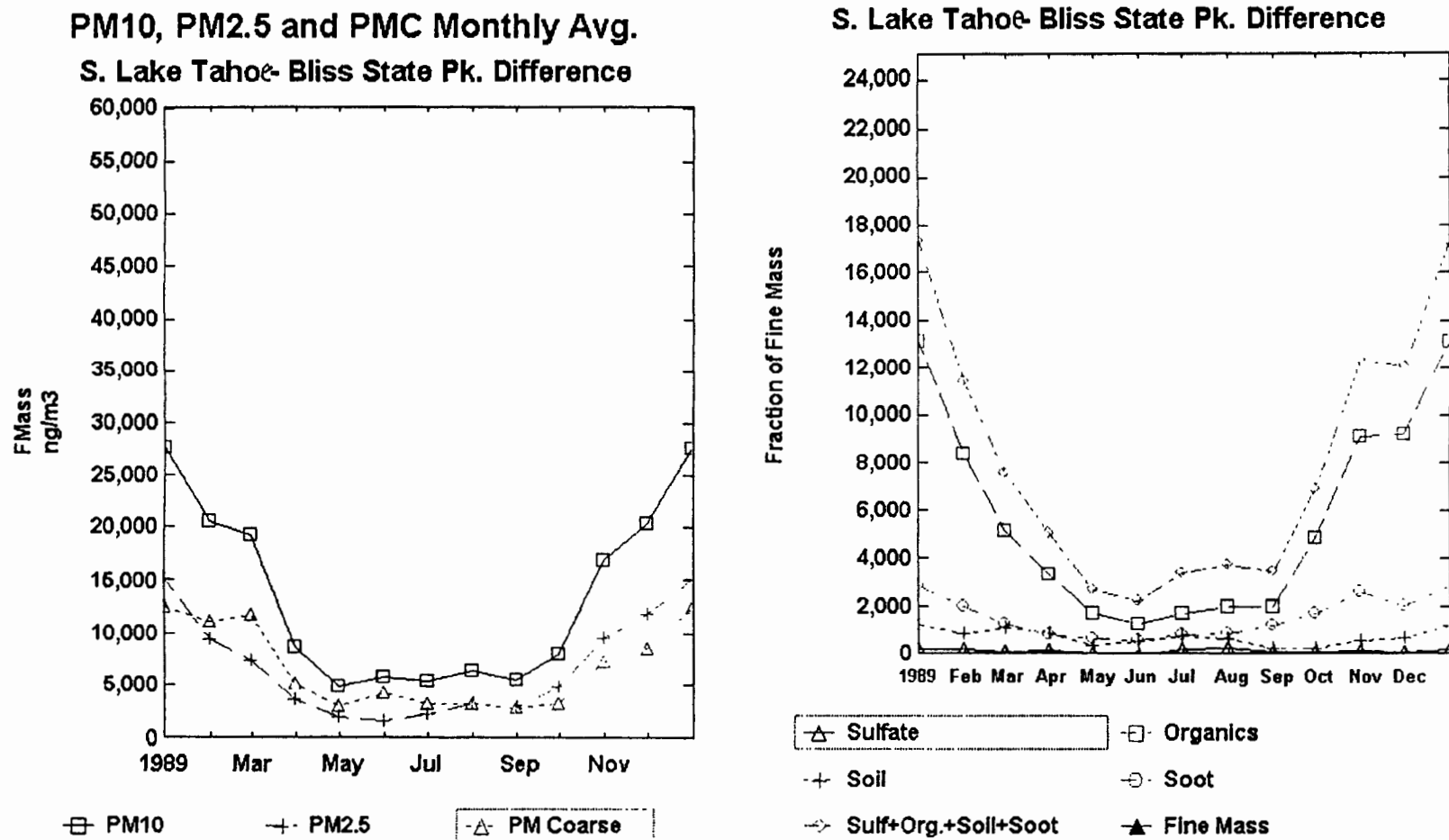


Figure 6-76. Excess aerosol concentration at South Lake Tahoe compared to Bliss State Park.

1 winter peak concentration. The chemical composition of the coarse mass is not known but  
2 both soil dust or the fine particle species are plausible.

3 The chemical composition of the valley excess fine particle mass concentration also  
4 shows a strong seasonality for organics and soot. In fact, the excess organics concentration  
5 in the winter ( $13 \mu\text{g}/\text{m}^3$ ) is almost an order of magnitude higher than the summer values.  
6 The seasonal concentration of excess fine particle soot is similar to that of the organics.  
7 However, the relative magnitude of winter organics compared to soot is higher in the winter  
8 (factor of five) than in the summer (factor of two). The concentration of fine particle sulfate  
9 is virtually identical for South Lake Tahoe and Bliss State Park. This implies that the South  
10 Lake Tahoe aerosol sources do not contain sulfur. It is also worth noting that the excess fine  
11 particle soil at South Lake Tahoe is below  $1 \mu\text{g}/\text{m}^3$ , which is a small fraction of the coarse  
12 mass. Thus, the crustal component of the South Lake Tahoe aerosol contributes to the  
13 coarse mass but not appreciably to the fine mass concentration.

14 In summary, there is a significant excess  $\text{PM}_{10}$  aerosol concentration S. Lake Tahoe  
15 compared to the adjacent Bliss State Park remote site, particularly during the winter season  
16 ( $28 \mu\text{g}/\text{m}^3$ ). The excess mass is about equally distributed between fine and coarse particles.  
17 The fine mass is largely composed of organics.

#### 18 19 **6.5.6.2 Salt Lake City, UT Sub-region**

20 Salt Lake City, Ogden, and Provo, UT are part of an airshed that is confined by tall  
21 mountains to the East, limiting the dispersion by westerly winds.

22 The seasonal average  $\text{PM}_{10}$  concentration at three AIRS sites in Salt Lake City,  
23 Ogden, and Provo, UT is shown in Figure 6-77b. All three sites show virtually identical  
24 seasonality, having peak concentrations during December through January. This confirms  
25 that the three sites belong to the same airshed with similar source pattern, meteorological  
26 dispersion and chemical transformation and removal processes.

27 The size segregated fine and coarse concentration data exhibit a dynamic seasonal  
28 pattern. Fine particles clearly dominate the high winter concentrations reaching 40 to  
29  $50 \mu\text{g}/\text{m}^3$ , compared to  $10 \mu\text{g}/\text{m}^3$  of summer values. This magnitude of fine mass  
30 concentration is among the highest recorded in the AIRS data system. Coarse particles are  
31 less seasonal and they are more important during the dry summer season. The formation of

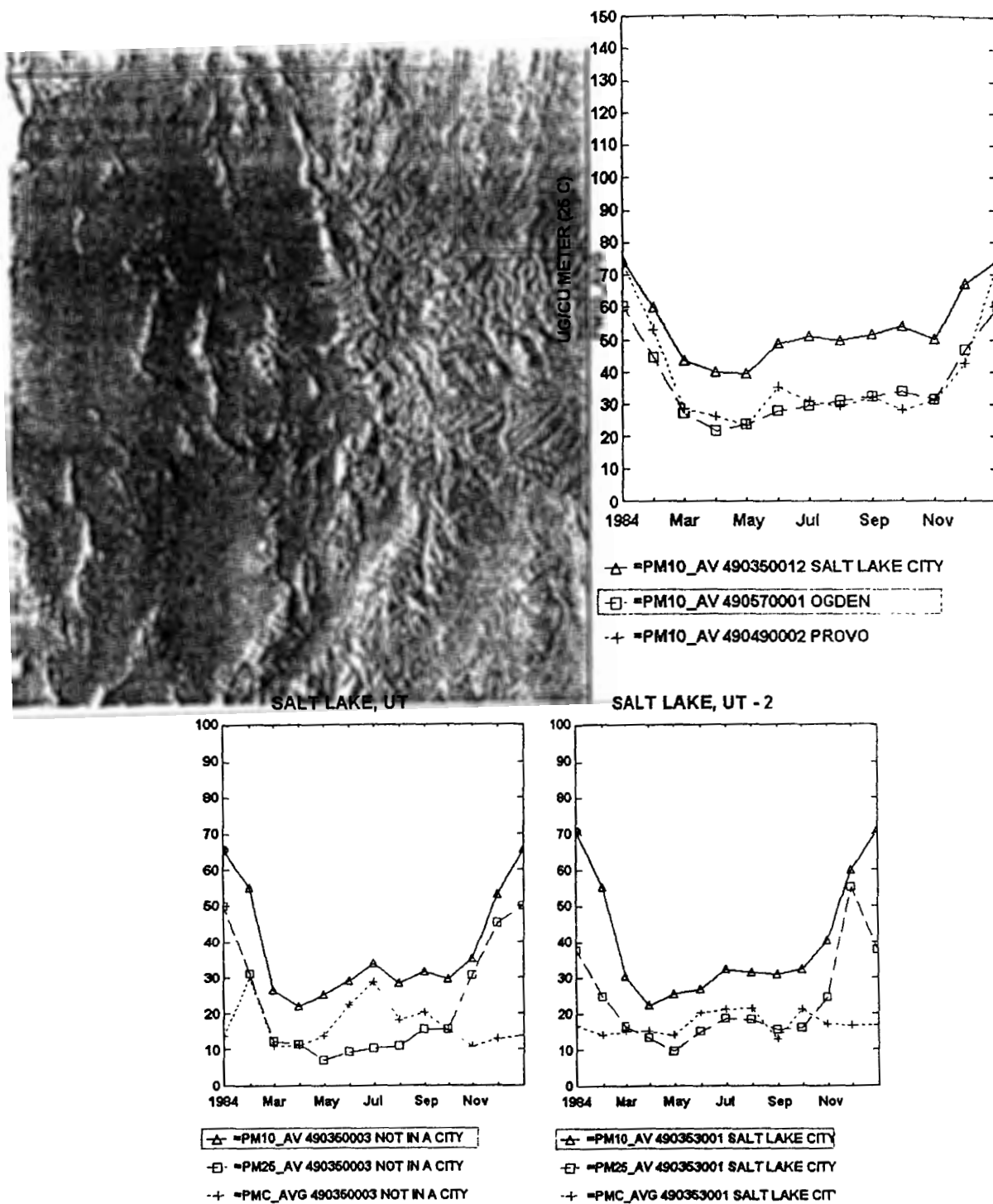


Figure 6-77. Aerosol concentration pattern near Salt Lake City.



sulfate and nitrate during winter inversion fogs near Salt Lake City, UT were studied by Mangelson et al., 1994.

#### 6.5.6.3 Denver, CO

The Denver “brown cloud” is a manifestation of high wintertime concentration of particles and gases. Several recent studies have focused on the characterization of the Denver brown cloud aerosols.

Size distribution measurements of winter Denver aerosol (Countess et al., 1981) show that on high pollution days that the MMAD of the accumulation mode aerosol was about  $0.31\text{ }\mu\text{m}$  with  $\sigma_g \pm 2.0$ . Wolff et al., 1980 found that on the average motor vehicles were responsible for 27% of the elemental carbon while wood burning was responsible for 39% of the elemental carbon.

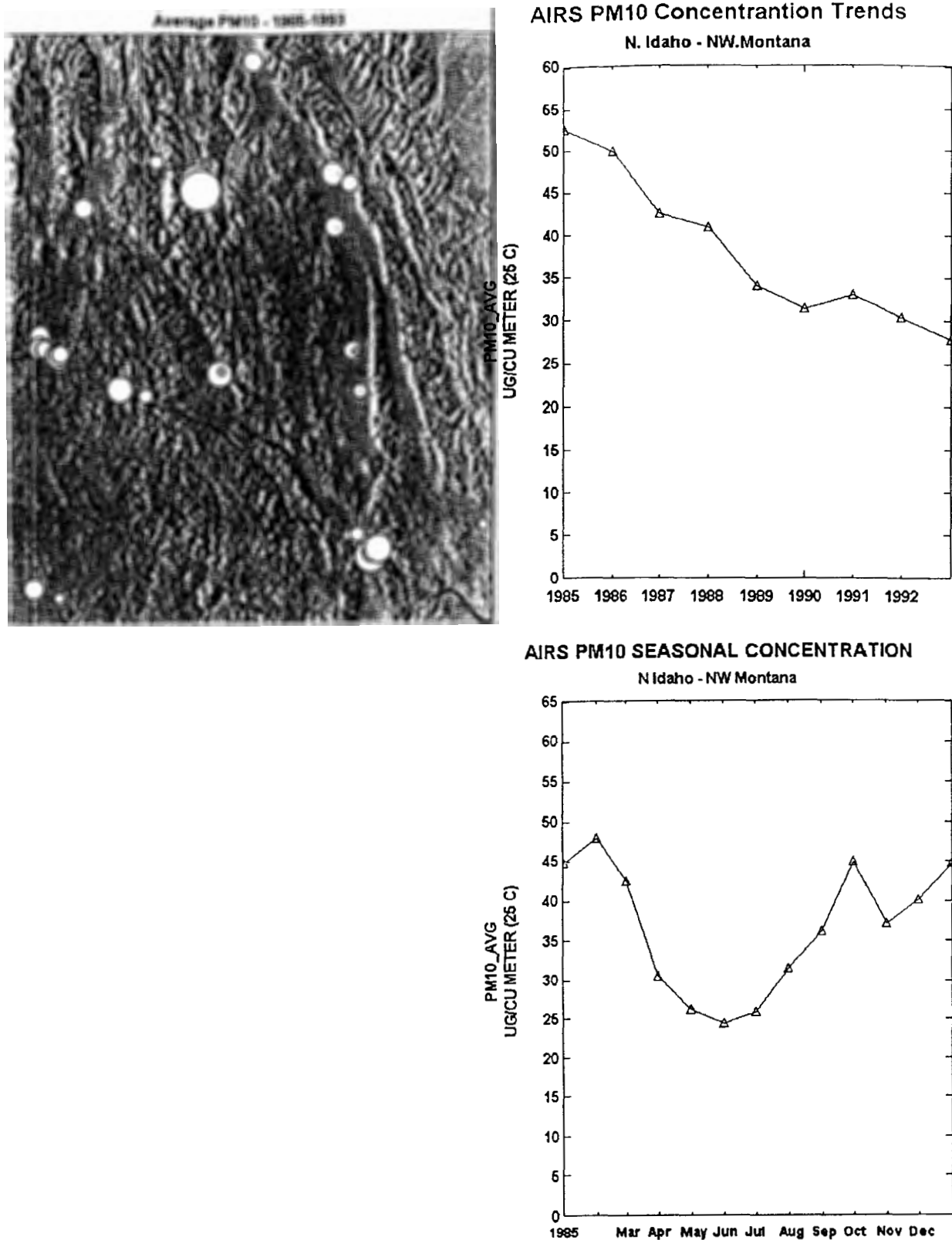
The chemical composition of wintertime Denver fine aerosol mass ( $16.4\text{ }\mu\text{g}/\text{m}^3$ ) (Sloane et al., 1991) shows the dominance of organic ( $8.1\text{ }\mu\text{g}/\text{m}^3$ ) and elemental carbon ( $2.6\text{ }\mu\text{g}/\text{m}^3$ ) over sulfate evidence that the fine particle sulfate and nitrates are bimodal, composed of  $0.2$  to  $0.3\text{ }\mu\text{m}$  and  $0.4$  to  $0.6\text{ }\mu\text{m}$  modes.

#### 6.5.6.4 Northern Idaho-Western Montana Sub-region

The mountainous northern Idaho and western Montana is characterized by deep valleys, absence of major industrial sources, or large urban-metropolitan areas. Nevertheless,  $\text{PM}_{10}$  monitoring sites in northern Idaho and western Montana report concentrations that are among the highest in the nation, as illustrated in Figure 6-78a, while adjacent sites are among the lowest. The large spatial concentration variability is evidently related to the rugged terrain. Most of the monitoring sites are located in the flat valleys.

The  $\text{PM}_{10}$  concentration trend (Figure 6-78b) is strongly downward, with a factor of two reduction (from  $54$  to  $27\text{ }\mu\text{g}/\text{m}^3$ ) between 1985 and 1993. The average seasonality of the sub-region is strongly winter peaked (Figure 6-78c) with a factor of two modulation between  $25$  and  $45\text{ }\mu\text{g}/\text{m}^3$ .

A typical example in northern Idaho (Figure 6-79a), where three adjacent sites show winter monthly averaged peak concentrations of  $50$  to  $85\text{ }\mu\text{g}/\text{m}^3$ . This is higher than the monthly average  $\text{PM}_{10}$  concentration anywhere in the eastern US.



**Figure 6-78.** Aerosol concentration pattern and trends in the N. Idaho-NW Montana subregion.

April 1995

6-134

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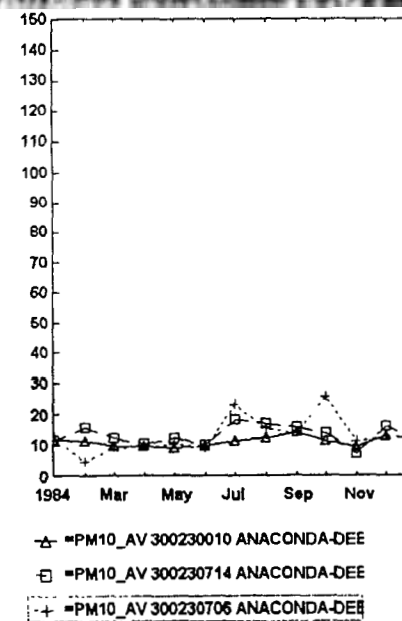
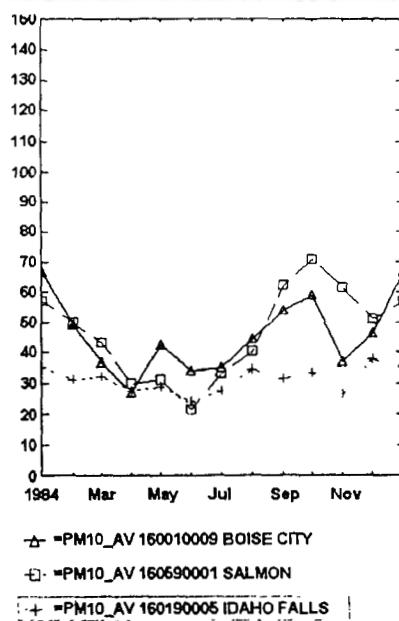
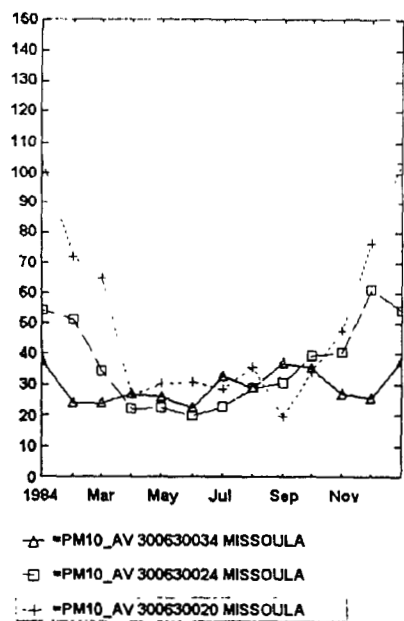
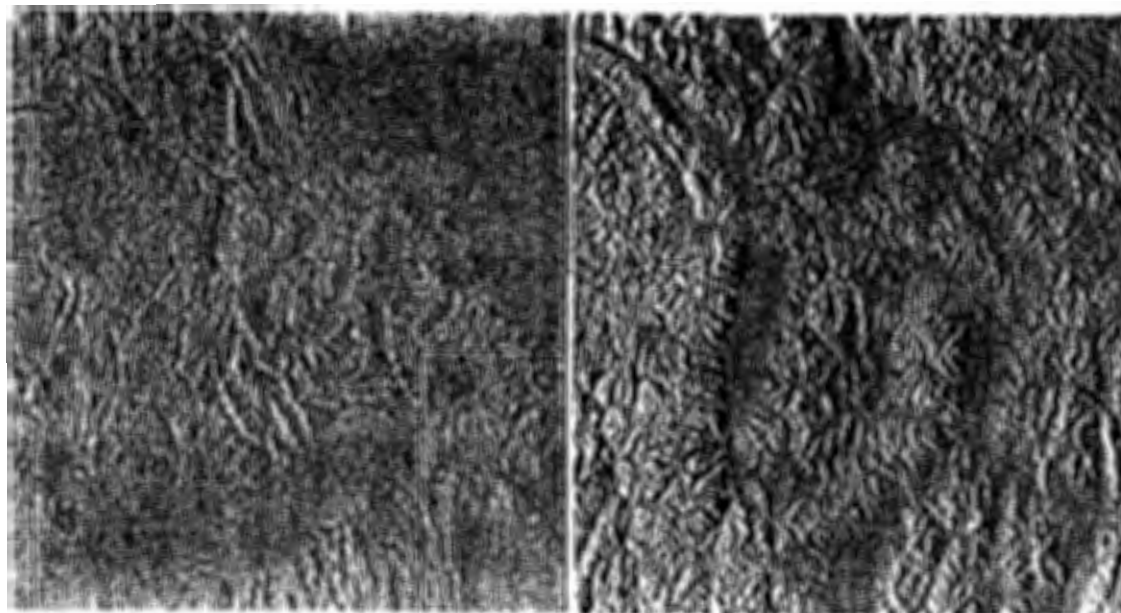
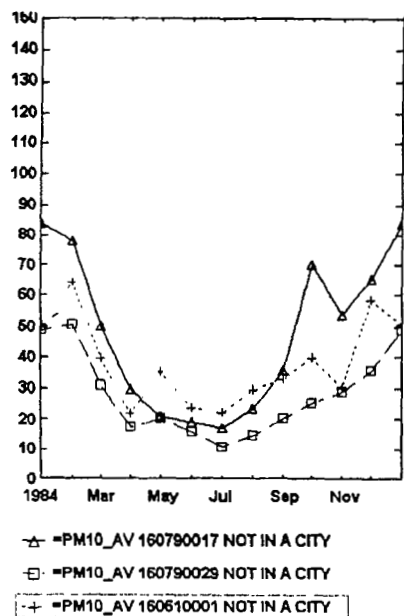


Figure 6-79. PM<sub>10</sub> concentration pattern at sites in N. Idaho-NW.

during December through February the concentrations are elevated to about  $50 \mu\text{g}/\text{m}^3$ . The third site (AIRS#300630034) shows the highest winter peak ( $> 100 \mu\text{g}/\text{m}^3$ ), but summer values that are comparable to the other two sites. The latter site is the closest to the city center. It is evident that in Missoula, MT high concentration gradients exist between the populated areas and remote sites. Boise and Salmon, ID (Figure 6-79e) also show elevated  $\text{PM}_{10}$  concentrations during the cold season. Idaho Falls, ID on the other hand, is seasonally uniform at about  $30 \mu\text{g}/\text{m}^3$ , which is comparable to the background (AIRS#300630020) Missoula, MT site.

Remarkably low  $\text{PM}_{10}$  concentrations of  $10 \mu\text{g}/\text{m}^3$  are reported at three  $\text{PM}_{10}$  monitoring sites near Anaconda-Deer, ID (Figure 6-79f). This is remarkable because the sites are in a valley, and that the characteristic winter peak is completely absent. This suggests that pristine, low,  $\text{PM}_{10}$  sites can exist in the northwestern valleys, and hence the region is not uniformly covered by wintertime haze or smoke.

#### **6.5.6.5 Washington-Oregon Sub-region**

The Pacific Northwest is also a mountainous sub-region that exhibits unique aerosol characteristics.  $\text{PM}_{10}$  monitoring sites in Seattle, Bellevue, and Tacoma, WA (Figure 6-80) show relatively low concentrations between 20 to  $40 \mu\text{g}/\text{m}^3$ , with the higher values occurring during the winter months. A much more pronounced seasonality of  $\text{PM}_{10}$  concentrations is recorded in southern Oregon, Medford, Grants Pass, and Klamath Falls, OR. These sites evidently belong to an airshed of which emissions, dispersion, and aerosol formation mechanisms are conducive for the formation of winter time aerosol ( $60$  to  $80 \mu\text{g}/\text{m}^3$ ).

Fine and coarse particle data collected over limited period in 1987 show that the winter peak of  $\text{PM}_{10}$  is entirely due to the strong winter peak of fine particle mass ( $50$  to  $100 \mu\text{g}/\text{m}^3$ ). Coarse mass, on the other hand, is seasonally invariant at about  $10$  to  $20 \mu\text{g}/\text{m}^3$ . Fine particles clearly are responsible for the winter peak. This is somewhat different from the observations at South Lake Tahoe, where the winter peak was attributed to both fine and coarse particles.

The size segregated aerosol data for Bend and Central Point, OR, show diminishing concentrations compared to Bedford, where the reduction of  $\text{PM}_{10}$  is mainly due to the decrease of the fine particle mass during the winter season.

April 1995

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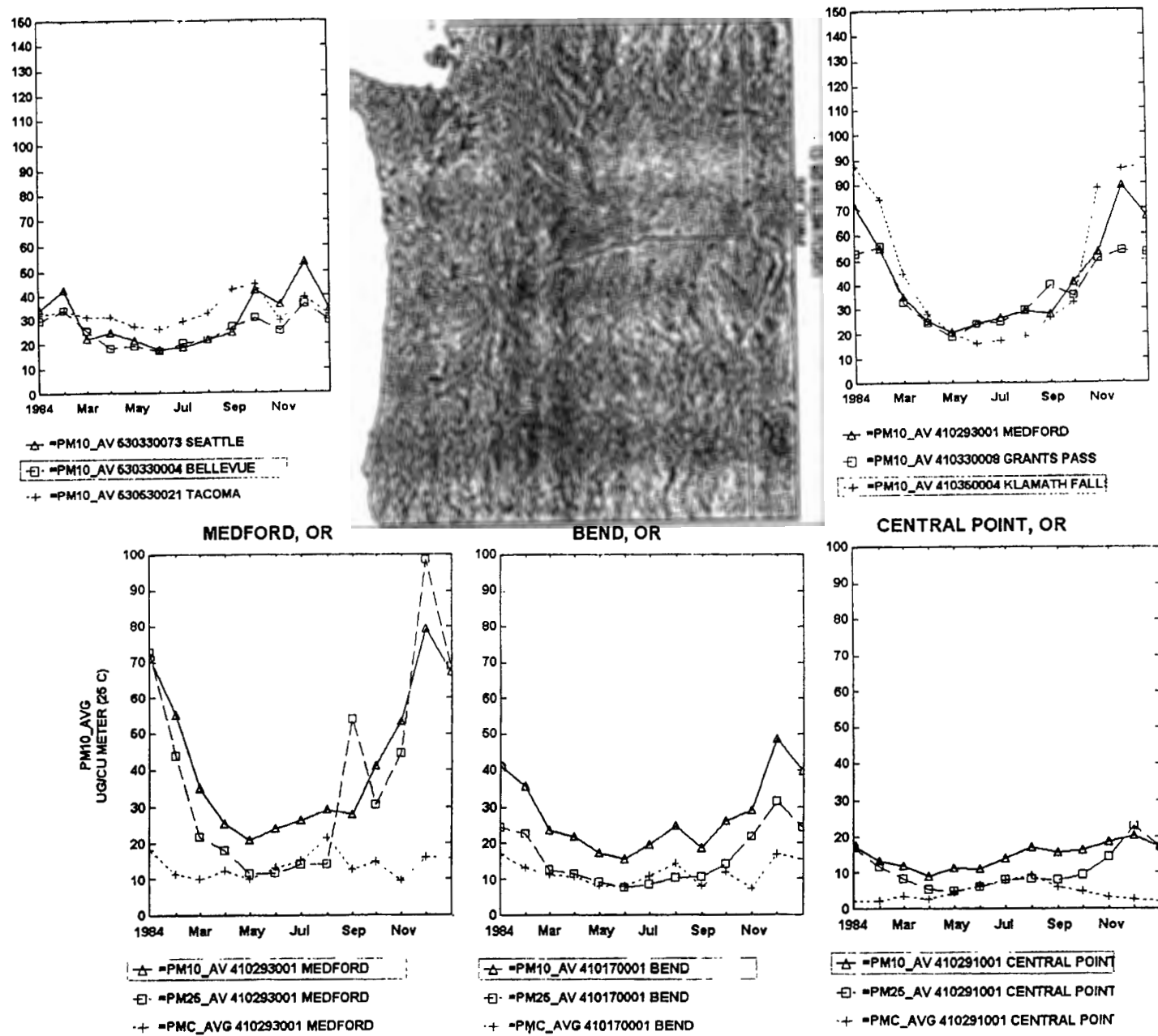


Figure 6-80. Aerosol concentration pattern in Washington State and Oregon.

## 6.5.7 Sub-regional Aerosol Pattern in the Southern California

The southern California region has two sub-regions, the San Joaquin Valley and the Los Angeles-South Coast Air Basin, discussed separately in sections below.

### 6.5.7.1 San Joaquin basin

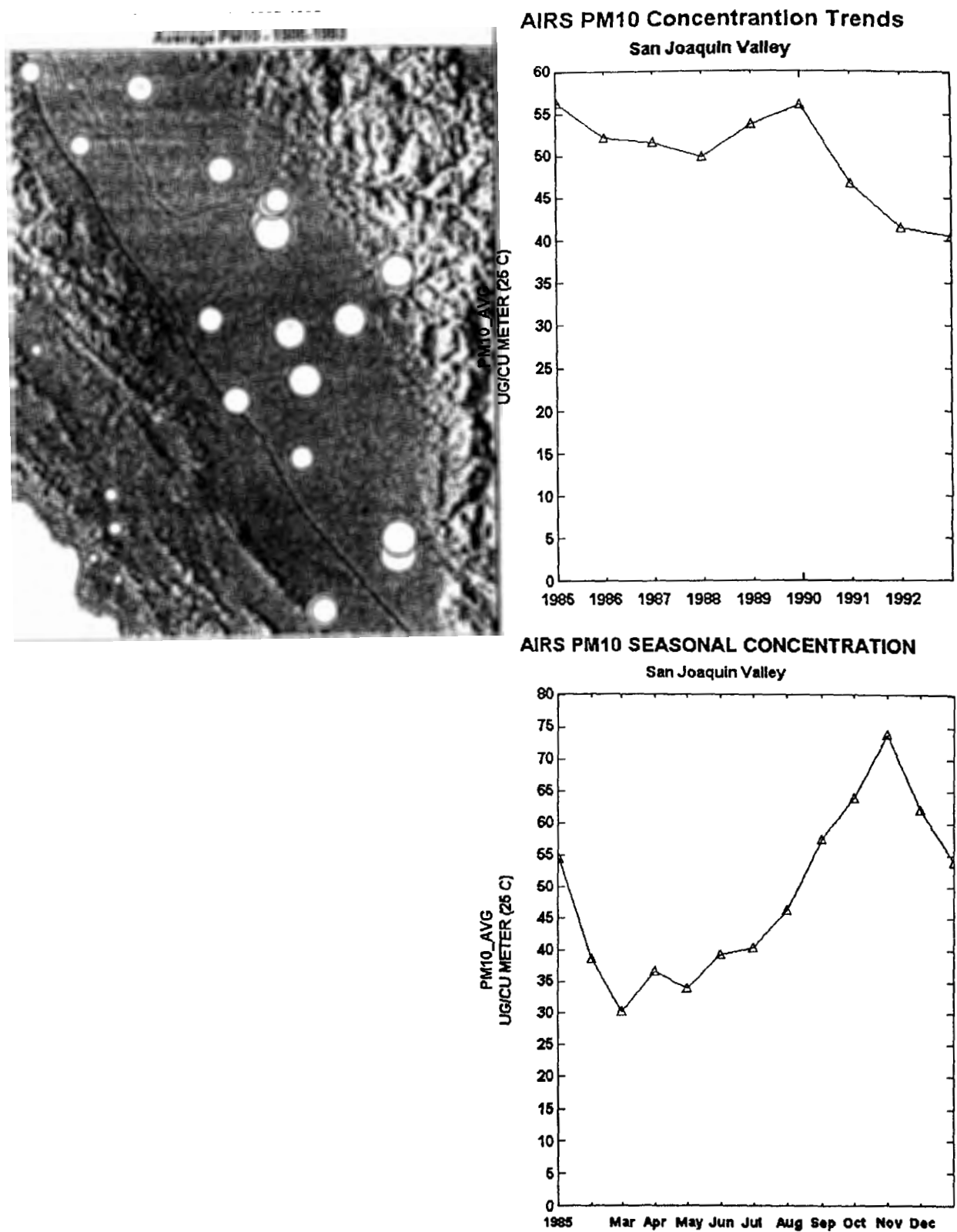
The wide air basin between the coastal mountain ranges of California to the west and the Sierra Nevada Mountains to the east shows a remarkably uniform  $PM_{10}$  concentrations as indicated on the map (Figure 6-81a).

There is evidence of  $PM_{10}$  concentration reduction from 55 to 40  $\mu g/m^3$ , but the trend is not conclusive (Figure 6-81b). The seasonal modulation amplitude over the San Joaquin Valley (Figure 6-81c) is about factor of 2.5 between the low spring concentration 30 to 35  $\mu g/m^3$ , and high fall concentration (60 to 70  $\mu g/m^3$ ). The unique feature of this seasonality is the fall peak which differs from the summer peak in the eastern United States and winter peak over the mountainous northwestern states.

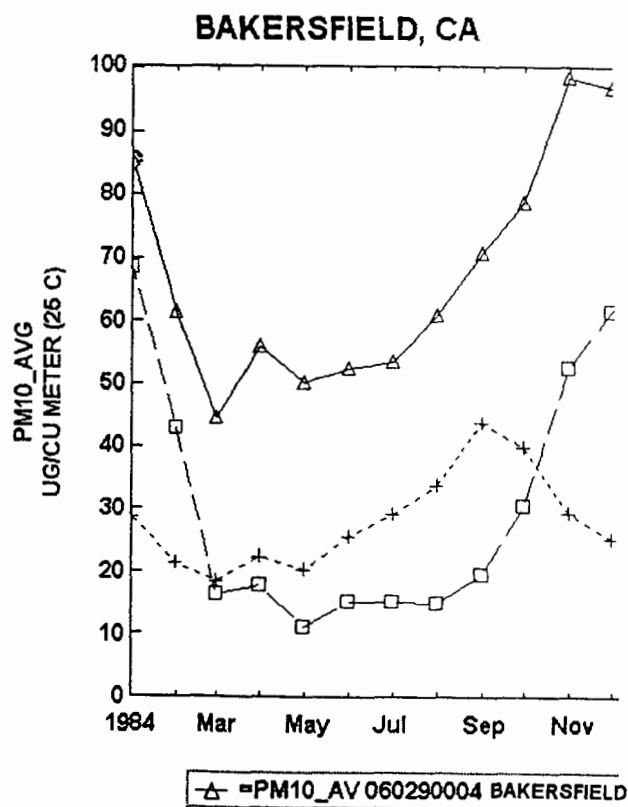
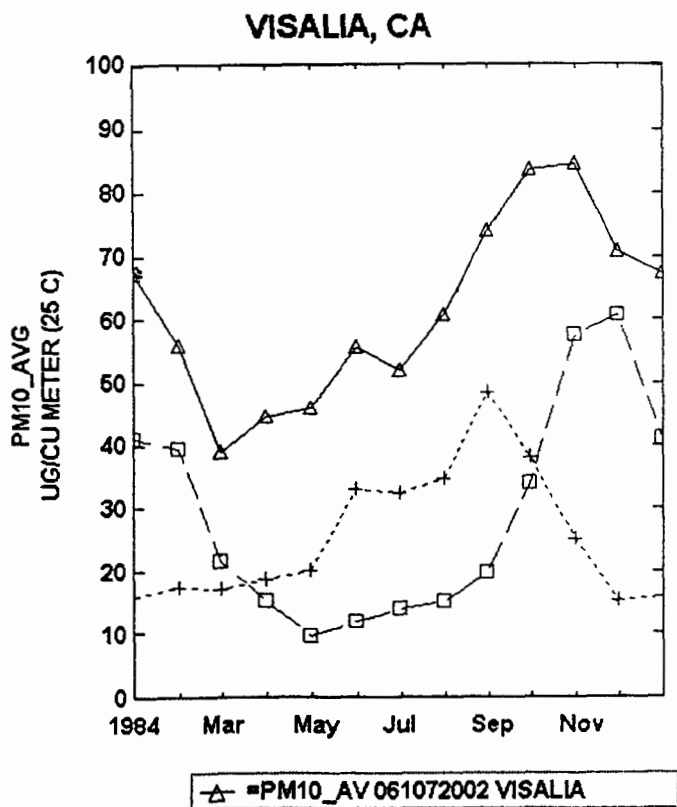
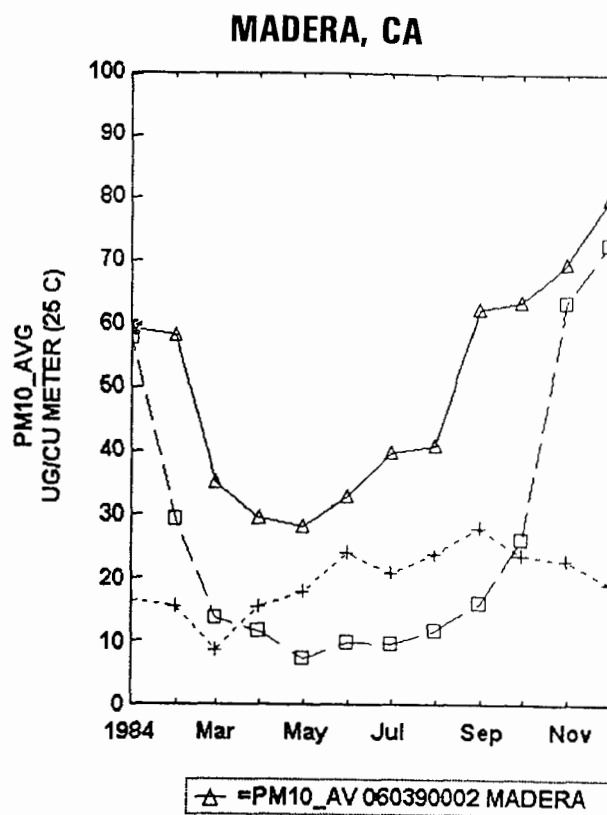
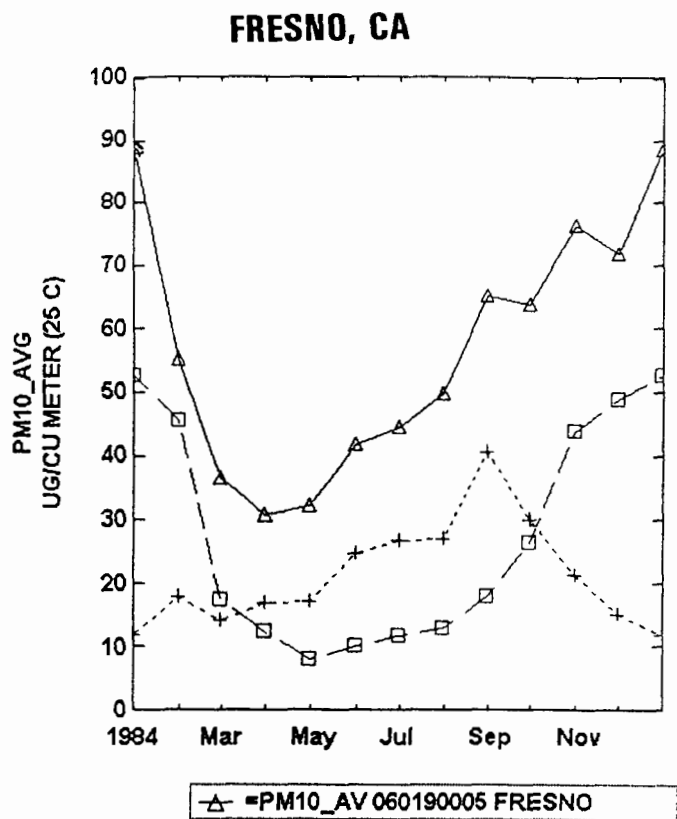
The AIRS database contains valuable size segregated fine and coarse particle concentration data within the San Joaquin Valley, as shown in Figure 6-82 for Fresno, Madera, Visalia, and Bakersfield, CA. These monitoring sites show virtually identical concentration pattern for fine and coarse mass. Both coarse and fine particles are important contributors to the San Joaquin Valley  $PM_{10}$  aerosol. However, their respective prevalence is phase shifted. Fine particles are most important during November through February winter season, while coarse particles prevail during June through November. As a consequence, in November, both coarse and fine particles are present causing the seasonal peak of  $PM_{10}$ . Conversely, during March through May, neither fine or coarse particles are abundant and the  $PM_{10}$  concentration is lowest during the spring season.

The temporal dynamics of the emissions, ventilation and aerosol formation in the San Joaquin Valley was a subject of detailed aerosol monitoring, and source apportionment studies.

The aerosol composition at non-urban sites (Chow et al., 1995) provide further characteristics of the central California aerosol pattern (Figure 6-82). A  $PM_{10}$  aerosol study was carried out at six sites in California's San Joaquin Valley from 14 June 1988 to 9 June 1989, as part of the 1988 to 1989 Valley Air Quality Study (VAQS). Concentrations of



**Figure 6-81. Aerosol concentration pattern and trends at San Joaquin Valley.**



**Figure 6-82. Fine, coarse and PM<sub>10</sub> concentration pattern in the San Joaquin Valley.**



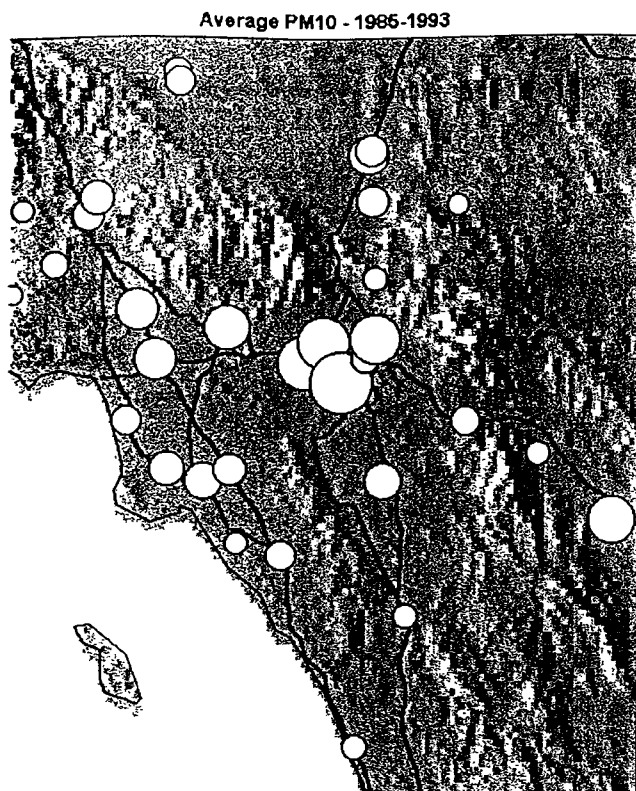
PM<sub>10</sub> and PM<sub>2.5</sub> mass, organic and elemental carbon, nitrate, sulfate, ammonium, and elements were determined in 24-h aerosol samples collected at three urban (Stockton, Fresno, Bakersfield) and three non-urban (Crows Landing, Fellows, Kern Wildlife Refuge) locations (Chow et al., 1993). The VAQS data indicate the federal 24-h PM<sub>10</sub> standard of 150 µg/m<sup>3</sup> was exceeded at four out of the six sites and for reasons which differ by season and by spatial region of influence. The annual average source contributions to PM<sub>10</sub> at Bakersfield, the site with the highest annual average, were 54% from primary geological material, 15% from secondary ammonium nitrate, 10 % from primary motor vehicle exhaust, 8% from primary construction, the remaining 4% is unexplained. The results of the source apportionment at all sites show that geological contributions dominate in summer and fall months, while secondary ammonium nitrate contributions derived from direct emissions of ammonia and oxides of nitrogen from agricultural activities and engine exhaust are largest during winter months. (Chow et al., 1992).

#### 6.5.7.2 Los Angeles-South Coast Air Basin

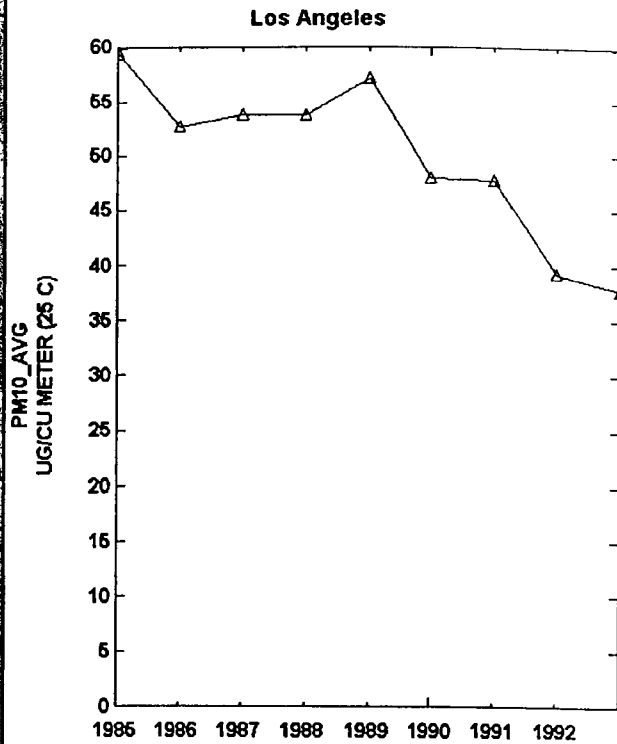
The Los Angeles basin is confined by the San Gabriel Mountains which limit the ventilation during westerly winds. Intensive emissions from automotive and industrial sources produce the notorious Los Angeles smog as a secondary photochemical reaction product of primary emissions. The map of the Los Angeles sub-region shows (Figure 6-83a) that the highest PM<sub>10</sub> concentrations are measured in the eastern half of the LA basin.

There has been a substantial reduction of sub-region average PM<sub>10</sub> concentration from 60 to 37 µg/m<sup>3</sup> from 1985 and 1993 (Figure 6-83b). The seasonality of the basin averaged PM<sub>10</sub> concentration shows a 50% amplitude, with the peak concentration (60 µg/m<sup>3</sup>) during October and the lowest values (40 µg/m<sup>3</sup>) during January through March (Figure 6-83c). Hence, this fall peaked seasonality is similar to the fall peak over the San Joaquin Valley.

Some unique characteristics of the Los Angeles basin are depicted in Figure 6-84. It shows that monitoring sites at different parts of the basin have markedly different seasonal concentration pattern. Hawthorne, near the Pacific Coast and Burbank in an inland valley have the highest concentration in late fall (November through January). On the other hand, Rubidoux in the eastern part of the basin exhibits the highest concentration in the late summer, July through October. It is likely, that the main cause of different seasonalities can



### AIRS PM10 Concentration Trends



### AIRS PM10 SEASONAL CONCENTRATION

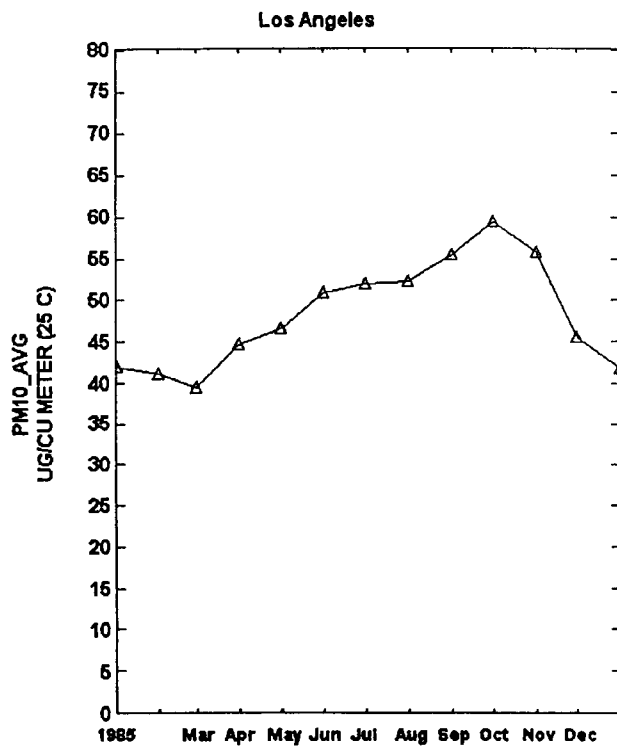


Figure 6-83. Aerosol concentration pattern and trends at Los Angeles.

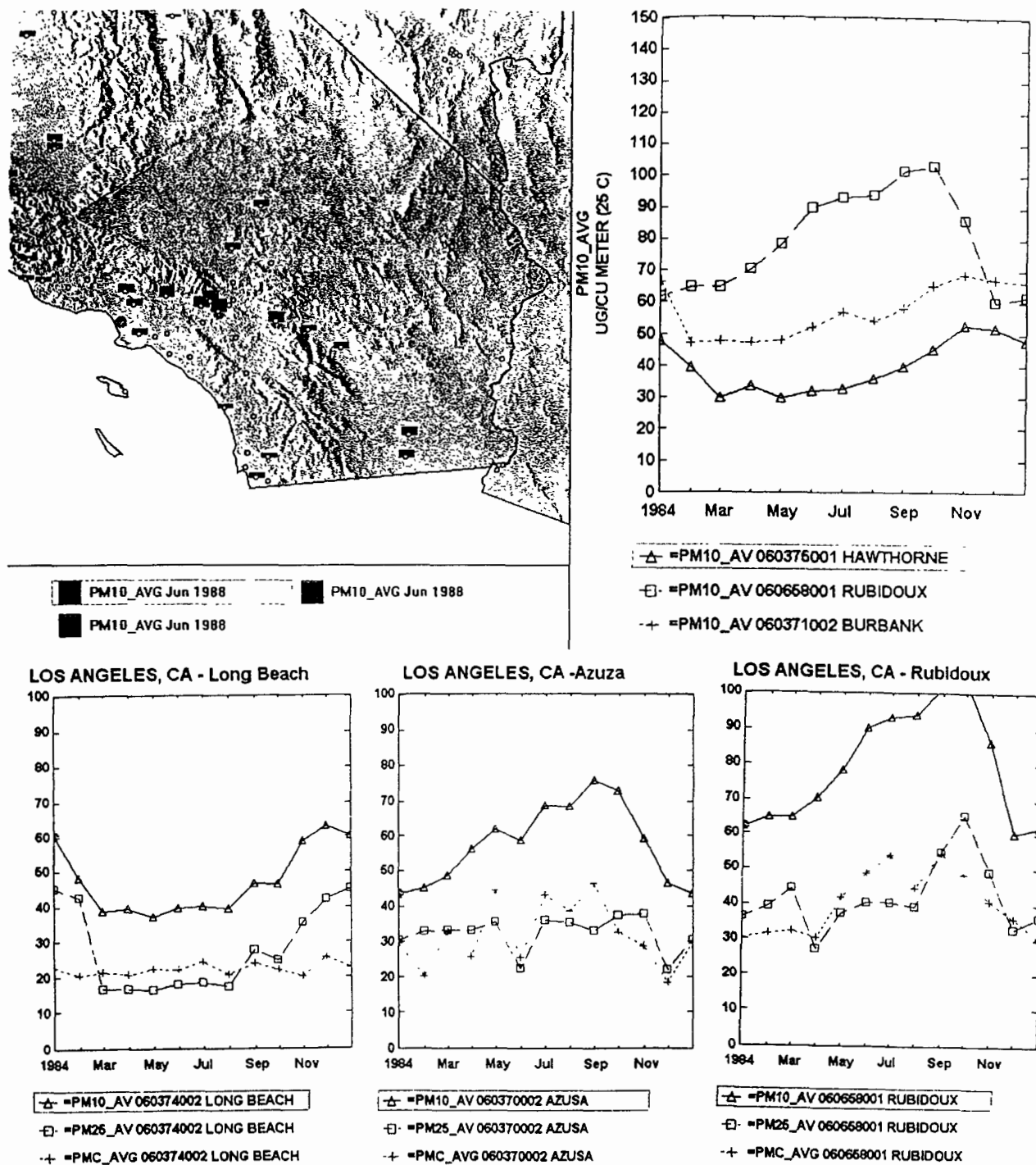


Figure 6-84. Fine, coarse and PM<sub>10</sub> concentration pattern near Los Angeles.

1 be found in the seasonally varying meteorological, transport, and chemical transformation  
2 pattern, rather than of emissions. The role of coarse and fine particles in the Los Angeles  
3 basin is also illustrated in Figure 6-84. At Long Beach, near the coast (adjacent to  
4 Hawthorne), the concentration of fine particles dominate the  $PM_{10}$  during the November  
5 through February winter season ( $40$  to  $50 \mu\text{g}/\text{m}^3$ ). Coarse particles at Long Beach are  
6 constant throughout the year at about ( $20 \mu\text{g}/\text{m}^3$ ). The size segregated aerosol samples at  
7 Azusa and Rubidoux in the eastern part of the basin, both show a  $PM_{10}$  peak during  
8 September through October, although the concentration are higher at Rubidoux. At both  
9 sites fine and coarse particles contribute roughly equally to the high  $PM_{10}$  concentrations.  
10 Thus, the  $PM_{10}$  aerosols over the smoggiest parts of the Los Angeles basin are not dominated  
11 by fine secondary aerosols but contributed by both fine and coarse particles.

12 The Los Angeles smog has been subject of extensive spatial, temporal, size and  
13 chemical composition studies even before the late 1960s (J. Colloid Interface Sci. (1972)  
14 volume 39, Hidy et al., 1980). More recently the LA aerosol characteristics have been  
15 further elucidated by Southern California Air Quality Study (SCAQS) (Watson et al., 1994;  
16 Chow et al., 1994; and other SCAQS studies).

17  $PM_{2.5}$  constituted one-half to two-thirds of  $PM_{10}$  at all sampling sites.  $PM_{10}$  mass  
18 concentrations were highest during the fall and were dominated by  $PM_{2.5}$ . Nitrate, sulfate,  
19 ammonium, and organic and elemental carbon were the most abundant species in the  $PM_{2.5}$   
20 fraction. The coarse particle fraction was composed of soil-related elements (e.g. aluminum,  
21 silicon, calcium, iron) at the inland sites and with marine-related elements (e.g. sodium,  
22 chloride) at the coastal sites. Average concentrations for most chemical compounds were  
23 higher during the fall than during the summer, except for sulfate which was more abundant  
24 in summer.  $PM_{2.5}$  nitrate and ammonium concentrations were negatively biased for daytime  
25 samples compared to nighttime samples, consistent with diurnal changes in temperature and  
26 the effect of these changes on the equilibrium between particulate ammonium nitrate and  
27 gaseous ammonia and nitric acid. (Chow et al., 1994).

28 *In situ*, time resolved analysis for aerosol organic and elemental carbon in Glendora,  
29 CA (Turpin et al., 1990) showed strong diurnal variations with peaks occurring the daylight  
30 hours. Comparison of the diurnal profile of organic carbon with those of elemental carbon  
31 provided evidence for the secondary formation of organic aerosol in the atmosphere. Turpin

1 et al., 1991 observed that secondary organic aerosol appears to have contributed roughly half  
2 of the organic aerosol in Pasadena during midday summer conditions.

3 Turpin and Huntzicker (1991) also found that the organic and elemental carbon  
4 concentrations exhibit strong diurnal variations. Peak concentrations occur during the  
5 daylight hours in the summer and at night in the fall. The maximum concentrations observed  
6 in the fall. The maximum concentrations observed in the fall (maximum total carbon,  
7  $88 \mu\text{g}/\text{m}^3$ ) were two to three times higher than the summer maxima (maximum total carbon,  
8  $36 \mu\text{g}/\text{m}^3$ ).

9 Gaseous nitric acid and fine particulate nitrate at Claremont, CA (Pierson and  
10 Brachaczek, 1988) both showed pronounced ( $\sim 10$  fold) diurnal variations, however coarse  
11 particles showed little diurnal variations.

12 Wolff et al., 1991 measured the smog aerosol pattern at Claremont, CA and Long  
13 Beach, CA, in the eastern and western Los Angeles basin, respectively. Claremont's air  
14 quality during the summer was characterized by high concentrations of photochemically  
15 produced pollutants including ozone, nitric acid, particulate nitrate, and particulate organic  
16 carbon (OC). The highest concentration of these species were experienced during the  
17 daytime sampling period (0600 to 1800) and were associated with transport from the western  
18 part of the basin. Long Beach' air quality during the fall was characterized by frequent  
19 periods of air stagnation that resulted in high concentrations of primary pollutants including  
20  $\text{PM}_{10}$ , OC and elemental carbon (EC) as well as particulate nitrate. Night -time levels of  
21 most constituents exceeded daytime levels due to poorer night-time dispersion conditions. At  
22 Claremont, OC and nitrate compounds accounted for 52% of  $\text{PM}_{10}$ , while at Long Beach  
23 they accounted for 67% of  $\text{PM}_{10}$ . On the average, there appears to be sufficient particulate  
24 ammonium to completely neutralize the nitrate and acidic sulfates.

25 Careful size distribution measurements in the Los Angeles basin (John et al., 1990)  
26 shed light on the size spectrum dynamics for ammonium, sulfate and nitrate. Three modes,  
27 two submicron and one coarse, were sufficient to fit all of the size distributions. The  
28 smallest mode, at  $0.2 \pm 0.1 \mu\text{m}$ , aerodynamic diameter, is probably a condensation mode  
29 containing gas phase reaction products. A larger mode  $0.7 \pm 0.2 \mu\text{m}$ , is defined as a droplet  
30 mode. Most of the inorganic particle mass was found in the droplet mode. The observed  
31 condensation and droplet modes characterize the overall size distribution in the 0.1 to  $1.0 \mu\text{m}$

range, previously described by Whitby and coworkers as a single accumulation mode (Whitby et al., 1972; Whitby, 1978). Wall et al., 1988 also found that in September 1985 at Claremont, CA fine particle nitrate was associated with ammonium, while coarse mode nitrate was associated with both ammonium and sodium. Sulfate was primarily in two submicrometer modes. Strong acid was associated with the smaller sulfate mode.

A clear demonstration of the effect of relative humidity and aerosol loading on atmospheric sulfate size distributions is given by Hering and Friedlander, 1982. Days of high relative humidity and aerosol loading correspond to high mass median diameters ( $0.54 \pm 0.07 \mu\text{m}$ ) for the sulfate while low relative humidity and low aerosol loadings correspond to small mass median diameters ( $0.2 \pm 0.02 \mu\text{m}$ ). According to their interpretation, the large ( $0.54 \mu\text{m}$ ) sulfate particles resulted from aqueous phase reactions of  $\text{SO}_2$ . The fine ( $0.2 \mu\text{m}$ ) sulfate resulted from homogeneous gas phase reactions leading to the nucleation of sulfuric acid particles.

McMurry and Stolzenburg, 1989 provide evidence that Los Angeles smog aerosols are externally mixed. Monodisperse ambient aerosols were often found to split into nonhygroscopic (nowater uptake) and hygroscopic portions when humidified. An average of 30% of the particles in the 0.2 to  $0.5 \mu\text{m}$  range were nonhygroscopic. However, the proportion of particles that were nonhygroscopic varied considerably from day to day and on occasions was 70 to 80% of the particles. The data show that for the hydrophilic aerosol, the larger particles ( $0.4$  to  $0.5 \mu\text{m}$ ) grew more when humidified than did smaller particles ( $0.05$  to  $0.2 \mu\text{m}$ ).

Murray and Zhang, 1989 reported the size distribution of ambient organic and elemental carbon near the Grand Canyon and in the Los Angeles basin. Virtually all of the carbon was found in the submicron range, some below  $0.1 \mu\text{m}$ . However, positive sampling artifacts for sub  $0.1 \mu\text{m}$  organics were considered significant.

At the Grand Canyon National Park, Zhang et al., 1994, showed that sulfates and carbonaceous particles were the major contributor to  $\text{PM}_{2.5}$  particle scattering during the three winter months and that their contributions were comparable. Scattering by nitrates and soil dust was typically a factor of five to ten smaller. The low pressure impactor measurements also showed that sulfur size distributions varies considerably ( $0.07$  to  $0.66 \mu\text{m}$ ).

1           Size distributions of aerosol phase aliphatic and carbonyl groups at Claremont, CA  
2 (Pickle et al., 1990) showed maxima in the 0.12 to 0.26  $\mu\text{m}$  and the 0.5 to 1.0  $\mu\text{m}$  size  
3 functions. For the aliphatic carbon absorbency, the ambient samples generally showed  
4 maxima in the 0.076 to 0.12  $\mu\text{m}$  size fraction. the authors attribute the carbonyl absorbance  
5 almost entirely attributed to products of atmospheric reactions and the aliphatic absorbencies  
6 in particles smaller than 0.12  $\mu\text{m}$  to automotive emissions.

7           Cahill et al., 1990 found that the sulfate aerosol size at Glendora, CA is smaller,  
8 0.33  $\mu\text{m}$  (MMD) during clear days compared to 0.5  $\mu\text{m}$  on smoggy days.

9           The size distributions of organic nitrate groups in ambient Los Angeles aerosol were  
10 typically bimodal (Mylonas et al., 1991). During periods of high photochemical activity, the  
11 maxima in the mass loadings were in the 0.05 to 0.075  $\mu\text{m}$  and the 0.12 to 0.26  $\mu\text{m}$  size  
12 fractions. During periods of low-moderate ozone concentrations in the distributions were  
13 shifted to slightly larger sizes, with maxima appearing in the 0.075 to 0.12  $\mu\text{m}$  and the 0.5 to  
14 1.0  $\mu\text{m}$  size fractions. A principal component analysis of the organonitrate loadings  
15 revealed strong correlations with ozone concentrations and with aerosol phase carbonyl  
16 loadings.

17           The analysis of coarse particles in Claremont, CA (Noll et al., 1990) show that the  
18 coarse particle mass could be divided into two categories: material that was primarily of  
19 crustal origin (Al, Ca, Fe, and Si) and material that was primarily of anthropogenic origin  
20 (Cd, Cu, Mn, Ni, Pb, and Zn). The mass of crustal material varied between 15 and 50% of  
21 the total coarse mass, while the mass of anthropogenic material was < 1%.

22           Chow et al., 1992 also conducted a neighborhood-scale study of  $\text{PM}_{10}$  source  
23 contributions in Rubidoux, CA elucidating the role of local soil dust.

24           The daily frequency distribution of the chemical components of the Los Angeles  
25 aerosol measured over a 1-year period were approximately lognormal (Kao and Friedlander,  
26 1994). For nonreactive aerosol components, the geometric standard deviation (GSD) is  
27 nearly constant at  $1.85 \pm 0.14$  even for components from different source types. An apparent  
28 bimodal frequency distribution for sulfates probably corresponds to the two differing reaction  
29 pathways by which gas-to-particle conversion occurs. However, the bimodal sulfate  
30 distribution function was not found at other Los Angeles sites (Kao and Friedlander, 1995).  
31 The authors suspect a relationship between GSD and the level of complexity of the stochastic

physical and chemical processes affecting the distributions of the individual species. They also point out that the chemical composition of the probable Los Angeles aerosol that corresponded to the peak in the (nearly) lognormal frequency distribution of the total mass is lower than the simple average chemical composition.

Twenty-four year (1958 to 1982) average elemental C concentrations at seven monitoring sites in the Los Angeles area are estimated to range from  $6.4 \mu\text{g}/\text{m}^3$  at downtown Los Angeles to  $4.5 \mu\text{g}/\text{m}^3$  at West Los Angeles. (Cass et al., 1984). At most monitoring sites studied, elemental C concentration were lower in recent years than during the late 1950s and early 1960s.

## **6.6 CHEMICAL COMPOSITION OF PM AEROSOLS AT URBAN AND NON-URBAN SITES**

This section summarizes available data for the composition of atmospheric particles in suburban, urban, and a few rural areas for comparison purposes. Emphasis has been placed on the Harvard six-city study and the inhalable particulate network (1980-1981). However, data for fine particle mass and elemental composition were available from these studies. Data for sulfate, nitrate, and elemental and organic carbon content are included from other studies to provide an overview of the chemical composition of the atmospheric aerosol in the United States. Tables, presented in Appendix 6A, provide relatively detailed representation of atmospheric properties of aerosols to which U.S. populations are exposed. Unfortunately, data this complete are generally collected over limited time periods and are not of sufficient duration to be useful for most epidemiological investigations. The tables do, however, provide insights as to the types of information that could be collected as part of future monitoring efforts in support of human exposure investigations.

A summary of all the aerosol sampling studies included in this compilation is given in Table 6A-1a and 6A-1b. Sampling studies have been grouped by geographical region roughly corresponding to the eastern, central and western U.S. Data are tabulated for the PM<sub>2.5</sub> ( $d < 2.5 \mu\text{m}$ ), the coarse fraction of PM<sub>10</sub> ( $2.5 \mu\text{m} < d < 10 \mu\text{m}$ ) and PM-10 ( $d < 10 \mu\text{m}$ ) size fractions of the ambient aerosol in Tables 6A-2a, 6A-2b, and 6A-2c. Compositional data for all size fractions were broken down into the following major components: sulfate, represented here as ammonium sulfate,  $(\text{NH}_4)_2\text{SO}_4$ ; carbon, as organic

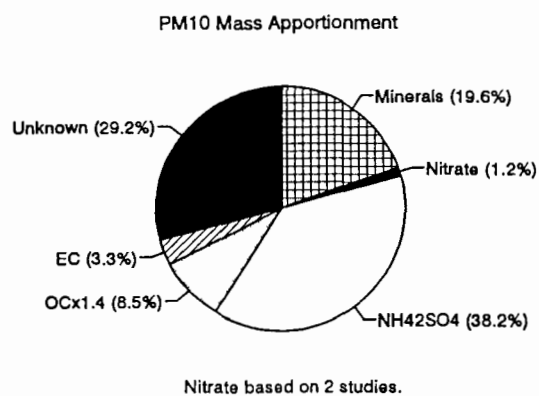
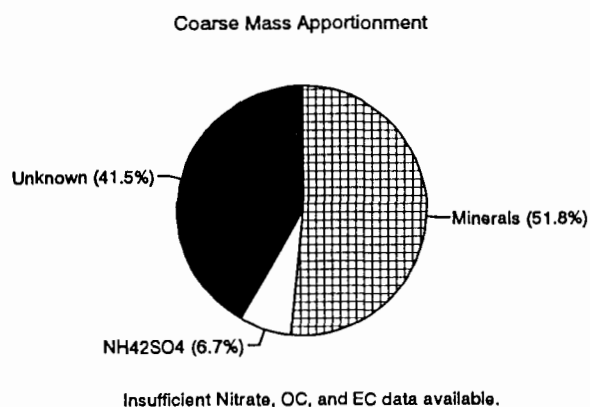
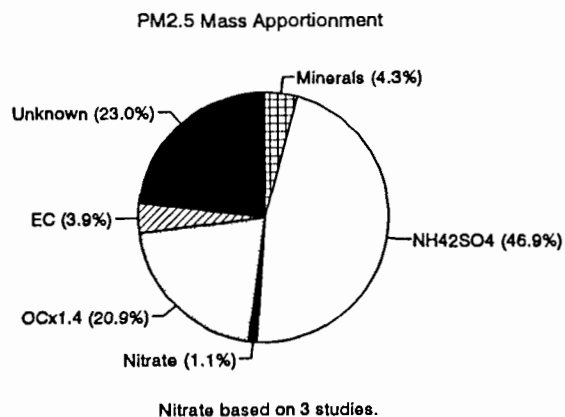


1 carbon ( $C_v$ ) which has been multiplied by a factor of 1.4 to account for the presence of  
2 oxidized species), and elemental carbon ( $C_e$ ); nitrate as  $NO_3^-$ ; and remaining trace elements  
3 which have been determined by XRF and or INAA. The masses of the trace elements from  
4 sodium through lead have been calculated by assuming they are in their most stable forms for  
5 conditions at the earth's surface. Reconstructed masses calculated in this way are shown by  
6 the entry, Sum, along with measured masses, and the ratio of the two are shown at the  
7 bottom of the individual summaries for each size fraction. Not all compositional categories  
8 were measured in the studies included in the Tables. The data are shown in graphical form  
9 in Figures 6-85a, 6-85b, and 6-85c.

10 As can be seen from inspection of Figure 6-85a for the eastern U.S., sulfate is the  
11 major identified component of mass for fine particles (46.9%), followed by carbon (24.8%),  
12 minerals (4.3%), and nitrate (1.1%). However, this last inference is based on only two  
13 studies in which nitrate was measured. Coarse particles are seen to consist mainly of mineral  
14 forming elements (51.8%) and sulfate (6.7%). Not enough data were available to determine  
15 abundances of carbon species and nitrate in the coarse fraction. A sizable fraction of both  
16 the fine (23.0%) and coarse (41.5%) particle mass is shown as unknown. This unknown  
17 mass is assumed to be mainly water, either bound as water of hydration or associated with  
18 hygroscopic particles. A small fraction of the mass, especially in the coarse fraction, may be  
19 present as carbonates. Carbonates are difficult to quantify, in part because of artifact  
20 forming reactions on filters with atmospheric  $CO_2$ . Stable carbonates can be identified by  
21 SEM, especially in regions where they are known to represent a substantial fraction of soil  
22 composition.

23 Fine particles in the central U.S. (Figure 6-85b) are seen to consist mainly of sulfate  
24 (37.9%) and minerals (9.4%) and elemental and organic carbon (66.1%) abundances. The  
25 reconstructed mass percentages sum to more than 100%. This is probably because of an  
26 overestimation of the carbon content which was based on only a few samples collected during  
27 winter in woodsmoke impacted areas. Coarse particles were found to consist mainly of  
28 minerals (62.8%), sulfate (4.2%) and an unknown fraction (33.0%). No nitrate or carbon  
29 data were available for the coarse fraction from the studies in the central U.S. However,  
30 during the spring and fall pollen becomes a significant fraction of the coarse particle  
31 composition.

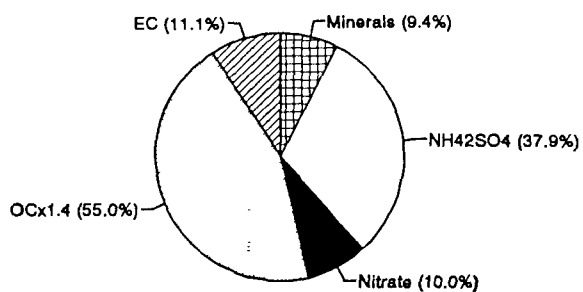
## EASTERN U.S.



**Figure 6-85a. Mass apportionment: Eastern U.S.**

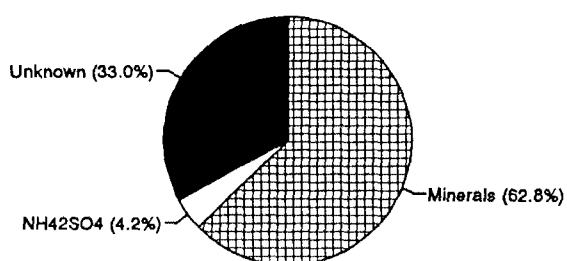
## CENTRAL U.S.

### PM2.5 Mass Apportionment



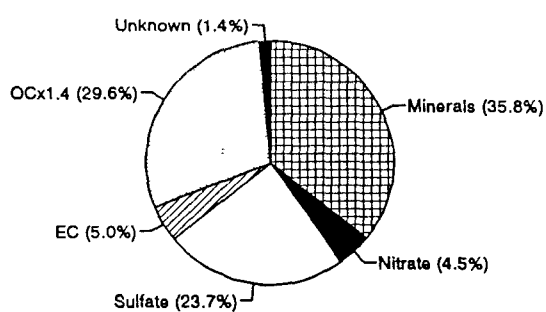
Reconstructed sum = 123%

### Coarse Mass Apportionment



Insufficient Nitrate, OC, and EC data available.

### PM10 Mass Apportionment

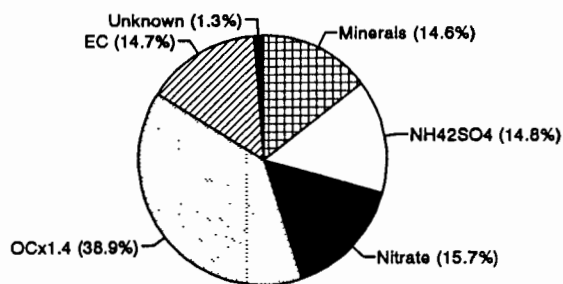


Nitrate based on 3 studies; OC and EC based on 4 studies.

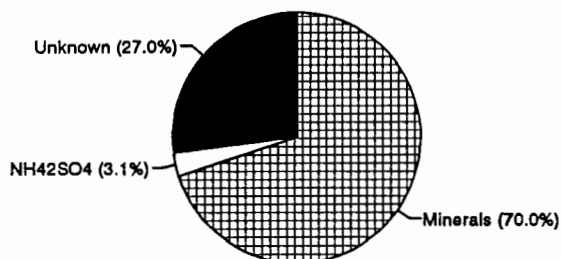
**Figure 6-85b. Mass apportionment: Central U.S.**

## WESTERN U.S.

PM2.5 Mass Apportionment

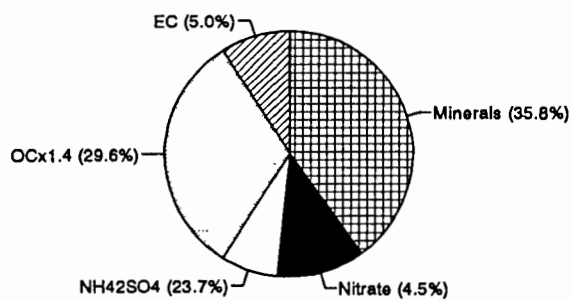


Coarse Mass Apportionment



Insufficient Nitrate, OC, and EC data available.

PM10 Mass Apportionment



Reconstructed sum = 106%

Figure 6-85c. Mass apportionment: Western U.S.

1 While gross fine particle composition appears to be broadly similar between the  
2 eastern and central U.S. on the basis of the few studies available, the fine particle  
3 composition is seen to be distinctly different in the western U.S. (Figure 6-85c). Elemental  
4 plus organic carbon species (53.6%) are the major identified component of mass, instead of  
5 sulfate (14.8%), and minerals and nitrate account for a larger fraction of total mass. While  
6 minerals are seen to account for most of the coarse particle mass (70.0%), insufficient data  
7 were available for elemental and organic carbon species to estimate their contributions to the  
8 coarse mass. Table 6A-3 shows a comparison of selected ratios of mass components for  
9 each of the three geographical regions of the U.S.

10 Many of the studies listed in Table 6A-3 involved data collected at more than one site  
11 within an airshed. Information about the variability of particle mass within an airshed can  
12 yield information about the nature of sources of the particles. The variability of mean  
13 concentrations measured at multiple sites within a study area is used as a measure of the  
14 intersite variability in fine particle composition and is shown in Table 6A-4.

15 Data for the chemical composition of the ambient aerosol has been summarized from  
16 the Harvard six-city study, the inhalable particle (IP) network and for a number of other  
17 studies around the country. As can be seen from inspection of the tables, data are not  
18 available to characterize the carbon or nitrate content of the ambient aerosol for many of the  
19 studies listed. Over the past 15 years woodstove emissions have become a significant  
20 contributor to fine particle mass during the winter (Stevens 1990).

## 23 **6.7 ACID AEROSOLS**

### 24 **6.7.1 Introduction**

25 Acid aerosols are secondary pollutants formed primarily through oxidation of sulfur  
26 dioxide ( $\text{SO}_2$ ), a gas emitted by the combustion of fossil fuels. Oxidation of  $\text{SO}_2$  forms  
27 sulfate ( $\text{SO}_4^{=}$ ), the major component of acid aerosols. Sulfate is formed to a lesser extent  
28 through the oxidation of sulfur species ( $\text{H}_2\text{S}$  and  $\text{CH}_3\text{SCH}_3$ ) from natural sources. The  
29 oxidation of  $\text{SO}_2$  occurs through a series of heterogeneous (gas-particle) or homogeneous (gas  
30 or aqueous) phase oxidation reactions that convert  $\text{SO}_2$  to sulfuric acid ( $\text{H}_2\text{SO}_4$ ) particles.  
31 The sulfate species are typically expressed in terms of total  $\text{SO}_4^{=}$ , with the acidic fraction

expressed in terms of titratable  $H^+$  and referred to as aerosol strong acidity.  $H^+$  is found in the fine particle size fraction (aerodynamic diameter ( $D_p$ )  $< 1.0 \mu m$ ) (Koutrakis and Kelly, 1993). Although recent research has shown a high correlation between  $SO_4^{=}$  and acidity, data from summertime sampling have shown that  $SO_4^{=}$  is not always a reliable predictor of  $H^+$  for individual events at a given site (Lipfert and Wyzga, 1993).

A major determinant of the lifetime of  $H^+$  in the atmosphere is the rate of neutralization by ammonia ( $NH_3$ ). Ammonia reacts with  $H_2SO_4$  to form ammonium sulfate  $[(NH_4)_2SO_4]$  and ammonium bisulfate ( $NH_4HSO_4$ ). The major sources of ammonia in the environment are animals and humans (Fekete and Gyenes, 1993). The then current state-of-knowledge regarding acid aerosols was reviewed by EPA in 1989 (U.S. Environmental Protection Agency, 1989) and Spengler et al. in 1990 (Spengler et al., 1990).

## 6.7.2 Geographical Distribution

In North America, ambient concentrations of  $H^+$  tend to be regional in nature with the highest concentrations found in the northeastern United States and southwestern Canada. Spengler et al. (1990) have collected information of maximum values of  $SO_4^{=}$  and  $H^+$  found across the U.S. and southern Canada. This information is shown in Table 6-3. Recent research has shown that regional transport is important to acid sulfate concentrations, as elevated levels of ambient  $H^+$  were measured simultaneously during a regional episode at multiple sites located from Tennessee to Connecticut (Keeler et al., 1991). It is commonly believed that the source region for most of the  $H^+$  precursors (primary inorganic pollutant gases —  $SO_2$  and  $NO_x$ ) is the Ohio River Valley (Liroy et al., 1980). The conversion of the primary gases to secondary pollutants takes place as the prevailing winds carry the precursors from the source region, northeastward to the northeastern United States and southwestern Canada. This type of northeasterly wind flow occurs on the backside (western side) of mid-latitude anti-cyclones (high pressure systems).

**TABLE 6-3. MAXIMUM  $\text{SO}_4^{2-}$  AND  $\text{H}^+$  CONCENTRATIONS MEASURED IN NORTH AMERICAN CITIES.  $\text{H}^+$  CONCENTRATIONS EXPRESSED AS " $\text{H}_2\text{SO}_4$ " EQUIVALENTS. "SC" INDICATES SEMI-CONTINUOUS MEASUREMENTS**

Location	Sample Duration (h)	Maximum Concentration	
		$\text{SO}_4^{2-}$ ( $\mu\text{g}\cdot\text{m}^{-3}$ )	$\text{H}_2\text{SO}_4$ ( $\mu\text{g}\cdot\text{m}^{-3}$ )
Lennox, CA	2-8	18	0.1
Smoky Mountains	12	17	10
High Point, NJ	6	37	18
Brookhaven, NY	3	24	10
Tuxedo, NY	1-12	41	9
St. Louis, MO	SC	25	7
St. Louis, MO	SC	43	34
Los Angeles, Ca	12	10	3
Harriman, TN	SC	47	18
Watertown, MA	SC	31	14
Fairview Lake, NJ	SC,4	27	12
Warren, MI	24	37	9
Whiteface Mt., NY	24	59	14
Toronto, Ontario, Canada	8,16	75	19
Allegheny Mt., PA	7,10	45	31
Laurel Mt., PA	7,10	56	42
Harriman, TN	24	28	14
St. Louis, MO	24	40	6
Topeka, KS	24	14	3
Watertown, MA	24	23	9
Steubenville, OH	24	56	18
Portage, WI	24	33	4
Kanawha Valley, WV	24	46	22
Dunville, Ontario, Canada	24	31	15
Hendersonville, TN	24	23	11
Livermore, CA	24	9	2
Morehead, KY	24	23	14
Monroeville, PA	24	42	18
Pembroke, ON, Canada	24	29	14
Springdale, AR	24	11	2
Newtown, CT	24	26	8
Allegheny Mt., PA	12	33	20
Uniontown, PA	12,24	52	39
State College, PA	12	47	25
Philadelphia, PA	24	39	9
Pittsburgh, PA	6,24	27	15

### 6.7.3 Spatial Variation (City-scale)

A study of acid aerosols and ammonia (Suh et al., 1992) found no significant spatial variation of  $\text{H}^+$  at Uniontown, Pennsylvania, a suburb of Pittsburgh. Measurements at the central monitoring site accounted for 92% of the variability in outdoor concentrations measured at various homes throughout the town. There was no statistical difference ( $p > 0.01$ ) between concentrations of outdoor  $\text{H}^+$  among five sites (a central site and four satellite sites) in Newtown, Connecticut (Thompson et al., 1991). However, there were differences in peak values which were probably related to the proximity of the sampling sites to ammonia sources. These studies suggest that long-term averages should not substantially differ across a suburban community, although peak values may differ significantly.

In small suburban communities outdoor concentrations of  $\text{H}^+$  are fairly uniform, suggesting that minor differences in population density do not significantly affect outdoor  $\text{H}^+$  or  $\text{NH}_3$  concentrations (Suh et al., 1992). In urban areas, however both  $\text{H}^+$  and  $\text{NH}_3$  exhibit significant spatial variation. Waldman et al. (1990) measured ambient concentrations of  $\text{H}^+$ ,  $\text{NH}_3$ , and  $\text{SO}_4^-$  at three locations in metropolitan Toronto. The sites, located up to 33 km apart, had significant differences in outdoor concentrations of  $\text{H}^+$ . Waldman and co-workers reported that the sites with high  $\text{NH}_3$  measured low  $\text{H}^+$  concentrations. However, the limited number of sampling sites did not allow for a conclusive determination of the relationship between population density, ammonia concentrations, and concentrations of acid aerosols.

An intensive monitoring study has been conducted during the summers of 1992 and 1993 in Philadelphia (Suh et al., 1994a). Twenty-four hour measurements of aerosol acidity ( $\text{H}^+$ ) sulfate and  $\text{NH}_3$  were collected simultaneously at 7 sites in metropolitan Philadelphia and at Valley Forge, 30 km northeast of the city center. The researchers reported that  $\text{SO}_4^-$  was evenly distributed throughout the measurement area but  $\text{H}^+$  concentrations varied spatially within metropolitan Philadelphia. This variation was related to local  $\text{NH}_3$  concentrations and the local population density (Figure 6-86). The amount of  $\text{NH}_3$  available to neutralize  $\text{H}^+$  increased with population density, resulting in lower  $\text{H}^+$  concentrations in more densely populated areas. The extent of the spatial variation in  $\text{H}^+$  concentrations did not appear to depend on the overall  $\text{H}^+$  concentration. It did, however, show a strong inverse association with local  $\text{NH}_3$  concentrations.



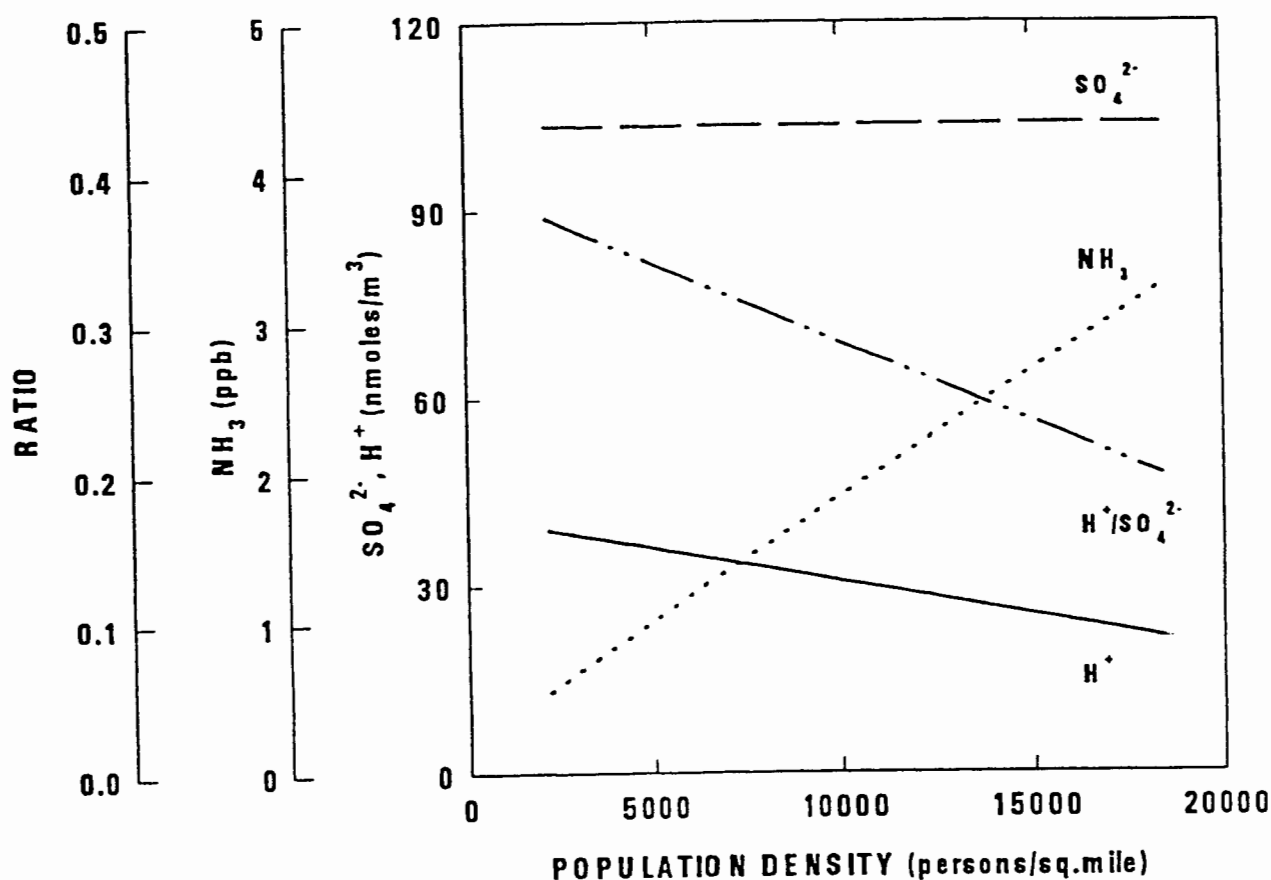


Figure 6-86. Mean air pollutant concentrations for days when winds were from the southerly direction plotted vs. population density. The solid line represents  $\text{H}^+$  concentrations; the long dashed line represents  $\text{SO}_4^{2-}$  concentrations; the dashed and dotted line represents the ration of  $\text{H}^+$  to  $\text{SO}_4^{2-}$  levels; and the dotted line represents  $\text{NH}_3$  concentrations. All data collected in Philadelphia, PA, during the summers of 1992 and 1993. Figure adapted from Suh et al. (1994a).

#### 6.7.4 Spatial Variation (Regional-scale)

Recent evidence has shown that meteorology and regional transport are extremely important to acid sulfate concentrations. Lamborg et al. (1992) measured  $\text{H}^+$  concentrations to investigate the behavior of regional and urban plumes advecting across Lake Michigan. Results suggested that aerosol acidity is maintained over long distances (up to 100 km or more) in air masses moving over large bodies of water. Lee et al. (1993) reported that  $\text{H}^+$

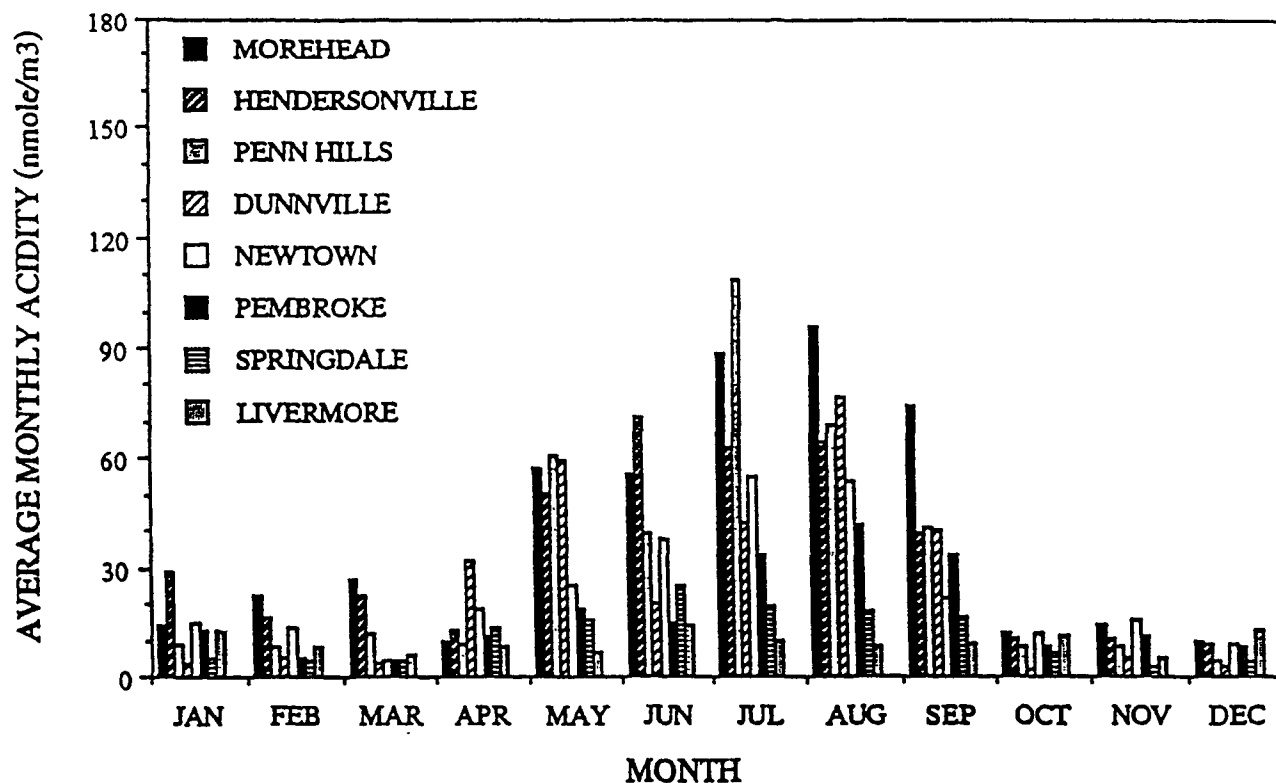
1 and  $\text{SO}_4^-$  concentrations measured in Chicago over a year were similar to levels measured in  
2 St. Louis. In an analysis of acid sulfate concentrations measured at Pittsburgh, State  
3 College, and Uniontown, Pennsylvania, Burton et al. (1995) reported high correlations for  
4  $\text{H}^+$  between all three locations. The three locations are separated by large distances  
5 (approximately 60 to 240 km) and have vastly different population densities.

### 6.7.5 Seasonal Variation

8 An analysis of results from Harvard's 24-city study (Thompson et al., 1991), which  
9 measured acid aerosols concentrations at 8 different sites across North America each year  
10 during a three year period, revealed that the summer  $\text{H}^+$  mean concentrations were  
11 significantly higher than the annual means at all sites. The results not only showed that at  
12 the sites with high  $\text{H}^+$  concentrations approximately two-thirds of the aerosol acidity  
13 occurred from May through September (Figure 6-87). Little or no seasonal variation was  
14 observed at sites with low acidity. These findings were supported by those of Thurston et al.  
15 (1992) in which  $\text{H}^+$  concentrations measured at Buffalo, Albany, and White Plains, New  
16 York were found to be highest during the summertime. Thurston and co-workers also  
17 reported that moderate concentrations of  $\text{H}^+$  could occur during non-summer months.

### 6.7.6 Diurnal Variation

20 Evidence exists of a distinct diurnal pattern in outdoor  $\text{H}^+$  concentrations. Wilson  
21 et al. (1991) examined concentration data for  $\text{H}^+$ ,  $\text{NH}_3$ , and  $\text{SO}_4^-$  from the Harvard 24-City  
22 Study for evidence of diurnal variability (Figure 6-88). This investigation found a distinct  
23 diurnal pattern for  $\text{H}^+$  concentrations and the  $\text{H}^+/\text{SO}_4^-$  ratio, with daytime concentrations  
24 being substantially higher than nighttime levels. Both  $\text{H}^+$  and  $\text{SO}_4^-$  concentrations peaked  
25 between noon and 6:00 pm. No such diurnal variation was found for  $\text{NH}_3$ . Wilson and co-  
26 workers concluded that the diurnal variation in  $\text{H}^+$  and  $\text{SO}_4^-$  was probably due to  
27 atmospheric mixing. Air containing high concentrations of  $\text{H}^+$  and  $\text{SO}_4^-$  mix downward  
28 during daylight hours when the atmosphere is unstable and well-mixed. During the night,  
29 ammonia emitted from ground-based sources neutralize the acid in the nocturnal boundary  
30 layer, the very stable lower part of the atmosphere, but a nocturnal inversion prevents the

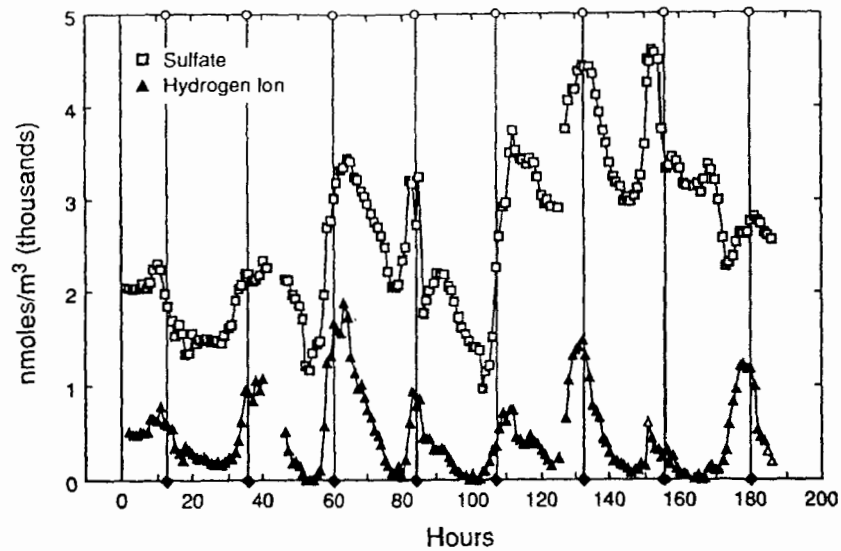


**Figure 6-87. Average monthly aerosol strong acidity for Year 1 sites of the Harvard 24-city study.**

Source: Thompson et al., 1991

- 1 ammonia from reacting with the acid aerosols aloft. Then in the morning as the nocturnal
- 2 inversion dissipates, the acid aerosols mix downward again as the process begins anew.
- 3 Spengler et al. (1986) also noted diurnal variations in sulfate and sulfuric acid concentrations
- 4 and suggested atmospheric dynamics as the cause.

### Harriman, TN, 8/12/84–8/19/84



### Harriman, TN Average August 12, 1984–August 19, 1984

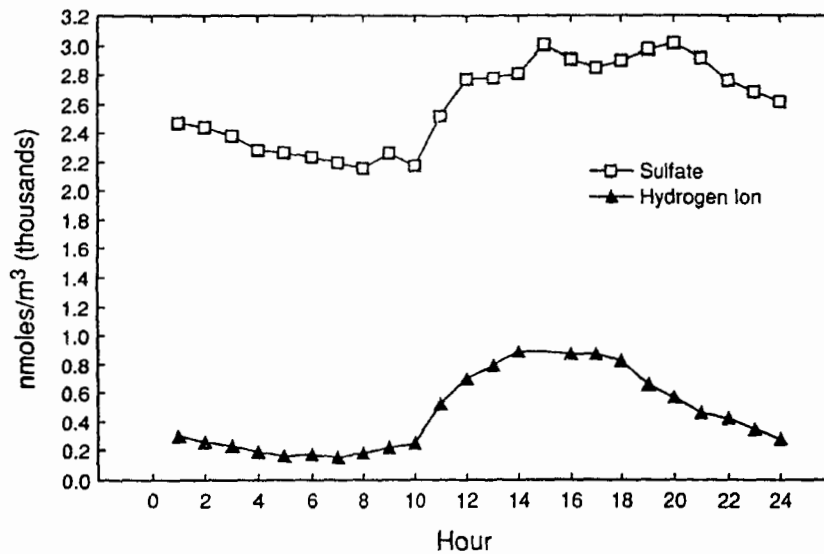


Figure 6-88. Diurnal pattern of sulfate and hydrogen ion at Harriman, TN; (a) weekly pattern, (b) daily average.

### 6.7.7 Indoor and Personal

Several studies have examined indoor concentrations of acid aerosols and personal monitoring. Brauer et al. (1989) monitored personal exposures to particles (including acidic sulfates) and gases in metropolitan Boston in the summer of 1988, and compared these to measurements collected at a centrally located ambient monitor. They found that personal concentrations of acidic aerosols and gases differed significantly from those measured at the centrally located site. Summer and winter concentrations of acid aerosols and gaseous pollutants also collected in Boston (Brauer et al., 1991) showed indoor/outdoor ratios of  $\text{H}^+$  to be 40-50% of the indoor/outdoor  $\text{SO}_4^{=}$  ratio indicating neutralization of the acid by the higher indoor  $\text{NH}_3$  levels, which were reported.

Indoor, outdoor, and personal acid aerosol monitoring was performed for children living in Uniontown, Pennsylvania, during the summer of 1990 (Suh et al., 1992). The indoor, outdoor, and personal measurements were compared to outdoor measurements collected from a centrally located ambient monitor. Personal concentrations were lower than corresponding outdoor levels but higher than indoor levels. Air conditioning was found to be an important predictor of indoor  $\text{H}^+$ , while  $\text{NH}_3$  was found to influence indoor and personal  $\text{H}^+$  concentrations. Similar results were obtained in a study of the relationships between indoor/outdoor concentrations of  $\text{H}^+$  and  $\text{NH}_3$  conducted in State College, Pennsylvania in 1991 (Suh et al., 1994b).

In a study characterizing  $\text{H}^+$  concentrations at child and elderly care facilities, Liang and Waldman (1992) measured indoor and outdoor acid aerosol concentrations. Results from this study showed that indoor/outdoor  $\text{H}^+$  and  $\text{SO}_4^{=}$  ratios were comparable to those measured inside residential buildings. Air conditioner use and indoor  $\text{NH}_3$  concentrations were again identified as important determinants of indoor  $\text{H}^+$  concentrations.

## 6.8 PARTICLE NUMBER CONCENTRATION

### 6.8.1 Introduction

Recent work has suggested that ultrafine particles may be responsible for some of the health effects associated with exposure to particulate matter (Section XX). The hypothesis for explaining a biological effect of ultrafine particles is based on the number,

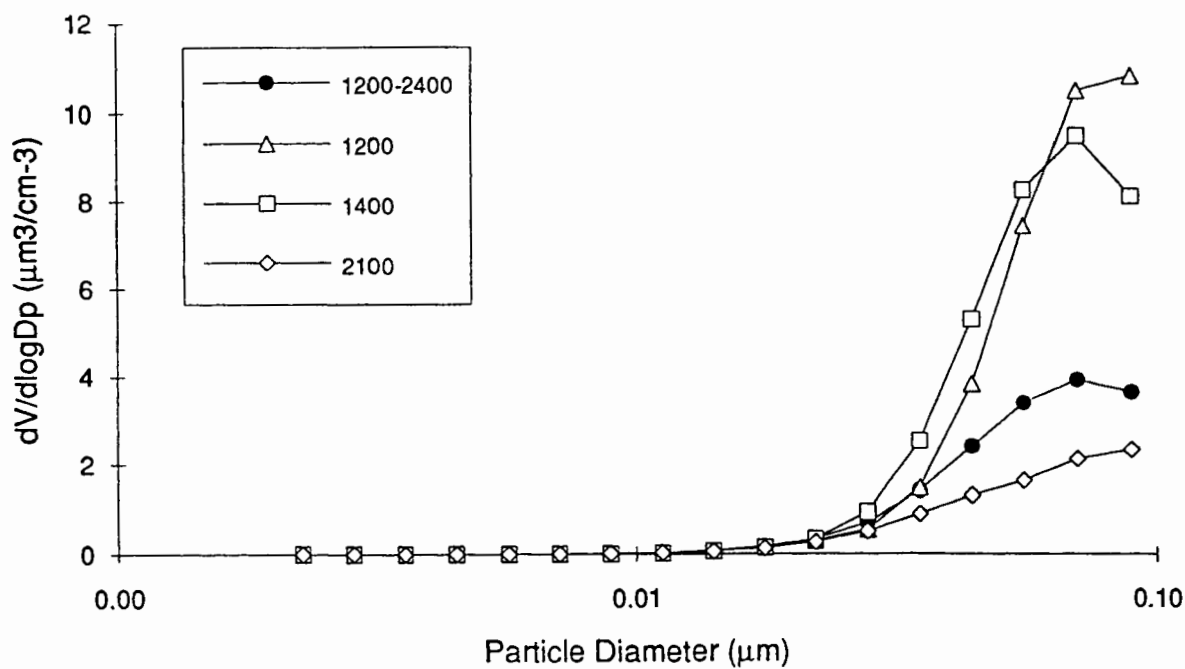
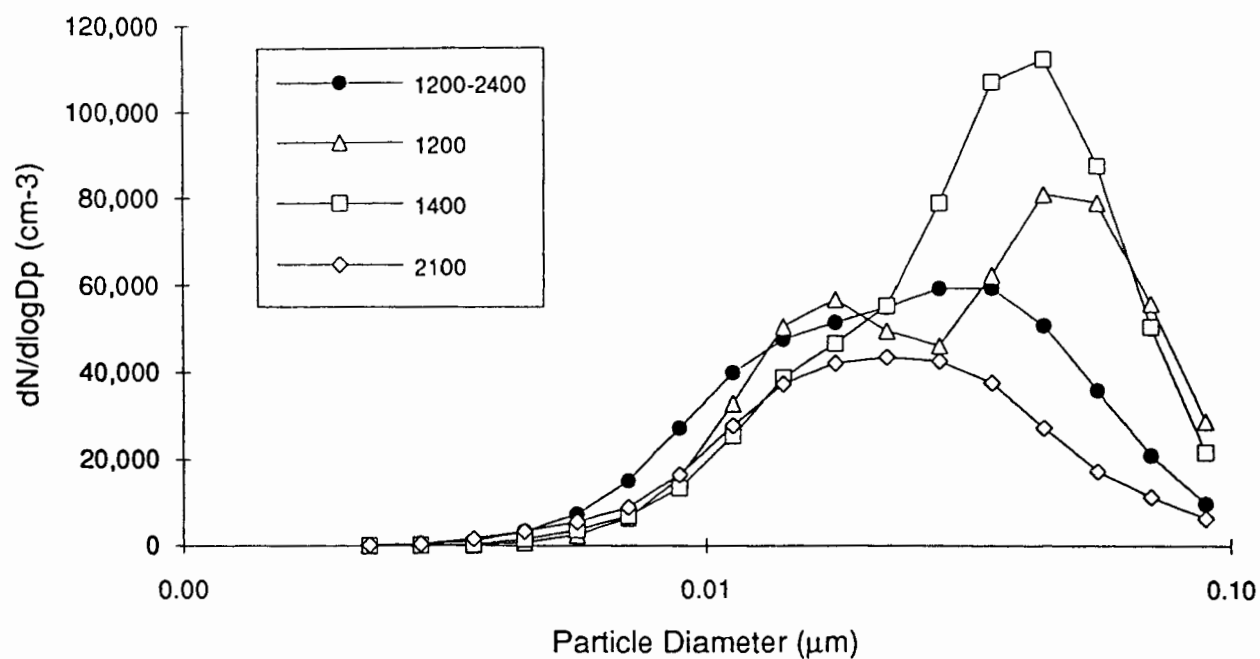
composition and size of particles rather than their mass (Seaton et al., 1995). This has led to an interest in the number concentration of ambient particles. This section examines data on particle number concentration and the relationship between particle number and particle mass or volume.

## **6.8.2 Ultrafine Particle Number-Size Distribution**

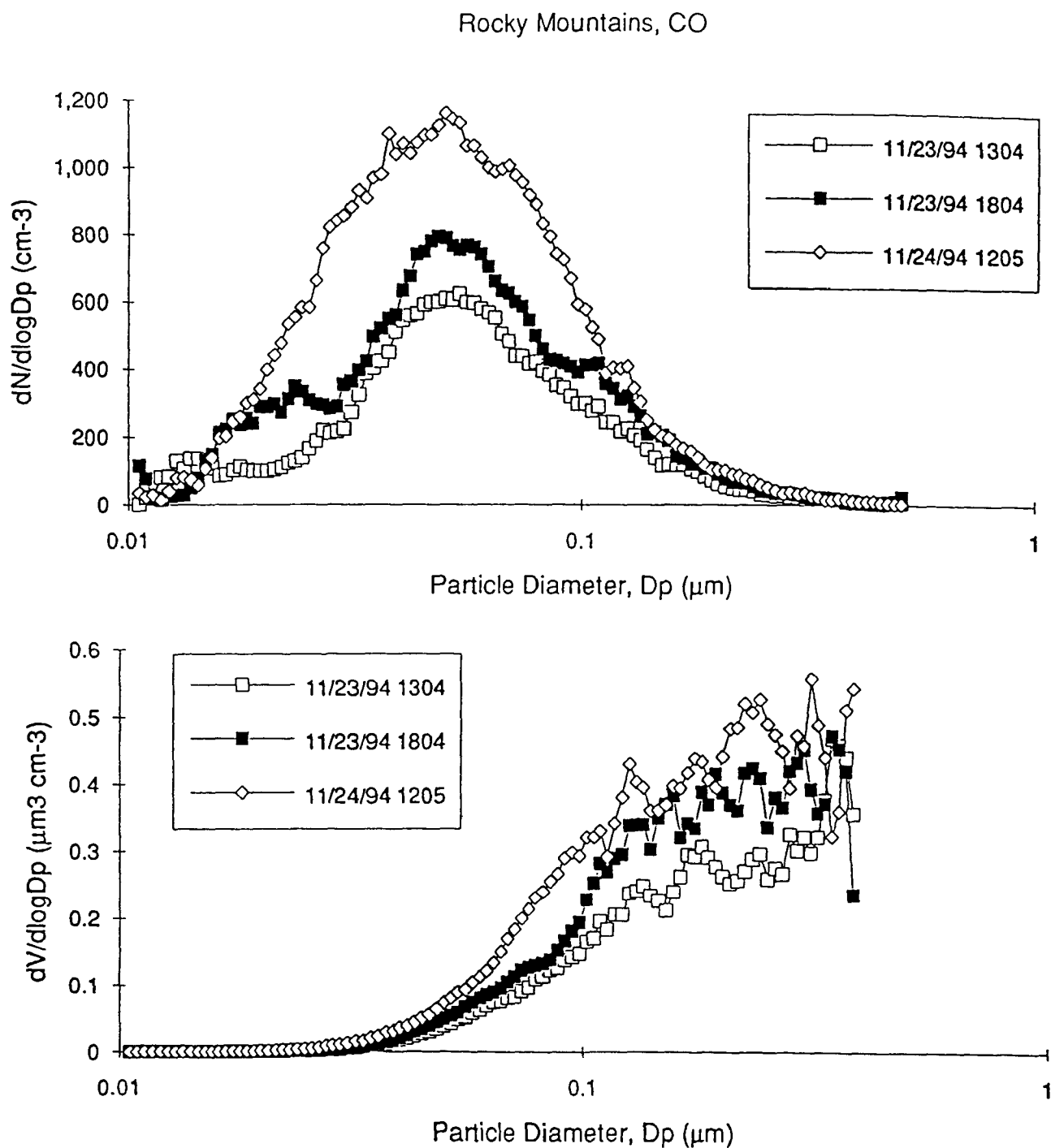
In the context of ambient particles, the term ultra fine particles refers to those particles with diameters below about  $0.1\ \mu\text{m}$ . Ultrafine aerosol size distributions from an urban site at Long Beach, California (Karch et al., 1987), and from a background site in the Rocky Mountains, Colorado (Kreidenwies and Brechtel, personal communication) are shown in Figures 6-89 and 6-90. Both of these sets of data were obtained by electrical mobility measurements. For the urban aerosols of Long Beach, the geometric mean number diameter can vary from  $0.012\ \mu\text{m}$  to  $0.043\ \mu\text{m}$ . Some of the ultrafine distributions, such as that shown for the 1,200 to 1,400 PST time period, are bimodal. The number concentrations were higher midday, as shown in Figure 6-91. For the background aerosols from Rocky Mountains the geometric mean diameter of the ultrafine aerosols was somewhat larger than for Long Beach, with geometric mean diameters ranging from  $0.047$  to  $0.075\ \mu\text{m}$  for periods without urban influence. A bimodal character for the ultrafine distribution was also observed for some measurements, as seen in Figure 6-90.

The contrast between urban and background ultrafine aerosol size distribution is demonstrated in Figure 6-92, where a change in the wind direction brought transport from an urban area to the background site at Rocky Mountains. Within a 2-h period, the number concentration increased from  $850\ \text{cm}^{-3}$  to  $19,000\ \text{cm}^{-3}$ , an increase of more than a factor of 20. In contrast, the volume distribution increased by less than a factor of 5. The number geometric mean diameter decreased from  $0.052\ \mu\text{m}$  for the background aerosol to  $0.024\ \mu\text{m}$  for the urban influenced aerosol. For the urban influenced size distributions, over 96% of the particle number was measured in particles below  $0.1\ \mu\text{m}$ , while 80% of the particle volume was associated with particles above that size.

## Long Beach, CA

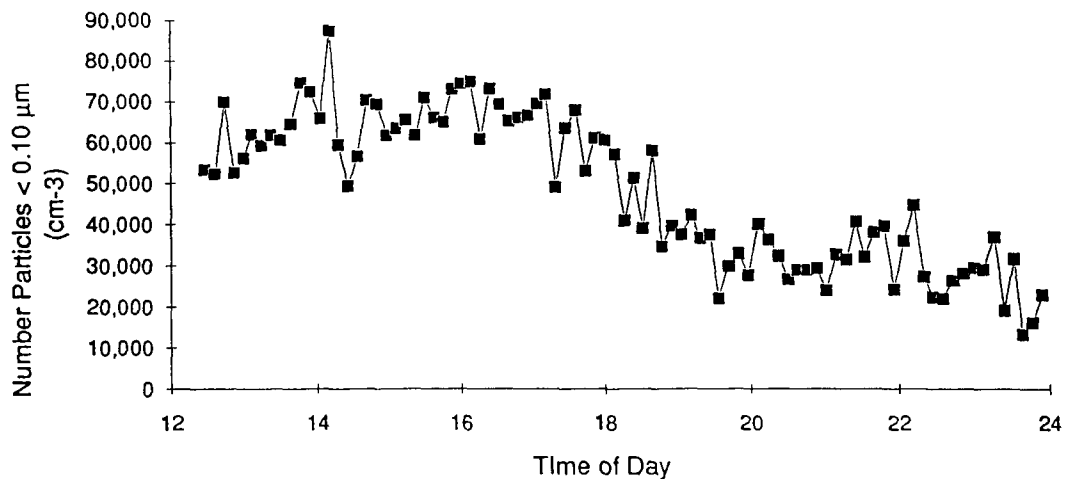


**Figure 6-89. Aerosol number and volume size distributions from an urban site at Long Beach, CA.**



**Figure 6-90. Aerosol number and volume size distributions from a background site in the Rocky Mountains, CO.**



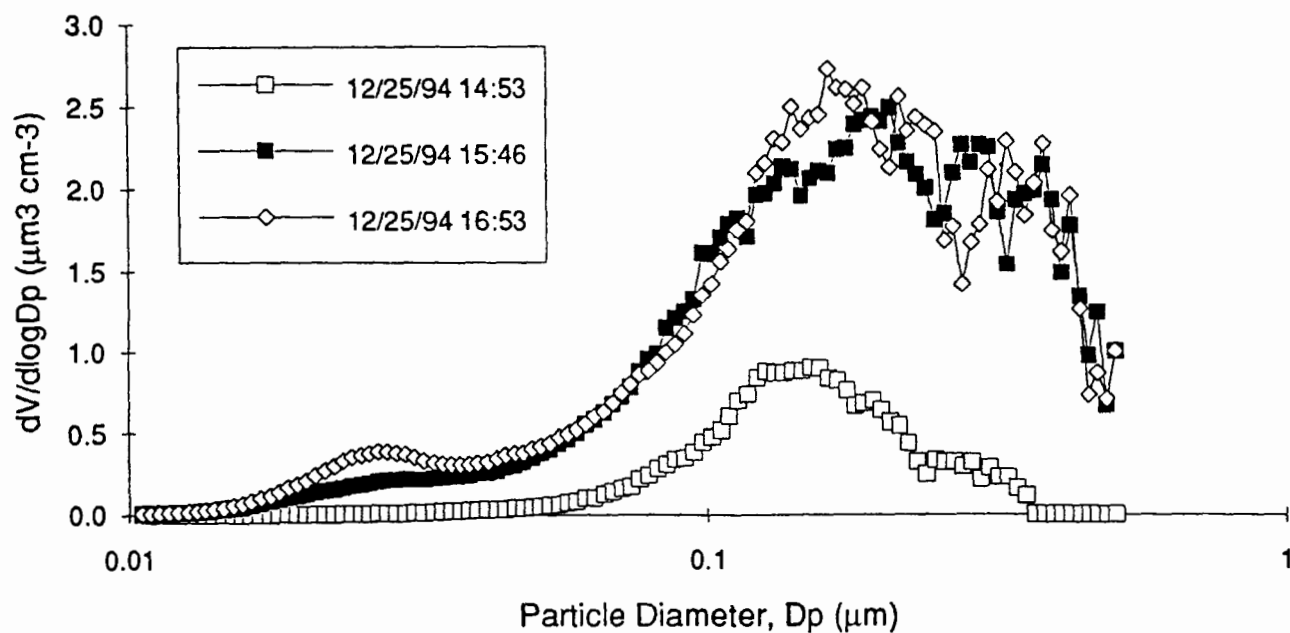
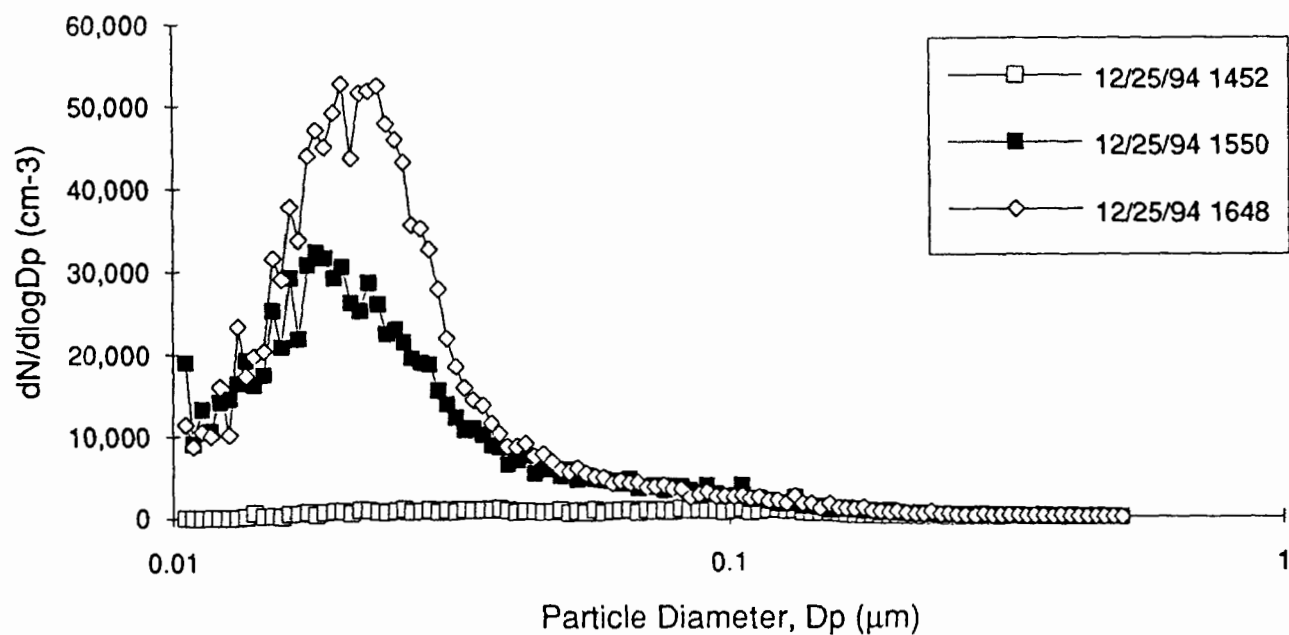


**Figure 6-91. Number concentrations as a function of time of day at Long Beach, CA.**

### 6.8.3 Relation of Particle Number to Particle Mass

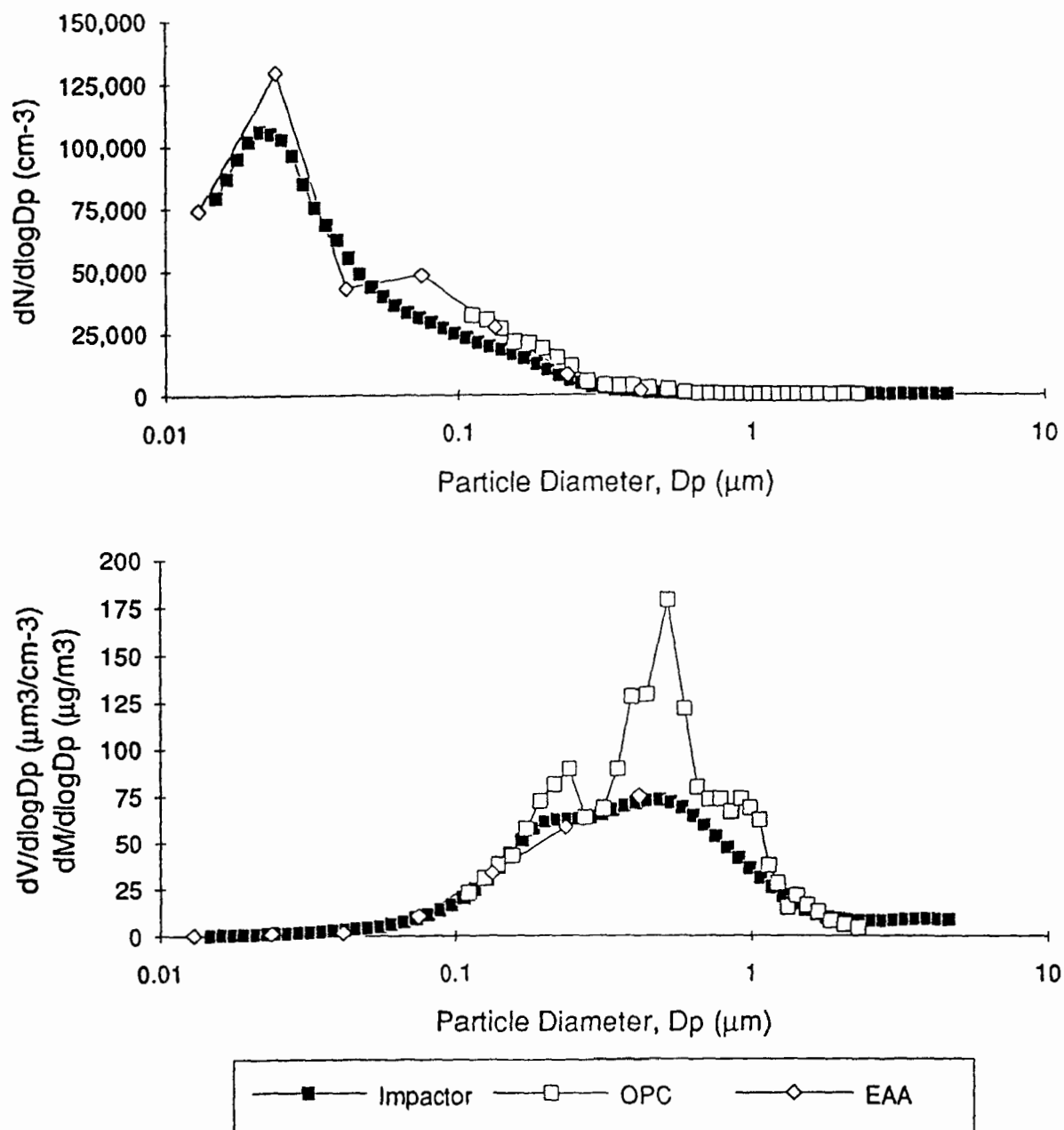
In general, the majority of airborne particle mass is associated with particles above 0.1  $\mu\text{m}$ , while the highest number concentration of particles is found in particles below 0.1  $\mu\text{m}$ . This can be seen in the recent data collected in the Los Angeles, CA shown in Figure 6-93. As with the data of Whitby and Sverdrup, the size distributions of Figure 6-93 show data collected by several instruments. Physical size distributions were measured with an electrical aerosol analyzer for particles between 0.01 and 0.4  $\mu\text{m}$ , and with a laser optical particle counter for particles between 0.14 and 3  $\mu\text{m}$  (Eldering and Cass, 1994). Additionally, Berner (John et al., 1989, 1990) and MOUDI impactors (McMurry, 1987) were used to measure the size distribution of inorganic ion species and carbonaceous species, and these data have been combined to give a total mass distribution from which the number distribution has been calculated assuming an effective aerosol density of 1.6 g/cm<sup>3</sup>, and

# Rocky Mountains, CO



**Figure 6-92. Number and volume size distributions at the Rocky Mountain site showing an intrusion of urban air.**

# Downtown Los Angeles



**Figure 6-93. Number and volume size distributions from Los Angeles, CA, showing comparison of three measurement techniques.**

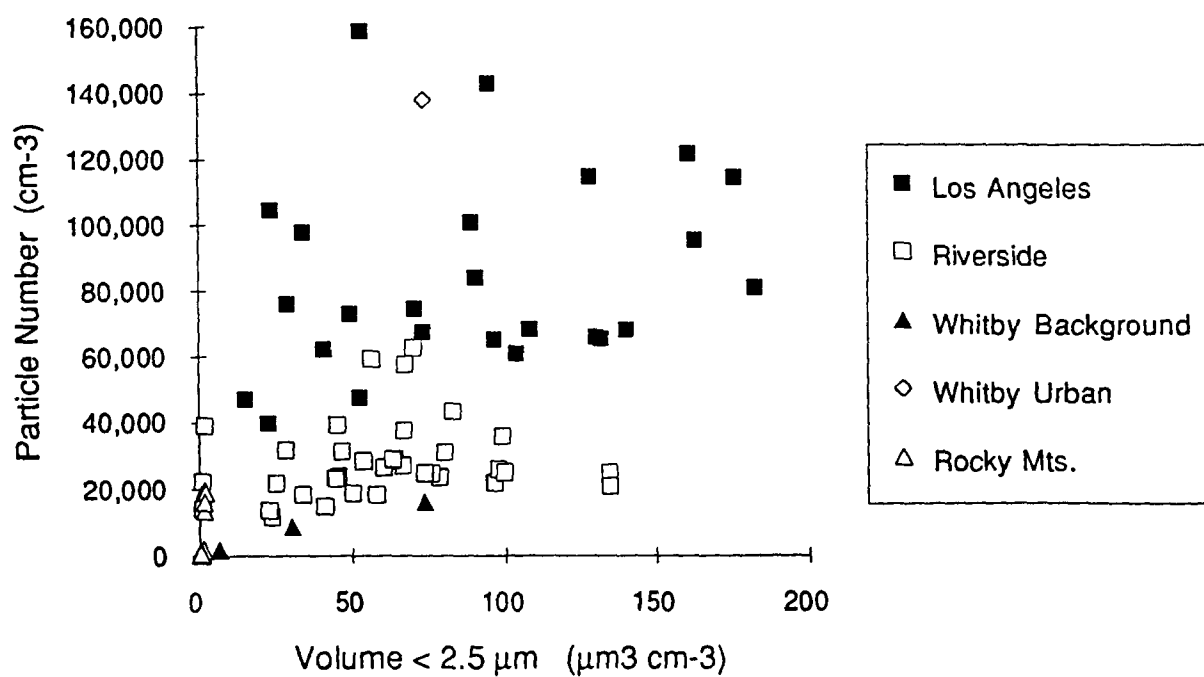
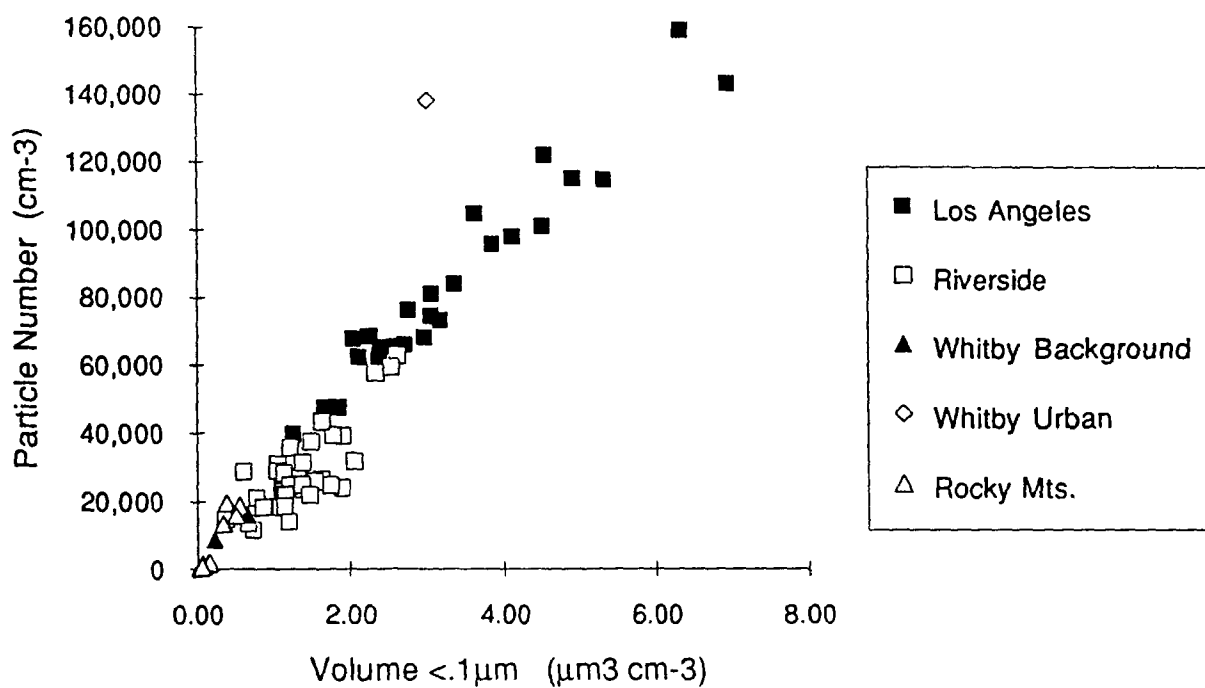
1 assuming that the water associated with the aerosol is 15% of the measured dry particle mass  
2 (see McMurry and Stolzenburg, 1989). The optical particle counter data were reduced using  
3 calibration with dioctyl sebacate aerosol, which has a refractive index ( $n = 1.45$ ) more  
4 closely related to that of ambient aerosol than does polystyrene latex ( $n = 1.59$ ) (Hering and  
5 McMurry, 1990). No fitting has been applied to match the different size distributions in the  
6 region of overlap.

7 Figure 6-93 shows the average of distributions collected over a six different days in the  
8 fall of 1987 in downtown Los Angeles, as part of the Southern California Air Quality Study.  
9 Particle number distributions emphasize the ultrafine particles, or "nuclei" mode. Volume  
10 distributions place importance on 0.1 to 1  $\mu\text{m}$  particles which are associated with the  
11 "accumulation" mode. For this average distribution 88% of the particle number is associated  
12 with particle below 0.1  $\mu\text{m}$ , but 99% of the particle volume is from particle above that size.  
13 Both the impactor and optical counter data indicate a weakly bimodal character for the  
14 accumulation mode aerosol.

15 For unimodal, log normal size distributions, the particle volume  $V$  is simply related to  
16 the particle number  $N$  by the relation:

$$V = \frac{\pi}{6} D_{gn}^3 \exp \left[ \frac{9}{2} \ln^2 \sigma_g \right] N$$

18  
19 where  $D_{gn}$  is the geometric number mean diameter, and  $\sigma_g$  is the geometric standard  
20 deviation. However, because of the multimodal character of ambient aerosol size  
21 distributions, one does not expect this simple relationship to hold in the atmosphere. The  
22 relationship between particle number and particle volume was examined for data from the  
23 Southern California Air Quality Study collected at Riverside, CA over 11 days in the  
24 summer of 1987, and at downtown Los Angeles in the fall of 1987 using the methods  
25 described above. As shown in Figure 6-94, particle number concentrations are correlated  
26 with the volume associate with particles below 0.1  $\mu\text{m}$ , but are not correlated with the total  
27 fine particle volume. Similar results are found for the data reported from Rocky Mountains,  
28 CO and for the data reported by Whitby and Sverdrup (1980).



**Figure 6-94. Relationship between particle number and particle volume; (a) volume < 0.1 μm, (b) volume < 2.5 μm.**

#### 6.8.4 Conclusion

The size distribution data for ultrafine aerosols in urban and continental background regions have geometric mean diameters which vary from 0.01 to 0.08, with the larger values found in background regions. Particle number concentrations may vary from less than 1,000/cm<sup>3</sup> at clean, background sites to over 100,000/cm<sup>3</sup> in polluted urban areas. Particle number concentrations are dominated by the ultrafine, "nuclei" mode aerosols. In contrast, the volume (or mass) of fine particles is associated with particles above 0.1  $\mu$ m, which are associated with the "accumulation" mode identified by Whitby and coworkers (Willeke and Whitby, 1975; Whitby and Sverdrup, 1980). Particle number concentrations are correlated with the volume of particles below 0.1  $\mu$ m. The number concentration of ultrafine particles results from a balance between formation and removal. The rate of removal by coagulation with accumulation mode particles will increase as the number (and mass and volume) of accumulation mode particles increases. Therefore, a correlation between number and accumulation mode volume or mass would not be anticipated. As expected no correlation is found between the total number concentration and the total fine particle mass or volume.

### 6.9 AMBIENT CONCENTRATIONS OF ULTRA-FINE METALS

#### 6.9.1 Introduction

Numerous pathways result in "ultra-fine" atmospheric aerosols, particles in the size range around 0.1  $\mu$ m diameter. These include both primary production processes, such as combustion, and secondary processes involving gas-to-particle conversion and subsequent growth by condensation and coagulation to larger particles. There are also numerous pathways that readily remove such particles from this mode, both by deposition and by growth in size into the "accumulation mode", broadly defined as the maximum in particle mass or volume that normally occurs in the range of particle diameters between 0.2 and 0.7  $\mu$ m (Whitby et al., 1978). The result is that in ambient conditions, the "ultra-fine" mode is generally indistinct or absent from mass or volume profiles of aerosol particles versus size. However, in some situations the ultra-fine mode can be the dominant size range for selected components of the atmospheric aerosol particles. This is the case for metallic aerosols in

1 which fine ( $D_p < 2.5 \mu\text{m}$ ) concentrations can be dominated by the ultra-fine mode despite the  
2 strength of the processes that tend to remove particles from this mode.

3 Removal processes are driven by the ability of ultra-fine particles to rapidly diffuse to  
4 surfaces, enhancing loss by deposition and by processes such as coagulation. The high  
5 surface area of ultra-fine particles, which is 5 times greater than an equal mass of particles at  
6  $0.5 \mu\text{m}$  diameter, also enhances growth to the accumulation mode by forming nuclei for  
7 condensation of volatile species. For these and other reasons, the mass of ultra-fine particles  
8 in the ambient atmosphere is generally much smaller than that of the accumulation mode,  
9 where removal rates of particles reach a minimum in non-cloud conditions. However, a  
10 distinct ultra-fine mode below  $0.1 \mu\text{m}$  diameter has been observed in quasi-ambient samples  
11 taken close to combustion sources, sometimes referred to as the "combustion mode" (Whitby  
12 et al., 1978).

13 While there is consensus that ultra-fine metals are abundantly produced and emitted into  
14 the atmosphere, there are not a lot of data on ambient concentrations of ultra-fine metals.  
15 The few direct measurements available can be extended with some confidence using indirect  
16 methods; i.e., from particle counting techniques that have size information but no chemical  
17 information, or from filter collection methods that have limited size information but detailed  
18 compositional information. Nevertheless, it is clear that more data on ultra-fine metals is  
19 urgently needed to gain confidence in the spatial and temporal concentration profiles of this  
20 key atmospheric component.

## 22 **6.9.2 Formation of ultra-fine particles**

23 Combustion theory establishes that high temperature processes are generally required to  
24 form ultra-fine metallic aerosols. Such processes are usually anthropogenic, although natural  
25 fires, volcanic eruptions, and other such events can contribute to ultra-fine transition and  
26 heavy metals in some circumstances. Table 6-4, taken from Seeker (1990), gives the  
27 temperature of formation of EPA-regulated metals (Federal Register, 1986) as a function of  
28 temperature, with and without chlorine available in the combustion process.

**TABLE 6-4. REGULATED METALS AND THE VOLATILITY TEMPERATURE  
(SEEKER, 1990)**

Metal	With no chlorine		With 10% chlorine in waste	
	Volatility temp, (°F)	Principal species	Volatility temp, (°F)	Principal species
Chromium	2935	CrO <sub>2</sub> /CrO <sub>3</sub>	2930	CrO <sub>2</sub> /CrO <sub>3</sub>
Nickel	2210	Ni(OH) <sub>2</sub>	1280	NiCl <sub>2</sub>
Beryllium	1930	Be(OH) <sub>2</sub>	1930	Be(OH) <sub>2</sub>
Silver	1660	Ag	1160	AgCl
Barium	1560	Ba(OH) <sub>2</sub>	1660	BaCl <sub>2</sub>
Thallium	1330	Tl <sub>2</sub> O <sub>3</sub>	280	TlOH
Antimony	1220	Sb <sub>2</sub> O <sub>3</sub>	1220	Sb <sub>2</sub> O <sub>3</sub>
Lead	1160	Pb	5	Pb
Selenium	605	SeO <sub>2</sub>	605	SeO <sub>2</sub>
Cadmium	417	Cd	417	Cd
Osmium	105	OsO <sub>4</sub>	105	OsO <sub>4</sub>
Arsenic	90	As <sub>2</sub> O <sub>3</sub>	90	As <sub>2</sub> O <sub>3</sub>
Mercury	57	Hg	57	Hg

Note the dramatic shift in temperature for several elements, including lead, for the chlorine-rich combustion scenario. A similar process has been used to prevent lead from coating surfaces in internal combustion engines using leaded gasoline. The process used chlorine and bromine-containing additives to form compounds such as PbBrCl which then leave the vehicles as ultra-fine aerosols.

Numerous theoretical and laboratory studies have shown that the typical size of metals derived from combustion is ultra-fine, (Friedlander, S.K., 1977; Senior, et al., 1982; Seeker et al., 1990). Analysis of particles from coal combustion by Natusch et al. (1974a, b) showed an additional aspect. There is a tendency for the condensing metal vapors to form relatively uniform thickness surface coatings on more refractory particles present in the combustion effluent stream. If the particles upon which the metals coat themselves are crustal, as in coal fly ash, this results in a final particle whose enrichment factor compared to crustal averages depends upon the initial size of the refractory particle-minor for large



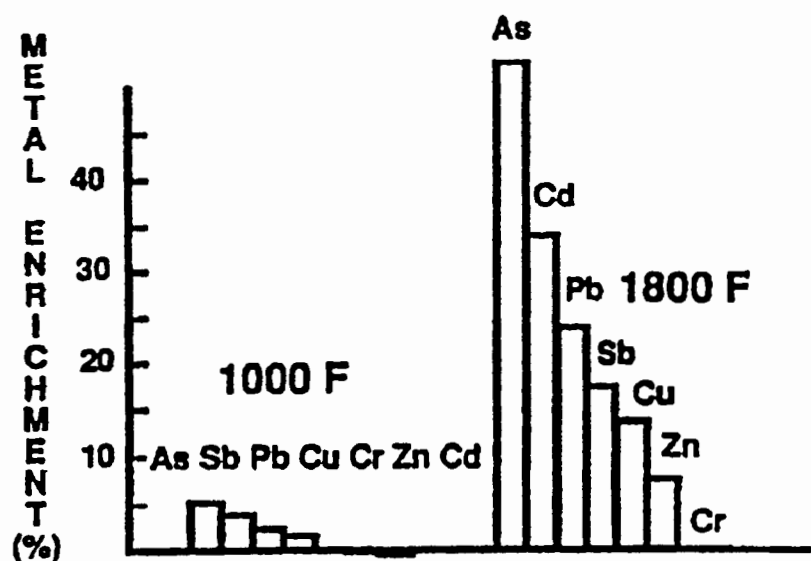
particles, extreme for ultra-fine particles (Davison et al., 1975). This result also places the (potentially) toxic metals on the biologically-accessible surface.

Thus, the presence of metals in a combustion process such as incineration of biological and chemical wastes or treatment of contaminated soils poses a problem. Raising the temperature of combustion high enough to completely ( $> 99.99\%$ ) destroy the biological and chemical species will also enhance the volatilization of metallic components in the feed stock, requiring more efficient removal methods for ultra-fine and accumulation mode metals. Figure 6-95 shows the enhanced volatilization of metals as the combustion temperature is raised from 1000 degrees F (540 C) to 1800 degrees F (980 C) (Seeker, 1990).

The combustion effluent can be partitioned into three components (Seeker, 1990; Barton et al., 1990); emitted (as fly ash), captured (assuming there is an attempt to capture fine particles), and collected in the bottom ash. Assuming no particle removal equipment is in place on the combustion process, emitted particles will include both the "emitted" component and most of the "captured" component. In an uncontrolled incineration facility, 96% of mercury, 88% of cadmium, 58% of lead, and 11% of copper might be emitted into the atmosphere. If control is attempted, the capture efficiency is only 25% for mercury, but is better for most other metals, ranging from 86% for cadmium to 91% for copper (Barton et al., 1990). In addition, the chemical state of the metals in the ultra-fine mode can vary from the more toxic phases (for example, arsenite versus arsenate) as a function of combustion conditions (Chesworth et al. 1994). Thus, we must expect that ultra-fine metallic components will be emitted from high temperature processes in both toxic and less toxic forms.

### **6.9.3 Techniques for collecting and analyzing ultra-fine metals**

Relatively little information exists on concentrations of ultra-fine metal particles in ambient air samples away from combustion sources. There are many reasons. The ultra-fine mode falls off rapidly away from the combustion source, due to the rapid migration of some types of ultra-fine particles into the accumulation mode, and increased dispersion as one moves away from the source. Many sources of ultra-fine metals use tall exhaust stacks, which enhances dispersion. The largest of the ultra-fine particles can overlap the smallest



**Figure 6-95. Impact of treatment temperature on the enrichment of metals in the fly ash after the thermal treatment of soils from a superfund site.**

particles of the much more abundant accumulation mode, roughly 0.2 to 0.7  $\mu$ m aerodynamic diameter. Particles must be size-separated using a device with a sharp cut point, usually a multistage physical impactor, that entails problems in particle collection and analysis. Since ultra-fine particles may hard and dry, adhesive coatings are essential in order to avoid particle bounce in the impactors. Particle bounce typically translates coarser particles onto finer stages, contaminating the ultra-fine particles with the enormously more abundant coarser particles. Finally, one can collect only a few monolayers of particles (at most) on the adhesive stages before particle bounce becomes important, assuming the particles themselves are not "sticky". A few monolayers of particles of 0.1  $\mu$ m diameter amounts to only about 50  $\mu$ g/cm<sup>2</sup> of total deposit. If one then desires to perform minor or trace elemental analysis of the deposit, one is then faced with analytical requirements that reach picogram ( $10^{-12}$  gm) sensitivities. This clearly limits analytical options.

For these reasons, much of the data available on the "ultra-fine" mode does not depend on compositional analysis. Most information on the presence of the ultra-fine

1 mode is derived from particle counting techniques such as the Electrical Mobility Analyzer  
2 (EMA), in situations in which the source is well known (source-enriched). This was the  
3 method pioneered in the 1972 ACHEX studies of Los Angeles (Whitby, 1978). Particle  
4 counting devices do not normally result in collection of particles in the ultra-fine mode in a  
5 manner suitable for compositional analysis, although some of the devices ("particle  
6 classifiers") could be modified to provide samples for subsequent compositional analysis, if  
7 desired. The same can be argued for devices such as diffusion batteries, but to date little has  
8 been done along this line in ambient conditions.

9 Integrated samples of fine particles can be collected on substrates suitable for  
10 analysis. While some optical information is available as one approaches the ultra-fine mode,  
11 most optical techniques do not work in the ultra-fine size range, which is well below the  
12 wavelength of light. A Scanning Electron Microscope (SEM) beam can still resolve particles  
13 in the ultra-fine mode although some details are lost. The ultra-fine mode can then be  
14 derived by particle counting techniques, either manual or automated, and metal composition  
15 can be found by x-ray analysis of the single particles. The enormous gain in signal to noise  
16 ratio by selecting individual particles off sets the loss of x-ray sensitivity (typically part per  
17 thousand) caused by use of the electron beams to induce the x-rays. SEM and electron  
18 microprobe analyses rarely achieve any better than one part per thousand sensitivity, but for  
19 single particles, this is often enough to classify them by source. Proton microprobes are, at  
20 present, not quite able to operate in the 0.1  $\mu$ m diameter region, but can perform Proton  
21 Induced X-ray Emission (PIXE) analysis to one part per million by mass on single particles  
22 as small as 0.3  $\mu$ m (Cahill, 1980).

23 Impactors are designed to separate particles by aerodynamic size in such a way  
24 as to allow compositional analysis. Yet here, too, the ultra-fine mode poses problems.  
25 First, most impactors can not operate effectively in the ultra-fine mode. The Stokes number  
26 for separation of a 0.1  $\mu$ m diameter particle from an air stream requires either extremely high  
27 jet velocities, extremely low pressures in the gas stream, or both. While such performance  
28 can be achieved in a physical impactor, most impactors used for ambient particle collection  
29 in the 1970's and early 1980's did not possess this capability. For example, the very popular  
30 cyclones and virtual impactors are ineffective below about 0.5  $\mu$ m diameter, and at ambient  
31 pressure, are unlikely to ever achieve performance in the ultra-fine regime. The Lundgren-

1 type impactors widely used in California studies (Lundgren et al., 1972; Flocchini et al.,  
2 1976; Barone et al. 1978) used 0.5  $\mu$ m as the lowest cut point. Everything smaller was  
3 collected on a filter. The Battelle-type samplers (Mercer, 1964) favored by other groups  
4 (Van Grieken et al., 1975) used a lowest cut point of 0.25  $\mu$ m diameter. Thus, while both  
5 these units generated copious information on aerosol composition, they could not separate  
6 ultra-fine aerosols from accumulation mode aerosols.

7 In the mid-1980's four new impactors were developed capable of resolving  
8 ultra-fine aerosols in ambient conditions; the Low Pressure Impactor, (LPI, Hering et al.,  
9 1978), the Berner Low Pressure Impactor (BLPI, Berner and Lurzer, 1980), the Davis  
10 Rotating-drum Unit for Monitoring impactor, (DRUM, Cahill et al., 1985; Raabe et al.,  
11 1988), and the Multiple Orifice Uniform Deposit Impactor (MOUDI, Marple et al. 1986).  
12 Battelle-type impactors were also modified to add two size cuts below 0.25  $\mu$ m diameter, but  
13 unlike the other four units, no certification of performance has been published to date on its  
14 performance in the ultra-fine region. The development of reliable, clean adhesive coatings  
15 such as Apiezon<sup>TM</sup>-L grease was also a major advance in the field (Wesolowski et al., 1978,  
16 Cahill, 1979), allowing separation of abundant soils from ultra-fine size ranges even in dry,  
17 dusty conditions. For nominally PM-10 soils, for example, a ratio of coarse to ultra-fine  
18 soils was measured at 6,600:1 at a temperature above 30 °C and low relative humidity, RH  
19 below 20 % (Cahill et al., 1985). Performances and specifications of all these units is  
20 included in a recent review paper (Cahill and Wakabayashi, 1993)

21 It is important to mention, however, that the motivation for development of  
22 this ultra-fine capability was not for extensive studies of ultra-fine metals, but rather to get a  
23 more complete picture of the accumulation mode behavior of sulfates, nitrates, organics, and  
24 other major components of the fine aerosol mix. Thus, compositional analysis was often  
25 limited to these species even when suitable samples had been collected. For example, many  
26 LPI samples were collected on stainless steel substrates, ideal for combustion analysis of  
27 sulfur, but unsuitable for analysis of transition metals by x-ray techniques.

#### 6.9.4 Observations of ultra-fine metals; Stack and source-enriched aerosols

Observations of ultra-fine metals in source or source-enriched situations lessens problems with dilution of the sample and identification of the source. This eases both particle collection and analysis. Figure 6-96 shows the results of such a study on a coal fired power plant (Maenhaut et al., 1993) using the Berner Low Pressure Impactor (BLPI). The extreme volatilization of selenium is clearly seen, which is also confirmed in aircraft sampling of power plant stacks. Note, however, that the enrichment factor is rather constant as a function of particle size for both sulfur and its chemical analog selenium. Other more refractory elements, on the other hand, are strongly enhanced in the ultra-fine mode as compared to coarser modes.

The BLPI cuts are as follows: Stage number 1-0.011 m diameter, 2-0.021, 3-0.032, 4-0.07, 5-0.17, 6-0.30, 7-0.64, 8-1.4, 9-2.6, 10-5.5, 11-10.7 m. All are for particle density 2.45 g/cm<sup>3</sup> and a temperature 120° C, the conditions of stack sampling in the coal fired power plant. Both these figures were normalized to Earth crustal averages. Thus, even a two order of magnitude rise in the normalized concentration may not result in a visible "combustion mode" since the mass of soil falls very rapidly as one moves towards ultra-fine particles. This is exactly what is predicted by the results of Natusch et al. (1974). Thus, source testing confirms combustion theory and the laboratory studies and predicts emissions of metals into the ultra-fine mode from many types of high temperature combustion sources.

#### Observations of ultra-fine metals: Ambient aerosols

##### *Direct observations*

Because of the difficulties in sampling and analysis, there are relatively few data on concentrations of ultra-fine ( $D_p$  0.1 m diameter) metals in ambient aerosols. Some quantitative determinations of ambient concentrations have become available in the past 15 years, however, generally as a result of a number of short but intensive aerosol studies. Examples include the extensive studies near the Grand Canyon, 1979 (Macias et al., 1981) to the Mohave Studies near the Grand Canyon NP, 1993, the Southern California Air Quality Study (SCAQs), 1985-1987 (Hering et al., 1990, Cahill et al., 1990, Cahill et al., 1992);

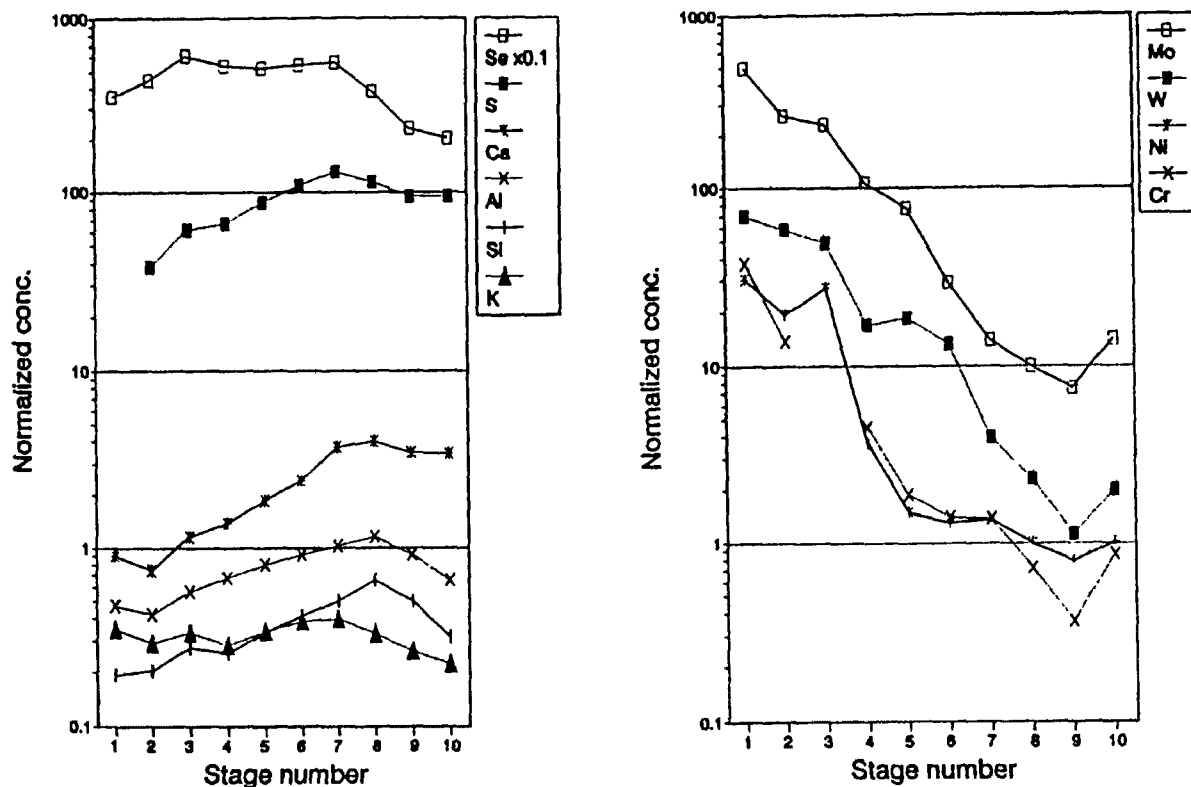


Figure 6-96. Average normalized concentrations as a function of stage number, for Se, S, Ca, al., Si, K, Mo, W, Ni, and Cr for five BLPI samples from a coal fired power plant. The smallest size mode is to the left, Stage number 1, 0.011 to Stage number 11, 10.7 m diameter. Normalization is to average crustal composition.

studies at Shenandoah (1991) and Mt. Rainier (1992) National Parks (Malm et al., 1993, Malm et al. 1994 b, Cahill and Wakabayashi, 1994), and others. While almost all of these studies used several different types of impactors with ultra-fine capabilities, relatively few were analyzed for trace metal content.

An example of a persistent ambient ultra-fine mode is shown in Figure 6-97 from data collected at Grand Canyon NP 1984 (Cahill et al., 1987). The ultra-fine mode behaves independently from the accumulation mode, in fact often showing a net anti-correlation in concentrations of sulfur as well as dramatic differences in metals (Table 6-5). The ultra-fine mode in Table 6-6 can be attributed to non-ferrous metal smelting activities in the region (Eldred et al. 1983, Small et al. 1981), which puts the nearest important sources a hundred miles away from the sampling site. The completely different behavior of the accumulation

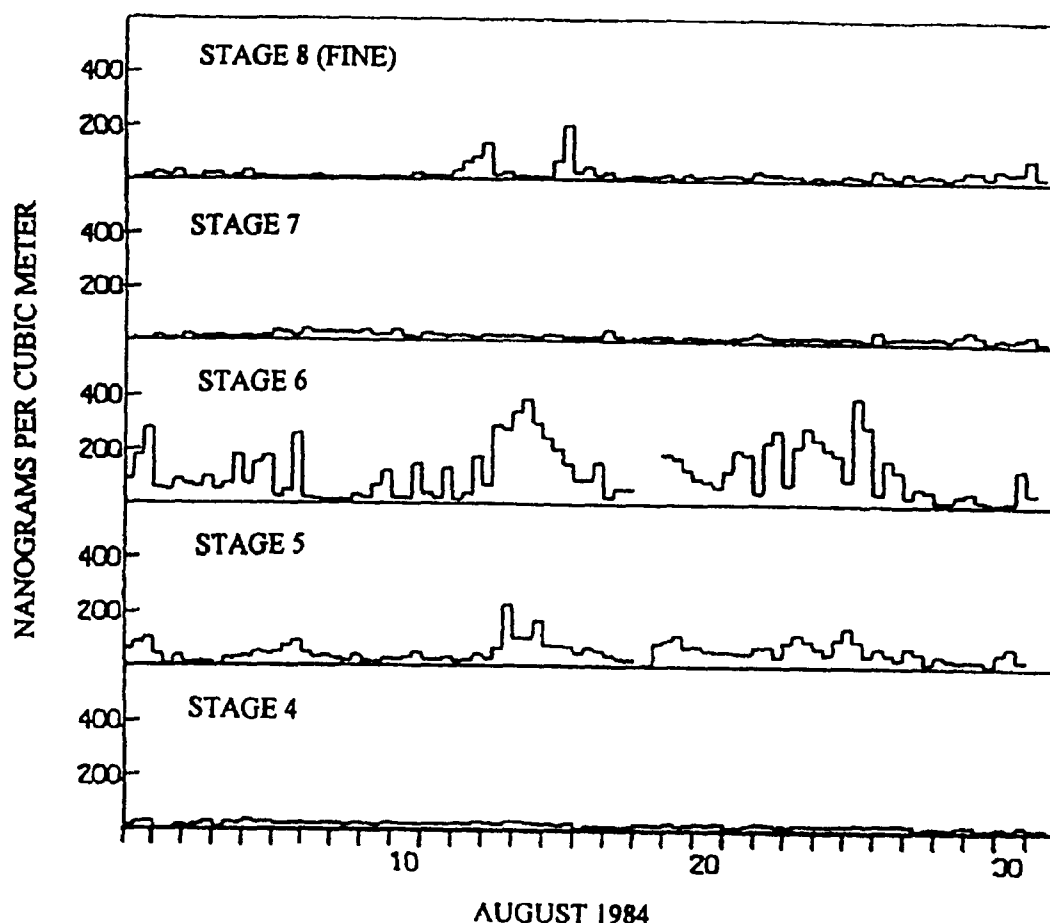


Figure 6-97. Fine and ultrafine sulfur at Grand Canyon NP, summer, 1984. The sulfur peaks on August 15 and August 16 were used for the compositional analysis in Table 3. Note that the size fractions are inverted, with the finest, Stage 8, at the top, 0.088-0.15  $\mu$ m diameter. The succeeding stages are at 0.24, 0.34, 0.56, to the coarsest, Stage 4, 1.15 to 2.4  $\mu$ m. The first three cut points are somewhat uncertain due to altitude and flow rate corrections. Final stage configurations are given in Raabe et al. (1989), which were used for all later studies using the DRUM.

and ultra-fine modes in this arid site also shows that mis-sizing by particle bounce is not significant.

Table 6-6 presents a summary of more recent data for major EPA-regulated metals (lead, nickel) and other metals, at Long Beach, CA, December, 1987 (SCAQs) and at Shenandoah NP, 1991. The elements span the range from refractory metals like nickel and vanadium to metals with low melting temperatures such as zinc and lead. These data were all taken with the same unit, the Davis Rotating-drum Unit for Monitoring (DRUM) using greased stages and a single orifice impactor (Cahill et al., 1985). The last two stages were

**TABLE 6-5. COMPOSITION OF THE AEROSOLS PRESENT AT GRAND CANYON NP IN SUMMER 1984, FOR THE TWO SULFATE EPISODES OF AUGUST 15 (ACCUMULATION MODE, STAGE 6) AND AUGUST 16 (ULTRA-FINE MODE, STAGE 8)**

Elements	Stage 8, 0.088-0.15 m (ng/m <sup>3</sup> )	Stage6, 0.15-0.60 m (ng/m <sup>3</sup> )
Sodium	420	10
Silicon and Aluminum	8	6
Sulfur	204	392
Chlorine	208	5
Potassium	59	3
Calcium	150	5
Titanium	2	4
Vanadium	2	3
Iron and nickel	2	2
Copper	100	1
Zinc	931	2
Arsenic	13	2
Bromine	2	2
Lead	63	4

modified from the Gand Canyon configuration as a result of theoretical and laboratory studies (Raabe et al., 1989), yielding 0.069 to 0.24 m for Stage 8, and 0.24 to 0.34 m diameter for Stage 7.

The DRUM data were used for several reasons: the DRUM's slowly rotating greased stages have a documented ability to handle large amounts of coarse, dry soils without contaminating the ultra-fine stages, (Cahill et al. 1985; Cahill and Wakabayashi, 1992), the elemental data are of unprecedented sensitivity for ambient ultra-fine trace metals (PIXE and synchrotron-XRF), there is a consistency of sampler type and protocols at very different locations, and there is more trace element data from the DRUM than from any other type of unit. These advantages outweigh its disadvantages; the DRUM does not have the ultra-fine sizing detail of either the LPI or BLPI impactor, or the ability to measure mass, ions and organic matter of the MOUDI or BLPI.



TABLE 6-6. MEASUREMENTS OF FINE AND ULTRA-FINE METALS

Site Name	Particle	Ultra-fine	Ultra-fine	Accumulation
Duration	Aerodynamic mode	mode	mode	Mode
Frequency	Diameters	From	From From	From From From
Dates		To	To To	To To To
	(Dae, micro-meters)	0.069 0.24	0.069 0.24 0.24 0.34	0.34 0.56 1.15 0.56 1.15 2.5
Long Beach, CA		Maximum	Mean	
6 days	Element	Values	Values	
6 samples/day		ng/m3	ng/m3 ng/m3	ng/m3 ng/m3 ng/m3
(11,12/87)	Vanadium	6.6	2.5 6.1	10.5 12.2 8.6
	Nickel	3.4	1.3 4.4	7.7 4.5 0.5
(Mean min.	Zinc	51	17.6 46.3	140.4 189.4 39
detectable	Selenium	MDL	MDL 0.32	3.00 1.40 0.65
limit - 0.3 ng/m3)	Lead	199	71.4 47.6	59.9 69.9 25.4
	Sulfur (est)		200 250	350 500 250
Shenandoah NP		Maximum	Mean	
21 days		Values	Values	
6 samples/day		ng/m3	ng/m3 ng/m3	ng/m3 ng/m3 ng/m3
(9/91)	Vanadium	1.2	0.24 0.67	0.52 0.30 0.80
	Nickel	1.2	0.58 0.48	0.13 0.03 0.01
(Mean min.	Zinc	3.8	1.42 2.16	2.60 1.92 1.66
detectable	Selenium	2.7	0.14 0.11	0.52 0.35 0.14
limit - 0.15 ng/m3)	Lead	50	5.38 5.49	3.01 10.87 16.06
	Sulfur		334 929	1235 1727 101
	(est) - estimated from graphs			

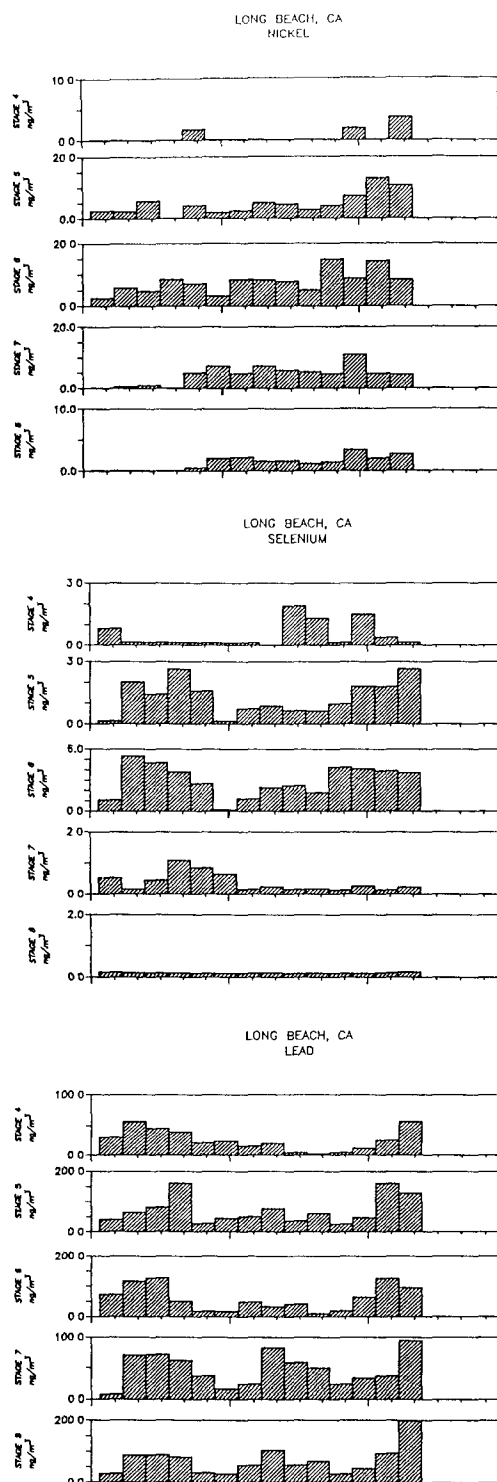
1 The analyses were done both by PIXE and by synchrotron-XRF (Cahill et al. 1992),  
2 with most of the trace metal data from the latter source. In order to obtain sulfate, multiple  
3 sulfur by 3.0. These average values, however, obscure a great deal of structure as a function  
4 of time.

5 The variability as a function of size and time is shown in Figure 6-98 for nickel,  
6 selenium, and lead in Long Beach, CA as part of the SCAQS studies of 1987. By 1987,  
7 much of the lead was no longer automotive, and there are significant changes in the ultra-fine  
8 fraction over periods of four to twelve hours. Note the behavior of ultra-fine metals; almost  
9 total absence for selenium, partial absence for nickel, and constant presence for lead.  
10 Almost all elements at almost every site shows similarly complex behavior. Thus, the  
11 summary of Table 6-11 can only include the most basic types of information on fine and  
12 ultra-fine metals in the atmosphere.

13 In addition to the limited US data, comparison data have also become available from  
14 foreign sources such as from the Kuwaiti oil fires (1991) and a study in Santiago, Chile,  
15 (1993). While the former is a unique situation, the Santiago data are especially useful since  
16 leaded gasoline is still routinely used in Chile and other countries, generating data impossible  
17 to obtain in the United States. Table 6-7 summarizes some of these data for a refractory  
18 element, nickel, and a volatile metal, lead.. However, the full data set includes 450 samples  
19 of four to six hour duration, each analyzed in five fine size fractions, generally with about  
20 20 elements found in each fraction, or approximately 40,000 individual elemental values.

21 Some general observations can be made from the data; first, there is an enormous  
22 variation in the concentration of fine and ultra-fine metals, sometimes spanning 4 or 5 orders  
23 of magnitude in a few days. Such behavior can be modeled by plumes of particles that  
24 sweep over the site episodically, as opposed to area or regional sources. Second, one often  
25 finds a mixture of ultra-fine and accumulation mode behaviors. However, these may be  
26 physically separated in time and size.

27 Lead in the United States follows a variety of very different patterns. In the rural  
28 samples, lead tends to be bimodal, with a coarse component above 1.0  $\mu$ m diameter and a  
29 very fine and ultra-fine mode below 0.34  $\mu$ m diameter. This can be modeled by a very fresh  
30 ultra-fine mode and a coarser mode associated with resuspended soil. Urban sites, however,  
31 both in the U.S. and in Santiago, show a strong ultra-fine mode and an accumulation mode.



**Figure 6-98. Fine and ultra-fine metals, nickel, selenium, and lead, in Long Beach, CA, December 10-13, 1987, in four hour increments. Stage 8 is ultra-76-fine, 0.069-0.24 m, then 0.34, 0.56, 1.15, 2.5 m D(ae).**

**TABLE 6-7. MEASUREMENTS OF FINE AND ULTRA-FINE METALS -  
LEAD AND NICKEL**

Site Name Duration Frequency Date	Element	Particle Aerodynamic Diameters  (Dae, micro- meters)	Ultra-fine.		Accumulation				
			From To	From To	From To	From To	From To		
			<b>0.069</b> <b>0.24</b>	0.24 0.34	0.34 0.56	0.56 1.15	1.15 2.5		
									MDL
Long Beach 6 days 4 samples/day (11/87)	Lead	Mean	<b>71.4</b>	47.6	59.9	69.9	25.4	0.45	
		Maximum	<b>199</b>	95	129	164	58		
	Nickel	Mean	<b>1.3</b>	4.4	7.7	4.5	0.5	0.22	
		Maximum	<b>3.4</b>	11.4	15.0	13.4	3.7		
									MDL
Shenandoah NP 21 days 6 samples/day (9/91)	Lead	Mean	<b>5.4</b>	5.5	3.0	10.9	16.1	0.2	
		Maximum	<b>50</b>	20	16	70	130		
	Nickel	Mean	<b>0.58</b>	0.48	0.13	0.03	0.01	0.09	
		Maximum	<b>1.20</b>	1.60	0.80	1.00	0.14		
									MDL
Mt. Rainier NP 28 days 6 samples/day (7,8/92)	Lead	Mean	<b>2.3</b>	6.5	2.0	3.4	6.7	0.5	
		Maximum	<b>6</b>	15	21	14	29		
	Nickel	Mean	Always less than MDL					0.07	
		Maximum	<b>MDL</b>	0.4	0.8	0.4	0.7		
									MDL
Santiago, Chile 14 days 6 samples/day (9/93)	Lead	Mean	<b>101</b>	53	38	108	41	8	
		Maximum	<b>920</b>	340	320	640	270		
									MDL
Kuwait 14 days 4 samples/day (6/91)	Lead	Mean	<b>429.9</b>	154.2	84.7	44.7	38.1	0.35	
		Maximum	<b>2580</b>	580	128	86	70		
	Nickel	Mean	<b>1.5</b>	2.5	4.3	3.7	6.0	0.22	
		Maximum	<b>5</b>	18	11	8	9		

MDL = minimum detectable limit at 95% confidence level, in ng/m<sup>3</sup>

Any resuspended soil mode is hidden under the extension of the accumulation mode above 1.0  $\mu$ m diameter.

Other metals at Long Beach, however, lack a distinct ultra-fine mode all the time (selenium) or part of the time (nickel), merely possessing an accumulation mode that closely mimics sulfates and other secondary species (Cahill et al., 1990). It is well known that nickel and vanadium were derived from high temperature combustion sources, and since each is highly refractory, they will occur primarily in an ultra-fine mode at the source. Thus, the similarity between the distributions of these elements and less refractory elements such as zinc can be understood through a rapid condensation and coagulation of the abundant secondary species around these metals, leading to an accumulation mode distribution as the secondary acidic species hydrate. Clearly, such processes are weaker at dry sites such as the arid west in summer (Table 6-6). On the other hand, Shenandoah NP has a mixture of urban and rural behavior, with occasional sharp peaks of ultra-fine metals (nickel) superimposed on an accumulation mode behavior (sulfur, selenium) but some coarse contribution (lead, vanadium). Only with a detailed study of meteorology and knowledge of emission sources can such ambient behavior be understood.

### *Indirect methods*

Lacking a large body of direct data on ultra-fine metallic aerosols, there are indirect ways to increase our knowledge of such aerosols;

1. Combustion studies have established the modes of formation of ultra-fine metallic aerosols, and,
2. Considerable ambient data exist that, when combined with known combustion processes, yield estimates for the concentration of ultra-fine metallic aerosols by time and locations.
3. In conditions of low ambient concentrations of particles and low humidity and , the ultra-fine mode has been shown to persist for many hours. (Cahill et al., 1985).

Thus, the numerous observations of fine ( $D_p < 2.5 \mu$ m) metallic aerosols in low humidity conditions can yield estimates of the presence of such metals in the ultra-fine mode and set upper limits on their concentrations. The relatively small number of actual measurements can then serve as tests or as confirmation of our level of understanding of

1 these biologically important aerosols. As an example, Figure 6-101 shows concentration  
2 profiles of sulfur, selenium, zinc, and arsenic, all of which can have ultra-fine modes in the  
3 western United States. Arsenic and zinc are annual averages, March, 1993 to February,  
4 1994, while the sulfur (for sulfate, times 3.0) and selenium are for summer, 1993. This was  
5 done to exhibit the correlation of these elements, which are chemically akin, during the  
6 eastern U.S. sulfate maximum each summer. The regional nature of the elements is very  
7 evident, as are certain strong sub-regional sources such as the copper smelter region of  
8 Arizona and New Mexico (arsenic).

9 The non-urban values shown in Figure 6-99, which are derived from the cleanest areas  
10 of the United States, are surprisingly relevant to urban areas in the same region for some of  
11 the species. Table 6-8 compares major and minor fine elements at Shenandoah NP, where  
12 there are detailed measurements of particle size, and Washington, DC, where such size  
13 information is lacking. Summer 1993 is the comparison period. Finally, two western sites  
14 are compared, both downwind of Los Angeles; San Geronio Wilderness, and Grand Canyon  
15 NP.

### 16 17 *Inhalation of ultra-fine metals*

18 An extensive literature exists on the deposition of fine metals in the human lung, much  
19 of which was derived from laboratory studies, some using radioactive tracer isotopes. But an  
20 example of one of the few direct measurement of lung capture by ambient ultra-fine metals is  
21 found in Dasaedeeler et al., 1977 and shown in Figure 6-100. The lower cut point is only  
22 0.25  $\mu$ m but even so, the increased capture efficiency of the lung for very fine and ultra-fine  
23 particles is clearly shown.

## 24 25 26 **6.10 SUMMARY**

27 There are few data on ambient concentrations of ultra-fine metals. The few direct  
28 measurements can be extended with some confidence using indirect methods; i.e., particle  
29 counting techniques that have size information but no chemical information, or filter  
30 collection methods that have limited size information but detailed compositional information.

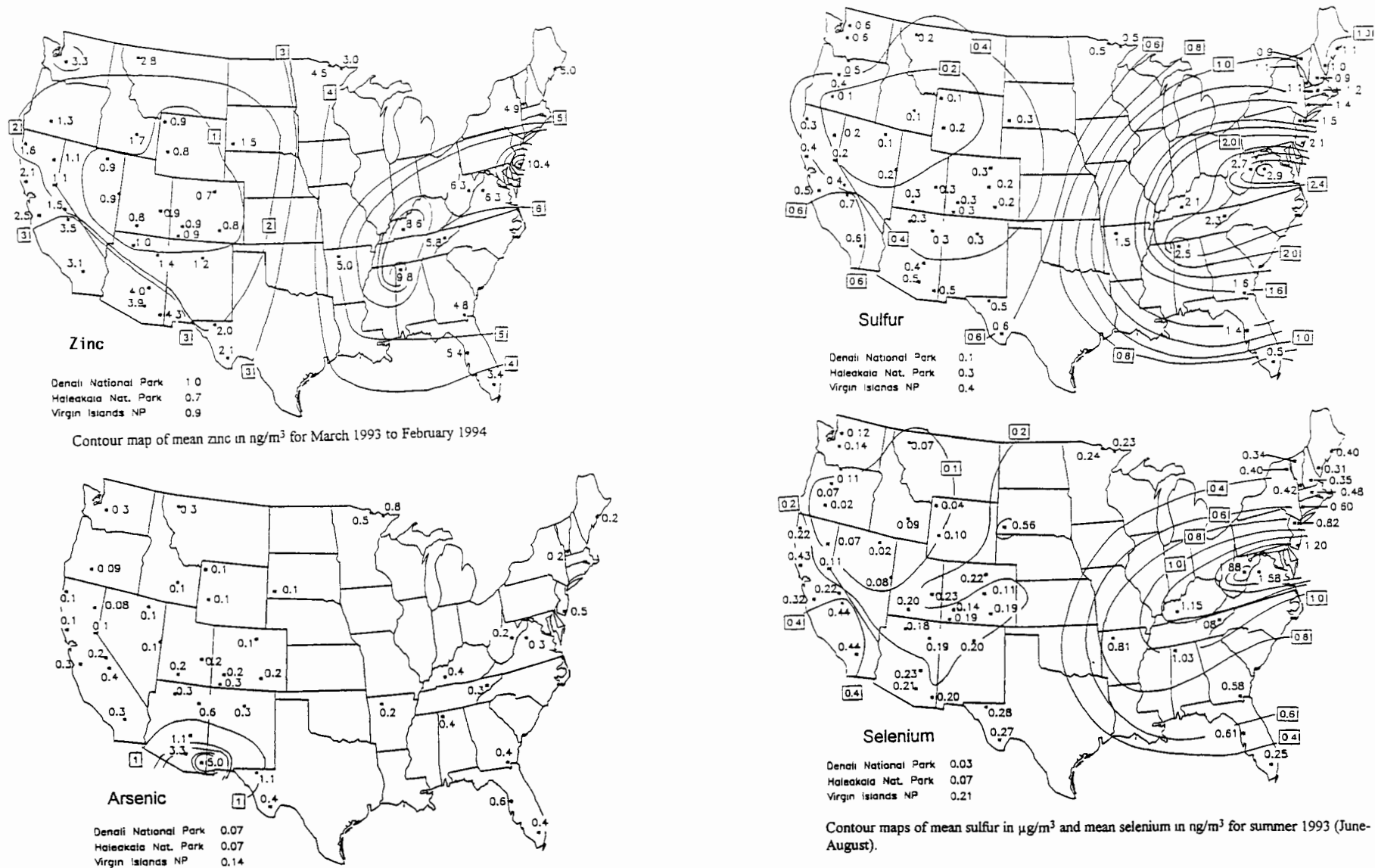
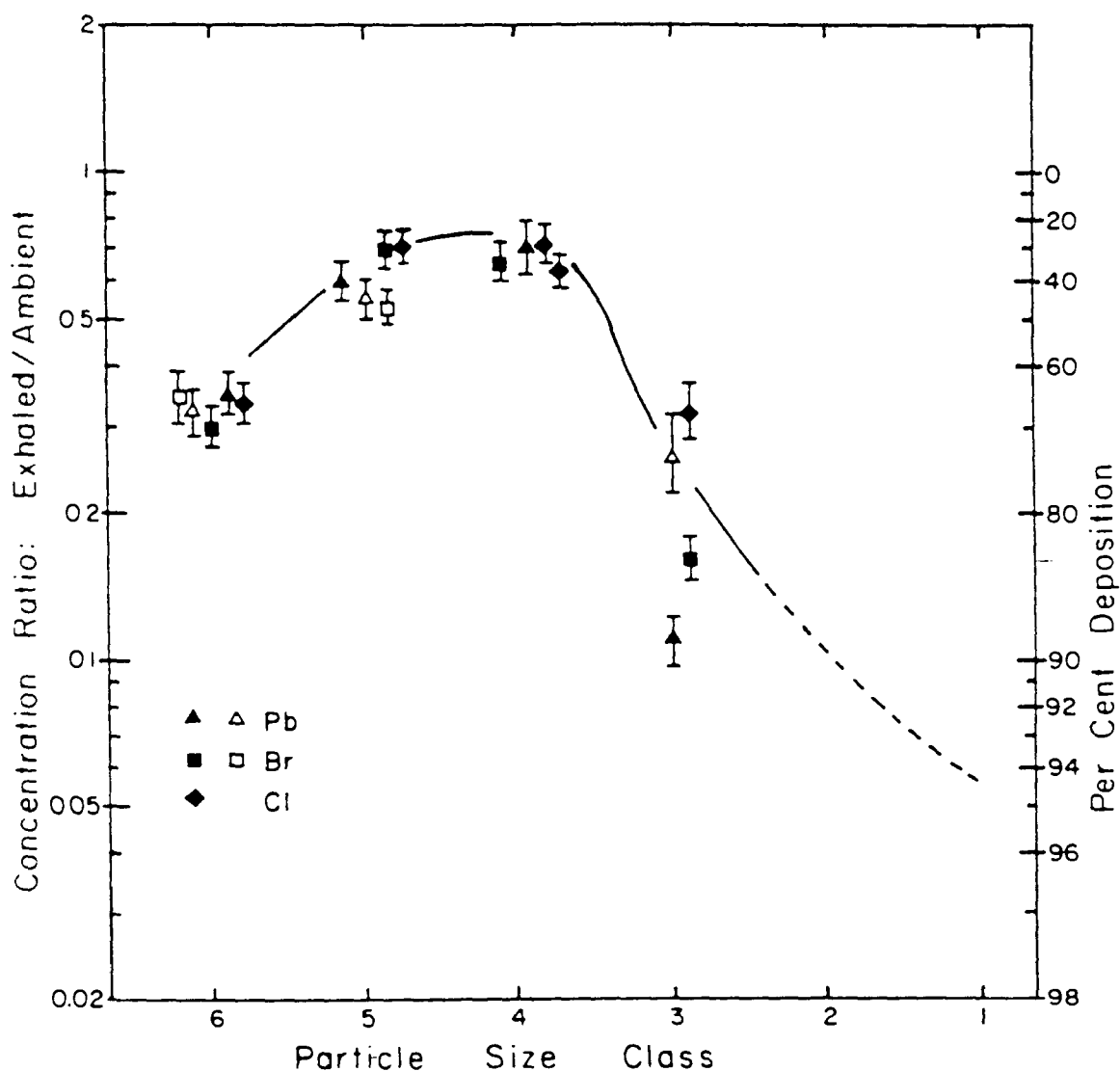


Figure 6-99. Patterns of zinc, arsenic, sulfur, and selenium in the United States.

**TABLE 6-8. COMPARISON OF SELECTED SPECIES, SHENANDOAH NP, AND WASHINGTON, DC, SAN GORGONIO WILDERNESS, CA, AND GRAND CANYON NP, SUMMER, 1993**

	Shenandoah	Washington	San Gorgonio	Grand Canyon
Concentration ( $\mu\text{g}/\text{m}^3$ )	NP	DC	Wilderness	NP
Mass - PM-10	31.00	34.90	21.70	9.37
Mass - PM-2.5	22.50	26.50	10.30	4.50
Composition PM-2.5 Mass				
Ammonium sulfate	11.80	14.60	2.55	1.09
Ammonium nitrate	0.40	1.47	4.44	0.25
Organic matter	2.84	5.42	3.88	1.22
Soil	1.41	1.55	0.86	0.63
Trace composition ( $\text{ng}/\text{m}^3$ )				
Nickel	0.24	0.97	0.18	0.09
Copper	1.06	3.37	0.76	0.30
Zinc	7.93	13.90	3.72	0.63
Arsenic	0.22	0.56	0.16	0.18
Selenium	1.58	2.48	0.44	0.18
Bromine	2.14	4.18	3.67	2.11
Lead	2.17	4.48	1.36	0.51
Bio-smoke tracer (non-soil fine potassium)	8.33	< 2.00	10.00	32.30
Optical Absorption (b(abs), $10^{-6} \text{ m}^{-1}$ )	19.60	41.90	13.90	5.40





**Figure 6-100.** Apparent deposition of automotive lead aerosol in the respiratory tract of one of the authors as determined by cascade impactor and PIXIE, as a function of aerodynamic diameter for >4, 4-2, 2-1, 1-0.5, 0.5-0.25, and <0.25  $\mu\text{m}$  particles of size classes 1, 2, 3, 4, 5, and 6, respectively. Extension of the curve to particles of diameter > 2  $\mu\text{m}$  (classes 2 and 1) is supported by separate experiments using chalk dust aerosol.

Source: Dasaedeeler et al., 1977.

1 Nevertheless, it is clear that more data on ultra-fine metals is urgently needed to gain  
2 confidence in the spatial and temporal concentration profiles of this key atmospheric  
3 component.

4 Ultra-fine metals are produced by a wide variety of anthropogenic activities and emitted  
5 into the ambient air. Ambient concentrations of such metals have been seen not only in urban  
6 settings but also at the cleanest sites in the United States. Concentrations are highly variable  
7 as a function of site and time. While ultra-fine metals have been seen to persist for many  
8 hours, or more, in the clean, dry environment of the arid west, they appear to be removed  
9 and/or transformed into the accumulation mode in polluted urban or humid rural sites.

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**APPENDIX 6A:**

**TABLES OF CHEMICAL COMPOSITION OF PM**



Table 1. Summary of PM2.5 Studies

EAST	Ref	Note	WEST	Ref	Note	CENTRAL	Ref	Note
Smoky Mtns	1		Boise	5	d	Albuquerque	5	d
Shenandoah	1		Tarrant CA	8	a	St. Louis	6,7	
Camden	2	b	Five Points CA	8	a	Steubenville	6,7	
Philadelphia	3		Riverside CA	8	a	Harriman	6,7	
Deep Creek	4	c	San Jose	8	a	Portage	6,7	
Roanoke	5	d	Honolulu	8	a	Topeka	6,7	
Raleigh	5	d	Winnemucca NV	8	a	Inglenook AL	8	a
Watertown	6,7		Portland	8	a	Braidwood IL	8	a
Hartford	8	a	Seattle	8	a	Kansas City KS	8	a
Boston	8	a	Southern California	9,31	g,h	Minneapolis	8	a
Res.Tr. Pk.	8	a	San Joaquin Valley	10	i	St. Louis	8	a
Charlotte	20	e	Phoenix	11	j	Kansas City MO	8	a
			Nevada	12	f	Akron	8	a
						Cincinnati	8	a
						Buffalo	8	a
						Dallas	8	a
						El Paso	8	a
						Denver	13	
						Urban Denver	14	m
						Non-urban Denver	14	aa
						Chicago	15	
						Houston	16	
						St. Louis	17	
						Harriman	17	
						St. Louis	18	k
						Steubenville	21	
						Brownsville	24	n
						Ontario	37	l

Table 1. Summary of Coarse Fraction Studies

EAST	Ref	Note	WEST	Ref	Note	CENTRAL	Ref	Note
Smoky Mtns	1	o	Tarrant CA	8	a,o	St. Louis	6,7	o,p
Shenandoah	1	o	Five Points CA	8	a,o	Steubenville	6,7	o,p
Camden	2	b	Riverside CA	8	a,o	Harriman	6,7	o,p
Philadelphia	3	ab	San Jose	8	a,o	Portage	6,7	o,p
Watertown	6,7	o,p	Honolulu	8	a,o	Topeka	6,7	o,p
Hartford	8	a,o	Winnemucca NV	8	a,o	Inglenook AL	8	a,o
Boston	8	a,o	Portland	8	a,o	Braidwood IL	8	a,o
Res.Tr. Pk.	8	a,o	Seattle	8	a,o	Kansas City KS	8	a,o
			Southern California	9,31	g	Minneapolis	8	a,o
			San Joaquin Valley	10	i	St. Louis	8	a,o
			Phoenix	11	j	Kansas City MO	8	a,o
						Cincinnati	8	a,o
						Buffalo	8	a,o

Table 1. Summary of Coarse Fraction Studies (Cont.)

EAST	Ref	Note	WEST	Ref	Note	CENTRAL	Ref	Note
						Dallas	8	a,o
						El Paso	8	a,o
						Denver	13	o
						Chicago	15	s
						Houston	16	o
						St. Louis	17	
						Harriman	17	
						St. Louis	18	k,r
						Brownsville	24	n
						Ontario	37	l

Table 1. Summary of PM10 Studies

EAST	Ref	Note	WEST	Ref	Note	CENTRAL	Ref	Note
Smoky Mtns	1	o,q	Tarrant CA	8	a,q	St. Louis	6,7	p,q
Shenandoah	1	o,q	Five Points CA	8	a,q	Harriman	6,7	p,q
Camden	2	b	Riverside CA	8	a,q	Steubenville	6,7	p,q
Philadelphia	3	ab	San Jose CA	8	a,q	Portage	6,7	p,q
Kingston	6,7	p,q	Honolulu HI	8	a,q	Topeka	6,7	p,q
Watertown	6,7	p,q	Winnemucca NV	8	a,q	Inglenook AL	8	a,q
Hartford	8	a,q	Portland OR	8	a,q	Braidwood IL	8	a,q
Boston	8	a,q	Seattle	8	a,q	Kansas City KS	8	a,q
Res.Tr. Pk.	8	a,q	Southern California	9,31	g,h	Minneapolis	8	a,q
			San Joaquin Valley	10	i	St. Louis	8	a,q
			Phoenix	11	j	Kansas City MO	8	a,q
			San Fran. Bay	29	v	Akron	8	a,q
			San Jose	29	w	Cincinnati	8	a,q
			Palm Springs	38	t	Buffalo	8	a,q
			Pocatello, ID	39		Dallas	8	a,q
			Tuscon	40	u	El Paso	8	a,q
			Rillito, AZ	42		Denver	13	q
						Chicago	15	s
						Houston	16	q
						St.Louis	17	
						Harriman	17	
						St. Louis	18	x
						Brownsville	24	
						Utah Valley	26	
						Ontario	37	l
						SE Chicago, IL	41	
						Ohio	43	y

## Table 1 Footnotes

- a. Inhalable Particle Network (IPN) Data. Only represents days of elevated concentrations, i.e., dichot filter loadings  $>50 \text{ ug/cm}^2$ .
- b. Data from Site 28 only.
- c. Average of all 6-hr samples.
- d. Avg over all day/nite samples.
- e. Average of all 12-hr samples at 2 incin. sites and 2 background sites.  
Only XRF values which exceeded associated uncertainties more than half the time at all four sites were included.
- f. Average from Sparks site and Reno site.
- g. Sampling only during intensive episodes.
- h. Averages based on 12-hr day/nite samples. There were 59 sampling days at Claremont and 23 sampling days at Long Beach.
- i. Avg over all sites: Stockton, Crow's Landing, Fresno, Kern, Fellows, and Bakersfield.
- j. Average of Central Phoenix, West Phoenix, and Scottsdale sites.
- k. Average of RAPS site 106.
- l. Average from Walpole, Windsor 1, and Windsor 2 sites.
- m. Average of 3 urban sites: Auraria, Federal, and Welby.
- n. Median VAPS values from Central site.
- o. 2.5-15  $\mu\text{m}$ .
- p. Coarse concentrations may be 30% or more underestimated due to losses from handling filters.
- q. PM15.
- r. 2.4-20  $\mu\text{m}$ .
- s. No upper size cutoff on VAPS inlet.
- t. Average of Palm Springs and Indio, CA.
- u. Avg. of Downtown Tuscon, Orange Grove, Craycroft, and Corona de Tuscon sites.
- v. Mean of annual avgs (1988-1992) from  $\sim 9$  sites in Alameda, San Francisco, and Santa Clara counties.
- w. 24-hr average of day/nite concentrations at two sites in San Jose.
- x. PM20. Average from RAPS site 106.
- y. Avg. of Follansbee, Mingo, Sewage Plant, Steubenville, and WTOV Tower sites.
- z. Average of urban sites: Fresno, Bakersfield and Stockton.
- aa. Average of non-urban sites: Brighton and Tower.
- ab. Castor Avenue site only.

Table 1 Appendix: Bibliography for PM Studies

Ref#	Sites	Dates	Types of Samples	Data	Comments
1	1) Smoky Mtns 2) Shenandoah Valley 3) Abastumani Mtns	1) Sept '78 2) Jul-Aug 80 3) 3-24 July79	F+C(2.5-15), EC, OC, SO <sub>4</sub> , Nitrate. 12-hr samples.	1) Comparison of avg F&C composition for 3 sites.	
2	Philadelphia - 3 sites	7/14-8/13 '82	F+C(2.5-10), EC, OC, SO <sub>4</sub> , NO <sub>3</sub> . 12-hr (0600-1800) and (1800-0600).	1) F+C composition at site 28. 2) 9-source CMB source app. for site 28. 3) Mass Balance for 3 sites.	
3	Philadelphia	7/25-8/14/94	Fine mass, elements, OC, EC, SD, uncert., from 4 sites	1) Measured PM <sub>2.5</sub> mass, OC, EC, elements, SD, unc. @ each site.	
4	Deep Creek Lake	August, 1983	Day/nite sampling (1000-2200, 2200-1000). Dichots. FM, CM, OC, EC, Gases, FP nitrate	1) Mean FP mass, OC, EC, nitrate, elements stratified by day/nite/all.	
5	1) Albuquerque 2) Raleigh 3) Boise 4) Roanoke	1) 12/84-3/85 2) 1/85-3/85 3) 12/86-3/87 4) 10/88-2/89	F & C (2.5-10) + Carbon, EOM, VOCs. 12-h samples, Day/night: 0700-1900, 1900-0700.	1) Mean comp. of F mass, EC, OC EOM, at 4 sites. 2) daytime/nighttime/24-hr avgs for key species at 4 sites.	No CP data presented; Sampling only in winter; focus on woodstove impact

6	Portage, Topeka, Harriman, Kingston, St. Louis, Steubenville, Watertown	'79-'81 Multi-season	FP & IP(2.5-15). 24-hr (midnite-midnite), every other day. No Carbon data.	1) Mean + -SE by city for F+C mass, metals. 2) Box-line plots by city showing means and percentiles for F+C mass, sulfate, Cl. 3) Time-series plots of F+C mass & tot Sulfate. 4) Data summaries only--no raw data.	Source of info on geographical and temporal PM composition variability.
7	Harvard 6-cities	1) 1977-85 TSP 2) '79-85 PM10 & PM2.5 3) '79-84 Sulfate		1) Table of Mean Air pollution values for 6 cities: TSP, Inhalable, Fine, Sulfate. No comp.	
8	IPN study --25 sites.	Throughout 1980.	F+C(2.5-15), 24-hr sample every 6th day. <u>Only moderately or highly-loaded samples were included.</u> No Carbon.	1) F+C mass for ~25 sites. 2) F+C mass, composition for 22 sites (No carbon)	
9	Los Angeles (SCAQS) 40 locations  <i>Aerosol composition</i>	Summer (11 episode days) and fall (7 episode days) 1987	Sequential 4-, 5-, and 7- hr PM2.5 and PM10 on summer episode days, and 4- and 6-hr samples in fall.  Mass, elements, ions, sulfate, nitrate, Carbon, ammonium.	1) Avg & Max PM10 and PM2.5 mass, ions, comp, Cv, Ce stratified into summer and fall. 2) Plots of temp and spatial variations of PM2.5 and PM10, PM2.5 nitrate. 3) $C_{tot}^i/EC$ for some sites	Temp and spatial variations of PM2.5 and PM10

10	San Joaquin Valley 6 sites  <i>Aerosol Composition</i>	6/88-6/89	24-hr PM10 & PM2.5 every 6 days.  Mass, elements, ions (K <sup>+</sup> , SO4 <sup>=</sup> , NH4 <sup>+</sup> , Na <sup>+</sup> ), EC, OC	1) Summary of annual geometric avg, arith. avg, max 24-h PM10 and PM2.5 mass by site.  2) Ann. Avg Mass and comp. for PM10 and PM2.5 by site.	PM10 highest in winter and dominated by F mass; C > 50% of PM10 in summer and fall. Data show spatial and temporal variations of PM10 and PM2.5
11	Phoenix PM Study	10/89 - 1/90	F&C mass, elements, uncertainties from 6 sites		
12	Phoenix 4 sites  Also comparison aerosol data from Denver, Reno, and Sparks	Sept'89 - Jan'90	6-hr samples, 2x/day, (0600-1200, 1300-1900) PM10 & PM2.5: mass, elements, HNO3, SO2, NH3, FP NO3 and SO4, ionic species, OC, EC.	1) temporal variation of PM2.5 mass at 4 sites. 2) Mean, SD, & Max: PM2.5, EC, OC, NO3, SO4 <sup>=</sup> , NH4 <sup>+</sup> and elements for 3 Phoenix sites 3) Same for Denver (11/87-1/88) 4) Same for Reno (11/86-1/87) 5) Same for Sparks (11/86-1-87)	Moudi size-resolved (0-5.6 μm in 9 bins) mass, NO3, SO4, OC, EC.
13	Denver	1/11-1/30/82	Dichotomous sampler, OC, EC, nitrate, sulfate	1) Measured PM2.5 and Coarse, elements, OC, EC, nitrate, day/night samples; light extinction.	Source apportionment for F&C particles and extinction.
14	Denver (SCENIC)	Nov'87-Jan'88	2x daily (0900-1600, 1600-0900). PM2.5 mass, comp, sulfate, nitrate, OC, EC, ionic species, gases	1) Avg, SD, Min, Max PM2.5 mass for 6 sites. 2) Avg, SD, Min, Max, for PM2.5 mass, ionic species, EC, OC, elements for 3 sites. 3) Source profiles 4) SCE for 4 sites by day and night	Source Apportionment study

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15	Chicago	July, 1994	VAPS & Dichot. FM, CM, OC, EC, elements, SO <sub>2</sub> , HONO, HNO <sub>3</sub> .	1) Avg VAPS mass, SD, uncert. for F & C, OC, EC.	
16	Houston	10-19 September 1980	Dichotomous sampler: 0.1-2.5, 2.5-15. 4 sites. Consecutive 12h samples.	1) Average F&C mass, elements, Carbon, NH <sub>4</sub> , NO <sub>3</sub> , Sulfate	Source apportionment.
17	St. Louis & Harriman	Sept'85-Aug'86	Daily F & C (2.5-10 $\mu$ m). Also SO <sub>2</sub> , NO <sub>2</sub> , and O <sub>3</sub> .	1) Mean, SD, range for PM <sub>10</sub> , PM <sub>2.5</sub> , SO <sub>4</sub> , H <sup>+</sup> , SO <sub>2</sub> , NO <sub>2</sub> , O <sub>3</sub> for both sites.	
18	St. Louis	7/76-8/76 (St.Louis)  RAPS data for St. Louis exist for 5/75-3/77 but were not in this article	F(<2.4) & C (2.4-20) 6-12 hr. No Carbon.	1) 2-mo avg of F+C mass, metals, sulfate, for one site. 2) F+C composition of selected samples (different sites) during events. 3) CMB apportionment of F+C fractions to 6 components (crustal shale, crustal limestone, ammonium sulfate, motor vehicles, steel, paint). 4) Plots of intercity variations in source component concentrations	1) Crude CMB source apportionment of FP with 6 sources.
19	1) Albuquerque 2) Denver	1) Jan 3-4, '83 2) Jan 19-20, '82	F & C (2.5-10) + Carbon, Nitrate & Sulfate (IC) 12-h samples, Day/Night: 0700-1900, 1900-0700.	1) Mean daytime and nighttime comp. of F&C, EC, OC, nitrate, sulfate, for each site. 2) Source app. of Denver winter FP composition.	More complete source app results in Lewis & Enfield paper.
20	Charlotte (2 incin sites and 2 control sites).	4/30-6/4/92 & 9/21-9/28/92.	VAPS F&C + Acid gases. no carbon. 12-hr samples	1) Mean ambient FP conc. +- XRF unc. @ 4 sites 2) CMB results for FP.	

21	Steubenville	Jan-Dec '84	24-hr, F+C. No Carbon	1) avg F mass + comp. 2) avg source contributions by SRFA 3) SRFA-derived source profiles	
22	Review of pm10 studies	1984-1990	PM10	1) SCE's for PM10 mass for ~ 15 studies	ambient PM10 data sources are cited but no data is presented
23	Phoenix	Jan 5-27, '83	F(<2.8)+C(>2.8). 1800-0800 hr samples.	1)avg F+C nighttime comp, mass, Cv,Ce, gases. 2) CMB of FP	
24	Brownsville -- residential and central sites.	Spring + Summer '93	1)FP MES indoor/outdoor 2) VAPS central site 3) Dichot central site	1) min, med, max for fine MES comp+mass 2) min, med, max F+C comp, mass for VAPS and dichot at central site	No <u>avg</u> values, only <u>median</u> .
25	Sparks, Reno, Verdi, NV (SNAPS)	4/86-3/87	1)PM2.5 & PM10 every 6th day. 24-hr samples. Also diurnal sampling.	1) Seasonal avg SCE for PM10 @ 3 sites. (geological, motor veh, construction, vegetative, sulfate, nitrate, OC, EC)	No raw data
26	Utah Valley (Linden site)	4/85-12/89	1) PM10 for 1736 days. Also, SO2, NO2, O3, acidity data.	1)avg PM10 = 47 ug/m3. sd=38, (min,max)=(1,365 ug/m3). 2) freq distribution of PM10 mass.	no comp. data. Highest pm10 during winter.
27	Santa Clara County	1980-1986: only Nov, Dec, Jan data used.	"COH" --coefficient of haze. [COH/PM10=1.87 or 1.64 ('85 and '86)].	1) Plots of COH vs daily mortality for 2-yr periods.	Examines relation between mortality and COH



28	San Joaquin Valley 6 sites  <i>Source apportionment</i>	6/88-6/89	24-hr PM10 & PM2.5 every 6 days.  Mass, elements, ionic species, Carbon,	1) Table of ann. avg SCE to PM10 and PM2.5 for data above, by site	For PM10 Mass, Sulfate, and Nitrate data, see ref 27.
29	SF Bay Area 2 sites	12/16/91-2/24/92	12-hr daily day & nite (0600-1800, 1800-0600) PM10 samples. Mass, elements, ions ( $K^+$ , $Cl^-$ , $SO_4^{=}$ , $NH_4^+$ , $Na^+$ ) Carbon, ammonium.	1) Table of ann avg PM10 mass, sulfate, nitrate statistics at 3 sites for 1988-1992 2) Avg & Max day & nite PM10 mass, ions, comp, EC, OC, for both sites 3) Source profiles 4) SCE pie charts for each site.	1. Highest PM10 mass during Nov, Dec, Jan. 2. Wood combust. contributes ~45% of PM10.
30	Los Angeles (SCAQS) 40 locations  <i>CMB Source Apport.</i>	Summer (11 episode days) and fall (7 episode days) 1987	Sequential 4-, 5-, and 7-hr PM2.5 and PM10 on summer episode days, and 4- and 6-hr samples in fall.  Mass, elements, ions, sulfate, nitrate, Carbon, ammonium.	1) Source profiles 2) PM10 SCE for summer and fall. 3) Diurnal SCE to PM10 at each site.	Data show diurnal changes in SCE for PM10 mass.

31	1) Claremont (SCAQS)  2) Long Beach (SCAQS)	1) Summer '87 (59d) 2) Fall '87 (23d)	Continuous 12-hr PM10 and PM2.5.  Mass, elements, ionic species, EC, OC	1) Mean, SD, & Max: PM10, FPM, CPM, EC, OC, NO <sub>3</sub> , SO <sub>4</sub> <sup>=</sup> , NH <sub>4</sub> <sup>+</sup> . 2) Mean values of above species during intensive and non-intensive periods. 3) Day/nite values of above 4) PM10 and PM2.5 mass balances 5) Summary of EC, OC data.	
32	CADMP -- 8 sites: Gasquet, Fremont, Bakersfield, Yosemite, Sequoia, Long Beach, Los Angeles, Azusa	Summer '88	2 samples every 6th day. 0600-01800,1800-0600. PM2.5, PM10. Mass, ionic species,	1) Graph of avg PM10 & PM2.5 mass and ratio @ 8 sites 2) Graphs of PM10 & PM2.5 ionic concentrations.	Ask Chow/Watson for raw data.
33	Central California - 53 sites in SF Bay area, Sacramento Valley, San Joaquin Valley, North and South Central Coast, Mountain Counties	1) 1989  2) July & August, 1988	PM10 every 6th day. Sulfate and nitrate measured on a subset of these samples.	1) 1989 Max and Avg PM10 mass, Sulfate, and Nitrate for ~ 53 sites. 2) Summertime '88 Avg, SD, and Max PM10 and PM2.5 Mass, comp, OC,EC, Ionic species, for 3 SJVAQS sites. [Annual data summary is in ref 20].	
34	Birmingham	1986-1989	Daily 24-hr PM10 mass. Also Ozone data.  No composition data.	1) Table of percentile points of the distribution of PM10, O3, T, DewPoint, Pneumonia, Chronic obstructive pulmonary disease. 2) Avg PM10 and O3 by season	Aside: Indoor/Outdoor ratios of 0.63 for PM10 were reported in Tuscon.

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35	Philadelphia	1973-1980	24-hr (midnite-midnite) TSP.  No composition data.	1) Table of percentile points of the distribution of TSP, SO <sub>2</sub> , T, DewPoint, Mortality.	
36	State College, PA	summer 1990	Indoor, outdoor, personal SO <sub>4</sub> =, H+, and NH <sub>3</sub>		Validation of personal exposure models
37	Southern Ontario 3 sites	Jan-Nov, 1991	24-hr, midnite-midnite, every 6th day. PM <sub>10</sub> dichot sampler.	1) Avg mass, elements, for F&C fractions, for 3 sites. NO OC, EC.	
38-43	Miscellaneous sites 14 sites	1984-1990	PM <sub>10</sub> concentrations.	1) Measured PM <sub>10</sub> mass and avg source contributions (up to 10 source categories).	Primary reference is Ref 10.

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PM2.5 COMPOSITION (24-h AVG)			EASTERN U.S.			Units = ug/m3				
Ref Site	1 Smoky Mtns	1 Shenandoah	2(b) Camden	3 Philadelphia	4(c) Deep Creek	5(d) Raleigh	5(d) Roanoke	6,7 Watertown	8(a) Hartford	8(a) Boston
Dates	9/20-26/78	7/23-5/08/80	7/14-8/13 '82	7/25-8/14/94	8/83	1/85-3/85	10/88-2/89	5/79-6/81	1980	1980
Hours			6am-6pm-6am		4x daily	7am-7pm-7am	7am-7pm-7am	0000-0000		
Dur	12	12	12	24	6	12	12	24	24	24
Number	12	28	50	21	98			354	2	1
Mass	24.00	27.00	28.70	32.18	40.00	30.30	19.90	14.90	26.75	34.80
OC	2.22	0.44	2.05	4.51	1.45	10.00	7.30			
EC	1.10	1.12	1.87	0.76	0.18	0.50	1.50			
Nitrate	0.30		<0.48		0.57					
Sulfate	12.00	13.60	11.20					6.50		
Acidity								20.3		
Al	<0.054	<0.105	0.053	0.114		0.009	0.176		0.035	
As	<0.003	<0.003	0.001		0.001	0.001	0.002			0.002
Ba										
Br	0.018	0.008	0.029	0.009	0.005	0.028	0.005	0.088	0.036	0.020
Ca	0.016	0.035	0.040	0.058	0.048	0.018	0.047	0.041	0.070	0.070
Cd			0.002							
Cl	<0.010	0.010	0.003	0.026		0.007	0.053	0.084		
Cr			0.002			0.000	0.001		0.003	0.004
Cu	0.003	0.005		0.007		0.020	0.007		0.043	0.035
Fe	0.028	0.054	0.091	0.127	0.058	0.044	0.114	0.074	0.125	0.121
K	0.040	0.061	0.101	0.060	0.044	0.159	0.177		0.171	0.096
Mg				0.023						
Mn			0.006	0.003	0.003	0.003	0.012	0.004	0.007	0.001
Mo			0.001			0.001	0.001			
Na			0.146	0.070	0.034					
Ni			0.011	0.007				0.009	0.010	0.012
P				0.015						0.009
Pb	0.097	0.052	0.249	0.019	0.048	0.096	0.027	0.329	0.510	0.285
Rb										
S	3.744	4.539	4.200	3.251	6.700	1.729	1.177	1.800	2.219	3.869
Sb			0.079		0.001					
Se	0.001	0.001	0.002	<0.002	0.003	0.002	0.002	0.001	0.001	0.001
Si	0.038	0.116	0.103	0.165	0.150	0.076	0.077	0.100	0.177	0.144
Sn			<0.012							
Sr			<0.002							
Ti	<0.006	<0.010	<0.027	<0.042					0.002	
V	<0.004	<0.010	0.013	<0.013	0.001	0.003	0.004	0.022	0.017	0.020
Zn	0.009	0.011	0.082	0.041	0.013	0.015	0.083		0.079	0.046

References are listed in Table 1 Appendix. Associated notes are explained in Table 1.

\* Values for this size fraction are calculated from the average measured values reported for the other two size fractions.



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6A-18

DRAFT-DO NOT QUOTE OR CITE

**PM2.5 COMPOSITION (24-h AVG) WESTERN U.S.****Units = ug/m3**

Ref Site	8(a) Res.Tr.Pk	9(g) Los Angeles	9(g) Los Angeles	10(i) San Joaquin Valley	11(j) Phoenix	5(d) Boise	12(f) Nevada	8(a) Tarrant CA	8(a) Five Points C	8(a) Riverside CA
Dates	1980	Summer'87	Fall'87	6'88-6'89	10/13/89-1/17/90	12/86-3/87	11/86-1/87	1980	1980	1980
Hours						7am-7pm-7a	00-2400			
Dur	24	4,5 and 7	4 and 6	24	6 h, 2x/day	12	24	24	24	24
Number	3	11 days	6 days	~35	~100 days		24	6	3	4
Mass	28.77	41.10	90.20	29.89	29.37	35.70	56.92	57.05	31.80	35.18
OC		8.27	18.46	4.87	10.10	12.70	19.97			
EC		2.37	7.28	3.24	7.47	1.70	15.17			
Nitrate		4.34	22.64	8.17	3.60		2.43			
Sulfate		9.41	4.38	3.00	1.33		1.67			
Acidity										
Al	0.073	0.035	0.250	0.152	0.130	0.102	0.275	0.177	0.239	0.036
As	0.002	0.022	0.015		<0.020	0.002	0.001			
Ba		0.015	0.043	0.012	<0.106		0.013			
Br	0.007	0.013	0.065	0.010	0.011	0.014	0.033	0.102	0.015	0.037
Ca	0.035	0.022	0.335	0.096	0.170	0.026	0.215	0.455	0.150	0.301
Cd				<0.007	<0.018					
Cl		0.093	0.453	0.094	0.365	0.122	0.145		0.004	0.009
Cr		0.022	0.025	0.003	0.003	0.001	0.002	0.002	0.001	
Cu	0.016	0.063	0.273	0.096	0.015	0.011	0.010	0.047	0.024	0.040
Fe	0.120	0.099	0.557	0.180	0.216	0.022	0.310	0.316	0.216	0.127
K	0.148	0.041	0.217	0.188	0.207	0.145	0.280	0.186	0.244	0.120
Mg		0.024	0.075							
Mn	0.003	0.016	0.043	0.006	0.023	0.002	0.015	0.032	0.005	0.007
Mo					<0.006	0.002				
Na		0.202	0.466							
Ni	0.001	0.005	0.007	0.016	0.003		0.006	0.003	0.025	0.007
P	0.042	0.060	0.046	0.007	<0.051		0.041		0.007	
Pb	0.106	0.038	0.185	0.029	0.039	0.045	0.115	0.619	0.087	0.376
Rb				0.001	<0.0025		0.001			
S	2.835	2.832	1.998	1.242	0.437	0.603	0.765	2.578	1.129	1.653
Sb				<0.002	<0.033					
Se	0.002	0.013	0.011	0.001	<0.002	0.001	0.000		0.001	0.001
Si	0.350	0.052	0.520	0.460	0.430	0.069	0.860	0.583	0.656	0.234
Sn				<0.015	<0.028					
Sr		0.019	0.028	0.002			0.004			
Ti		0.005	0.060	0.017	<0.030		0.043	0.010	0.005	
V		0.006	0.007	0.015	<0.016	0.001	0.009		0.006	0.003
Zn	0.018	0.090	0.298	0.078	0.056	0.019	0.033	0.095	0.016	0.029

References are listed in Table 1 Appendix. Associated notes are explained in Table 1.

\* Values for this size fraction are calculated from the average measured values reported for the other two size fractions.

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6A-19

DRAFT-DO NOT QUOTE OR CITE

**PM2.5 COMPOSITION (24-h AVG)****CENTRAL U.S.****Units = ug/m3**

Ref	8(a)	8(a)	8(a)	8(a)	8(a)	5(d)	13	14(m)	14(aa)	15
Site	San Jose CA	Honolulu	Winnemucca	Portland	Seattle	Albuquerque	Denver	Urban Denver	Non-urban Denver	Chicago
Dates	1980	1980	1980	1980	1980	12/84-3/85	1/11-30/82	11/87-1/88	11/87-1/88	7/94
Hours						7am-7pm-7am	6am-6pm-6a	9am-4pm-9am	9am-4pm-9am	0800-0800
Dur	24	24	24	24	24	12	12	7 & 17	7 & 17	24
Number	6	1	5	4	1		~ 26	~ 136	~ 150	16
Mass	36.28	21.10	9.68	37.18	10.70	20.60	20.73	19.67	10.35	13.57
OC						13.20	7.11	7.25		5.39
EC						2.10	2.15	4.41		1.31
Nitrate							2.22	3.96		
Sulfate							2.06	1.55		
Acidity										
Al	0.123	1.127	0.361	0.581	0.002	0.077	0.394	0.037		0.046
As	0.001			0.012	0.006		<0.002			<0.003
Ba							0.031			<0.091
Br	0.188	0.017	0.006	0.093	0.019	0.085	0.103	0.018		0.004
Ca	0.089	1.024	0.243	0.154	0.037	0.059	0.047	0.058		0.045
Cd							0.006	0.005		<0.029
Cl	0.050	0.518		0.021		0.036	0.052	0.141		0.011
Cr	0.003	0.004		0.009	0.002		<0.009	0.003		<0.005
Cu	0.043	0.018	0.026	0.072	0.024		0.010	0.017		0.011
Fe	0.148	0.726	0.231	0.270	0.098	0.045	0.079	0.111		0.089
K	0.248	0.371	0.149	0.218	0.080	0.074	0.079	0.077		0.061
Mg										0.012
Mn	0.006	0.020	0.003	0.052	0.004		0.011	0.012		0.005
Mo						0.000				<0.002
Na										0.022
Ni	0.006	0.002	0.001	0.027	0.006		0.003	0.002		<0.001
P	0.013	0.002		0.017	0.006		0.043			0.008
Pb	0.891	0.071	0.042	0.422	0.215	0.237	0.326	0.075		0.027
Rb							<0.003			
S	0.852	0.313	0.358	1.944	0.831	0.507	0.709	0.642		1.321
Sb								0.004		<0.042
Se				0.001	0.001			0.001		<0.001
Si	0.292	2.363	0.914	0.377	0.092	0.076	0.277	0.272		0.074
Sn								0.006		<0.049
Sr							<0.003	0.001		
Ti		0.063	0.009	0.005			<0.027	0.009		<0.029
V	0.002	0.001		0.014						<0.009
Zn	0.061	0.011	0.011	0.081	0.059	0.007	0.046	0.031		0.052

References are listed in Table 1 Appendix. Associated notes are explained in Table 1.

\* Values for this size fraction are calculated from the average measured values reported for the other two size fractions.

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6A-20

DRAFT-DO NOT QUOTE OR CITE

# **PM2.5 COMPOSITION (24-h AVG)**

## **CENTRAL U.S.**

**Units = ug/m3**

Ref Site	16 Houston	6,7 Harriman	17 Harriman	6,7 Kingston	6,7 Portage	6,7 Topeka	8(a) El Paso	8(a) Inglenook	8(a) Braidwood	8(a) Kansas City KS
Dates	9/10-19/80	5/80-5/81	9/85-8/86	5/80-6/81	3/79-5/81	8/79-5/81	1980	1980	1980	1980
Hours		0000-0000		0000-0000	0000-0000	0000-0000				
Dur	12	24	24	24	24	24	24	24	24	24
Number	20	256	330	169	271	286	10	8	1	8
Mass	38.60	20.80	21.00	24.60	11.00	12.50	27.16	32.03	28.20	25.66
OC	5.68									
EC	1.42									
Nitrate	0.59									
Sulfate	14.61	8.10	8.70		6.81	6.05				
Acidity		36.1	36.1		10.5	11.6				
Al	0.123						0.155	0.082	0.089	0.091
As	<0.005						0.025	0.001		0.003
Ba	0.048									
Br	0.055	0.038		0.044	0.011	0.045	0.070	0.040	0.003	0.027
Ca	0.155	0.150		0.120	0.045	0.250	0.332	0.326	0.084	0.519
Cd	<0.003									
Cl	0.032	0.021		BQL	0.027	0.031		0.003		
Cr	<0.005						0.001	0.002		0.004
Cu	0.028						0.036	0.032	0.024	0.032
Fe	0.162	0.120		0.097	0.049	0.090	0.134	0.281	0.071	0.189
K	0.119						0.127	0.408	0.052	0.311
Mg										
Mn	0.014	0.017		0.010	0.003	0.004	0.004	0.037	0.001	0.006
Mo										
Na	<0.38									
Ni	0.004	BQL		BQL	BQL	BQL	0.001	0.001	0.001	0.002
P	0.028							0.008		0.013
Pb	0.465	0.180		0.194	0.061	0.163	0.481	0.309	0.041	0.180
Rb	<0.002									
S	4.834	2.500		2.400	1.400	1.100	0.823	2.655	2.060	1.816
Sb	0.006									
Se	<0.002	0.002		0.002	0.001	0.000	0.002	0.001	0.001	0.001
Si	0.210	0.120		0.200	0.075	0.190	0.436	0.685	0.220	0.434
Sn	<0.005									
Sr	<0.002									
Ti	<0.014						0.003			0.004
V	<0.008	BQL		BQL	BQL	BQL				
Zn	0.084						0.055	0.133	0.011	0.034

References are listed in Table 1 Appendix. Associated notes are explained in Table 1.

\* Values for this size fraction are calculated from the average measured values reported for the other two size fractions.

PM2.5 COMPOSITION (24-h AVG)									CENTRAL U.S.			Units = ug/m3		
Ref Site	8(a) Minneapolis	8(a) Kansas City MO	8(a) Akron	8(a) Cincinnati	8(a) Buffalo	8(a) Dallas	8(a) St. Louis	18(k) St. Louis	6,7 St. Louis	17 St. Louis	6,7 Steubenville			
Dates	1980	1980	1980	1980	1980	1980	1980	8-9/76	9/79-6/81	9/85-8/86	4/79-4/81			
Hours									0000-0000					
Dur	24	24	24	24	24	24	24	6-12	24	24	24			
Number	6	3	7	2	14	4	5		306	311	499			
Mass	15.50	16.77	36.09	29.80	38.75	28.93	23.06	34.00	19.00	17.70	29.60			
OC														
EC														
Nitrate														
Sulfate									8.10	8.00	12.80			
Acidity									10.3	9.7	25.2			
Al			0.046	0.062	0.192	0.111	0.119	0.203						
As	0.004	0.007	0.012	0.013	0.009	0.033	0.003	0.002						
Ba								0.020						
Br	0.047	0.064	0.039	0.024	0.003	0.223	0.025	0.132	0.078		0.042			
Ca	0.103	0.213	0.110	0.062	0.218	0.691	0.090	0.132	0.101		0.097			
Cd								0.004						
Cl								0.087	0.052		0.092			
Cr	0.001	0.002	0.010	0.003	0.002	0.005		0.006						
Cu	0.035	0.021	0.037	0.024	0.026	0.043	0.018	0.029						
Fe	0.087	0.140	0.609	0.174	0.671	0.248	0.076	0.275	0.190		0.590			
K	0.092	0.142	0.268	0.136	0.310	0.125	0.126	0.261						
Mg														
Mn	0.005	0.006	0.085	0.011	0.033	0.015	0.002	0.036	0.021		0.029			
Mo														
Na														
Ni	0.001	0.001	0.006	0.004	0.008	0.002	0.002	0.004	0.003		0.005			
P			0.059	0.043	0.060	0.018	0.020	0.001						
Pb	0.308	0.369	0.412	0.343	0.359	1.066	0.277	0.688	0.327		0.216			
Rb								0.000						
S	0.907	0.763	3.419	2.876	3.706	1.514	2.333	4.655	2.100		4.700			
Sb								0.006						
Se	0.001		0.008	0.005	0.005		0.002	0.004	0.002		0.005			
Si	0.169	0.177	0.522	0.328	0.241	0.442	0.170	0.458	0.160		0.290			
Sn								0.009						
Sr								0.002						
Ti			0.009	0.003		0.007		0.112						
V					0.001	0.002		0.002	BQL		0.011			
Zn	0.045	0.046	0.150	0.053	0.078	0.054	0.023	0.101						

References are listed in Table 1 Appendix. Associated notes are explained in Table 1.

\* Values for this size fraction are calculated from the average measured values reported for the other two size fractions.

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6A-22

DRAFT-DO NOT QUOTE OR CITE

PM10 COMPOSITION (24-hr AVG)									
EASTERN U.S.									
Units = ug/m3									
Ref	1(o,q)*	1(o,q)*	2(b)*	3(ab)*	4(c)	5(d)	5(d)	6,7(p,q)	8(a,q)
Site	Smoky Mtns	Shenandoah	Camden	Philadelphia	Deep Creek	Raleigh	Roanoke	Watertown	Hartford
Dates	9/20-26/78	7/23-5/08/80	7/14-8/13 '82	7/25-8/14/94	8/83	1/85-3/85	10/88-2/89	5/79-6/81	1980
Hours			6am-6pm-6am		4x daily	7am-7pm-7a	7am-7pm-7a	0000-0000	
Dur	12	12	12	24	6	12	12	24	24
Number	12	28	50	21	98			354	2
Mass	29.60	34.40	40.10	40.60				24.20	54.60
OC	2.22	0.44	2.05	4.51					
EC	1.10	1.12	2.29	0.76					
Nitrate	0.30		0.57						
Sulfate	12.00	14.38	11.20					8.94	
Acidity									
Al	BQL	0.311	0.603	0.439					1.910
As	BQL		0.001						3.458
Ba									0.003
Br	0.023	0.011	0.044	0.012				0.110	0.082
Ca	0.338	0.339	0.400	0.479				0.250	0.045
Cd			0.002						1.139
Cl	BQL	0.189	0.072	0.073				0.389	0.302
Cr			0.002						0.011
Cu	0.003	0.011		0.021					0.069
Fe	0.146	0.212	0.581	0.479				0.350	1.195
K	0.148	0.190	0.252	0.160					1.733
Mg				0.126					0.481
Mn		BQL	0.017	0.010				0.009	0.028
Mo			0.001						0.030
Na			0.146	0.206					
Ni	BQL	BQL	0.015	0.009				0.011	0.015
P				0.042					0.033
Pb	0.111	0.061	0.303	0.032				0.405	0.681
Rb									0.462
S	3.744	4.539	4.430	3.251				2.000	2.647
Sb			0.260						4.371
Se	0.001	0.001	0.002					0.001	0.001
Si	0.618	0.929	1.713	1.098				1.100	0.001
Sn			BQL						4.694
Sr			0.002						6.904
Ti	0.018	0.017	0.065	0.030					0.096
V	BQL	BQL	0.020					0.022	0.025
Zn	0.009	0.017	0.112	0.092					0.133

References are listed in Table 1 Appendix. Associated notes are explained in Table 1.

\* Values for this size fraction are calculated from the average measured values reported for the other two size fractions.

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6A-23

DRAFT-DO NOT QUOTE OR CITE

**PM10 COMPOSITION (24-hr AVG)****WESTERN U.S.****Units = ug/m3**

Ref Site	8(a,q) Res.Tr.Pk	9(g) Los Angeles	9(g) Los Angeles	10(i) San Joaquin Valley	11(j)* Phoenix	5(d) Boise	12(f) Nevada	8(a,q)* Tarrant CA	8(a,q)* Five Points CA	8(a,q)* Riverside CA
Dates	1980	Summer'87	Fall'87	6'88-6'89	10/13/89-1/17/90	12/86-3/87	11/86-1/87	1980	1980	1980
Hours						7am-7pm-7a	00-2400			
Dur	24	4,5 and 7	4 and 6	24	6 h, 2x/day	12	24	24	24	24
Number	3	11 days	6 days	~35	~100 days		24	6	3	4
Mass	36.93	67.40	98.70	74.05	62.45			100.90	124.37	106.20
OC		11.61	23.35	10.59	14.56					
EC		3.19	8.49	5.62	8.30					
Nitrate		9.47	27.50	10.55	4.46					
Sulfate		11.28	5.39	3.62	2.34					
Acidity										
Al	0.679	0.758	0.847	3.570	2.67			2.407	7.317	3.549
As	0.002	0.007	0.019		BQL					
Ba		0.070	0.127	0.051	0.01					
Br	0.010	0.016	0.072	0.015	0.01			0.149	0.019	0.065
Ca	0.121	0.585	1.190	1.057	2.10			4.543	1.786	5.082
Cd					BQL					
Cl		1.119	0.880	0.487	0.56				0.026	0.173
Cr	0.002	0.023	0.042	0.010	0.01			0.007	0.007	0.005
Cu	0.026	0.022	0.178	0.087	0.04			0.077	0.037	0.061
Fe	0.302	0.836	2.192	1.633	1.47			1.257	3.275	2.015
K	0.216	0.237	0.460	0.820	0.88			0.441	1.437	1.081
Mg		0.335	0.287		BQL					
Mn	0.006	0.033	0.063	0.037	0.05			0.067	0.055	0.049
Mo					BQL					
Na		1.632	0.518		BQL					
Ni	0.001	0.005	0.005	0.010	0.01			0.006	0.037	0.013
P	0.042	0.187	0.099	0.059	0.05			0.002	0.155	0.144
Pb	0.119	0.084	0.251	0.061	0.06			0.786	0.105	0.489
Rb				0.004	BQL					
S	3.058	3.353	2.262	1.463	0.62			2.888	1.422	2.373
Sb					BQL					
Se	0.002	0.008	0.010	0.001	BQL				0.001	0.001
Si	1.737	2.040	2.162	8.037	7.44			5.791	16.657	7.778
Sn					BQL					
Sr		0.018	0.024	0.014	0.01					
Ti	0.021	0.077	0.165	0.147	0.14			0.093	0.277	0.182
V		0.005	0.009	0.014	BQL				0.013	0.003
Zn	0.025	0.114	0.293	0.094	0.09			0.147	0.032	0.059

References are listed in Table 1 Appendix. Associated notes are explained in Table 1.

\* Values for this size fraction are calculated from the average measured values reported for the other two size fractions.

April 1995

6A-24

DRAFT-DO NOT QUOTE OR CITE

**PM10 COMPOSITION (24-hr AVG)****CENTRAL U.S.****Units = ug/m3**

Ref Site	8(a,q)* San Jose CA	8(a,q)* Honolulu	8(a,q)* Winnemucca	8(a,q)* Portland	8(a,q)* Seattle	8(a,q)* Albuquerque	13(q)* Denver	14(m) Urban Denver	14(aa) Non-urban Denver	15(s)* Chicago
Dates	1980	1980	1980	1980	1980	12/84-3/85	1/11-30/82	11/87-1/88	11/87-1/88	7/94
Hours						7am-7pm-7am	6am-6pm-6am	9am-4pm-9am	9am-4pm-9am	0800-0800
Dur	24	24	24	24	24	12	12	7 & 17	7 & 17	24
Number	6	1	5	4	1		~ 26	~ 136	~ 150	16
Mass	66.68	46.90	65.42	117.55	36.00		56.46			28.54
OC							7.11			5.39
EC							2.15			1.31
Nitrate							2.22			
Sulfate							2.45			5.46
Acidity										
Al	2.053	2.992	6.925	6.932	2.296		3.294			0.269
As	0.001			0.014	0.008		<0.004			<0.0043
Ba							0.089			<0.130
Br	0.250	0.023	0.010	0.121	0.033		0.127			0.011
Ca	0.771	1.981	2.177	1.459	0.585		0.705			0.761
Cd							0.018			<0.041
Cl	0.480	1.456	0.176	0.197	0.228		1.287			0.047
Cr	0.009	0.009	0.006	0.019	0.005		<0.018			<0.0073
Cu	0.071	0.025	0.043	0.109	0.041		0.018			0.017
Fe	1.214	1.384	1.995	2.059	1.001		1.033			0.432
K	0.508	0.665	1.200	0.805	0.231		0.727			0.161
Mg										0.118
Mn	0.027	0.034	0.044	0.108	0.022		0.031			0.013
Mo										<0.0041
Na										0.022
Ni	0.014	0.005	0.003	0.036	0.007		0.008			<0.0018
P	0.045	0.002		0.028	0.006		0.155			0.035
Pb	1.119	0.093	0.063	0.537	0.292		0.424			0.032
Rb							0.005			
S	1.109	0.571	0.573	2.371	0.952		0.709			1.363
Sb							<0.004			<0.059
Se				0.001	0.001		<0.004			<0.0017
Si	5.506	6.129	12.817	12.505	4.424		7.737			0.813
Sn							<0.004			<0.070
Sr							0.009			
Ti	0.086	0.130	0.173	0.191	0.091		0.09			0.019
V	0.002	0.001		0.018			<0.004			<0.013
Zn	0.105	0.019	0.026	0.119	0.093		0.085			0.090

References are listed in Table 1 Appendix. Associated notes are explained in Table 1.

\* Values for this size fraction are calculated from the average measured values reported for the other two size fractions.

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6A-25

DRAFT-DO NOT QUOTE OR CITE

PM10 COMPOSITION (24-hr AVG)						CENTRAL U.S.		Units = ug/m3		
Ref	16(q)*	6,7(p,q)	17*	6,7(p,q)	6,7(p,q)	6,7(p,q)	8(a,q)*	8(a,q)*	8(a,q)*	8(a,q)*
Site	Houston	Harriman	Harriman	Kingston	Portage	Topeka	El Paso	Inglenook	Braidwood	Kansas City KS
Dates	9/10-19/80	5/80-5/81	9/85-8/86	5/80-6/81	3/79-5/81	8/79-5/81	1980	1980	1980	1980
Hours	0000-0000		0000-0000		0000-0000	0000-0000				
Dur	12	24	24	24	24	24	24	24	24	24
Number	20	256	330	169	271	286	10	8	1	8
Mass	63.40	32.50	30.00	35.40	18.20	26.40	76.21	72.45	56.90	70.33
OC	8.78									
EC	1.42									
Nitrate	2.22									
Sulfate	15.52	11.14	8.70	13.63	7.29	6.60				
Acidity			36.1							
Al	1.216						2.903	2.508	2.020	2.144
As	<0.015						0.037	0.001	0.002	0.003
Ba	0.139									
Br	0.091	0.052		0.056	0.014	0.055	0.103	0.061	0.006	0.036
Ca	2.935	1.800		0.960	0.380	2.400	3.964	2.924	1.490	4.371
Cd	<0.012									
Cl	0.398	0.050		0.018	0.083	0.031	0.043	0.003		
Cr	0.007						0.004	0.006	0.002	0.010
Cu	0.046						0.083	0.059	0.044	0.048
Fe	0.766	0.690		0.360	0.230	0.580	0.946	1.474	0.727	0.989
K	0.289						0.623	0.717	0.355	0.660
Mg										
Mn	0.035	0.038		0.027	0.009	0.020	0.027	0.078	0.018	0.026
Mo										
Na	<1.49									
Ni	0.008	0.001		ND	0.001	0.001	0.002	0.003	0.002	0.005
P	0.128							0.030	0.014	0.013
Pb	0.589	0.237		0.234	0.074	0.203	0.672	0.388	0.054	0.237
Rb	<0.006									
S	4.83	2.500		2.400	1.500	1.200	1.072	2.969	2.632	2.031
Sb	0.006									
Se	<0.003	0.002		0.002	0.001	0.000	0.003	0.001	0.002	0.001
Si	3.200	2.000		1.900	0.980	2.500	5.813	6.997	5.987	4.976
Sn										
Sr										
Ti	0.036						0.080	0.116	0.083	0.076
V	<0.045	ND		ND	ND	ND				
Zn	0.142						0.112	0.188	0.023	0.060

References are listed in Table 1 Appendix. Associated notes are explained in Table 1.

\* Values for this size fraction are calculated from the average measured values reported for the other two size fractions.



April 1995

6A-26

DRAFT-DO NOT QUOTE OR CITE

# **PM10 COMPOSITION (24-hr AVG)**

## **CENTRAL U.S.**

**Units = ug/m3**

Ref Site	8(a,q)* Minneapolis	8(a,q)* Kansas City MO	8(a,q)* Akron	8(a,q)* Cincinnati	8(a,q)* Buffalo	8(a,q)* Dallas	8(a,q)* St. Louis	18(x)* St. Louis	6,7(p,q) St. Louis	17* St. Louis	6,7(p,q) Steubenville
Dates	1980	1980	1980	1980	1980	1980	1980	8-9/76	9/79-6/81	9/85-8/86	4/79-4/81
Hours									0000-0000		0000-0000
Dur	24	24	24	24	24	24	24	6-12	24	24	24
Number	6	3	7	2	14	4	5		306	311	499
Mass	46.35	58.43	70.90	62.95	83.32	61.55	56.82	62.00	31.40	27.60	46.50
OC											
EC											
Nitrate											
Sulfate									11.14	8.00	17.60
Acidity										9.7	
Al	2.191	2.284	2.555	2.972	3.000	1.405	3.956	1.412			
As	0.005	0.010	0.015	0.013	0.009	0.039	0.004	0.003			
Ba								0.054			
Br	0.069	0.093	0.064	0.041	0.015	0.274	0.046	0.179	0.099		0.052
Ca	1.674	3.967	1.541	1.374	2.768	4.127	1.874	2.949	1.600		1.120
Cd								0.005			
Cl	0.293	0.530	0.572	0.103	0.728	0.029	0.053	0.344	0.145		0.303
Cr	0.003	0.006	0.024	0.005	0.017	0.010	0.001	0.015			
Cu	0.057	0.036	0.055	0.038	0.048	0.066	0.032	0.043			
Fe	0.831	1.119	2.249	1.057	2.711	0.968	0.663	1.493	0.770		2.200
K	0.402	0.503	0.592	0.499	0.516	0.335	0.417	0.653			
Mg											
Mn	0.031	0.031	0.129	0.032	0.111	0.035	0.019	0.071	0.040		0.068
Mo											
Na											
Ni	0.002	0.003	0.011	0.007	0.017	0.004	0.004	0.009	0.005		0.008
P			0.059	0.080	0.060	0.018	0.020	0.099			
Pb	0.406	0.478	0.509	0.442	0.467	1.318	0.372	0.877	0.415		0.259
Rb								0.002			
S	1.131	1.043	3.870	3.265	4.471	1.754	2.612	5.188	2.300		5.500
Sb								0.007			
Se	0.001		0.008	0.005	0.005		0.002	0.005	0.002		0.005
Si	4.848	4.986	5.531	6.961	2.916	3.652	4.638	4.928	2.100		2.300
Sn								0.010			
Sr								0.009			
Ti	0.062	0.074	0.116	0.099	0.051	0.058	0.058	0.587			
V					0.001	0.002		0.006	ND		0.013
Zn	0.072	0.086	0.219	0.201	0.121	0.084	0.044	0.175			

References are listed in Table 1 Appendix. Associated notes are explained in Table 1.

\* Values for this size fraction are calculated from the average measured values reported for the other two size fractions.

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6A-27

DRAFT-DO NOT QUOTE OR CITE

COARSE COMPOSITION (24-hr AVG)				EASTERN U.S.			Units = ug/m3			
Ref Site	1(o) Smoky Mtns	1(o) Shenandoah	2(b) Camden	3(ab) Philadelphia	4(c) Deep Creek	5(d) Raleigh	5(d) Roanoke	6,7(o,p)* Watertown	8(a,o) Hartford	8(a,o) Boston
Dates	9/20-26/78	7/23-5/08/80	7/14-8/13 '82	7/25-8/14/94	8/83	1/85-3/85	10/88-2/89	5/79-6/81	1980	1980
Hours			6am-6pm-6am		4x daily	7am-7pm-7a	7am-7pm-7am	0000-0000		
Dur	12	12	12	24	6	12	12	24	24	24
Number	12	28	50	21	98			354	2	1
Mass	5.60	7.40	11.40	8.42				9.30	27.85	105.60
OC			<3.00							
EC			0.42							
Nitrate			0.57							
Sulfate		0.78	<0.90					2.44		
Acidity										
Al	<0.300	0.311	0.550	0.325					1.875	3.458
As	<0.001	<0.002								0.001
Ba										
Br	0.005	0.003	0.015	0.003				0.022	0.046	0.025
Ca	0.322	0.304	0.360	0.421				0.209	0.864	1.069
Cd			<0.006							
Cl	<0.012	0.179	0.069	0.047				0.305	0.302	0.301
Cr			<0.009						0.008	0.004
Cu	<0.005	0.006		0.014					0.026	0.023
Fe	0.118	0.158	0.490	0.352				0.276	1.070	1.612
K	0.108	0.129	0.151	0.100					0.310	0.533
Mg				0.104						
Mn		<0.006	0.011	0.006				0.006	0.021	0.029
Mo										
Na				0.136						
Ni	<0.002	<0.003	0.004	0.002					0.005	0.022
P				0.027					0.033	0.016
Pb	0.014	0.009	0.054	0.013				0.076	0.171	0.177
Rb										
S	<0.560	<0.711	0.230	BQL				0.200	0.428	0.502
Sb			0.181							
Se	<0.0006	<0.001	<0.0015	BQL						
Si	0.580	0.813	1.610	0.933				1.000	4.517	6.760
Sn			<0.009							
Sr			0.002							
Ti	0.018	0.017	0.065	0.030					0.094	0.154
V			0.007	BQL					0.008	0.008
Zn	<0.004	0.006	0.030	0.052					0.054	0.054

References are listed in Table 1 Appendix. Associated notes are explained in Table 1.

\* Values for this size fraction are calculated from the average measured values reported for the other two size fractions.

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6A-28

DRAFT-DO NOT QUOTE OR CITE

**COARSE COMPOSITION (24-hr AVG)****WESTERN U.S.****Units = ug/m3**

Ref Site	8(a,o) Res.Tr.Pk	9(g)* Los Angeles	9(g)* Los Angeles	10(i)* San Joaquin Valley	11(i) Phoenix	5(d) Boise	12(f) Nevada	8(a,o) Tarrant CA	8(a,o) Five Points CA	8(a,o) Riverside CA
Dates	1980	Summer'87	Fall'87	6'88-6'89	10/13/89-1/17/90	12/86-3/87	11/86-1/87	1980	1980	1980
Hours						7am-7pm-7a	00-2400			
Dur	24	4,5 and 7	4 and 6	24	6 h, 2x/day	12	24	24	24	24
Number	3	11 days	6 days	~ 35	~ 100 days		24	6	3	4
Mass	8.17	26.30	8.50	44.17	33.09			43.85	92.57	71.03
OC		3.34	4.89	5.71	4.46					
EC		0.82	1.21	2.38	0.84					
Nitrate		5.13	4.86	2.38	0.86					
Sulfate		1.87	1.01	0.62	0.37					
Acidity										
Al	0.606	0.723	0.597	3.418	2.539			2.230	7.078	3.513
As		BQL	0.004	0.000	<0.002					
Ba		0.055	0.084	0.040	<0.077					
Br	0.003	0.003	0.006	0.006	0.002			0.047	0.004	0.028
Ca	0.086	0.563	0.854	0.961	1.929			4.088	1.636	4.781
Cd					<0.016					
Cl		1.026	0.426	0.393	0.194				0.022	0.164
Cr	0.002	0.002	0.017	0.007	0.008			0.005	0.006	0.005
Cu	0.010	BQL	BQL	BQL	0.021			0.030	0.013	0.021
Fe	0.182	0.737	1.635	1.453	1.259			0.941	3.059	1.888
K	0.068	0.196	0.243	0.632	0.669			0.255	1.193	0.961
Mg		0.311	0.212	0.000						
Mn	0.003	0.017	0.021	0.031	0.032			0.035	0.050	0.042
Mo					<0.005					
Na		1.431	0.052	0.000						
Ni		BQL	BQL	BQL	0.003			0.003	0.012	0.006
P		0.127	0.053	0.052	0.038			0.002	0.148	0.144
Pb	0.013	0.046	0.066	0.032	0.022			0.167	0.018	0.113
Rb					0.003					
S	0.223	0.520	0.264	0.222	0.178			0.310	0.293	0.720
Sb					<0.030					
Se		BQL	BQL	0.000	<0.002					
Si	1.387	1.988	1.642	7.577	7.013			5.208	16.001	7.544
Sn					<0.026					
Sr		BQL	BQL	0.012	0.014					
Ti	0.021	0.072	0.106	0.130	0.121			0.083	0.272	0.182
V		BQL	0.003	BQL	<0.014				0.007	
Zn	0.007	0.024	BQL	0.016	0.034			0.052	0.016	0.030

References are listed in Table 1 Appendix. Associated notes are explained in Table 1.

\* Values for this size fraction are calculated from the average measured values reported for the other two size fractions.

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6A-29

DRAFT-DO NOT QUOTE OR CITE

**COARSE COMPOSITION (24-hr AVG)****CENTRAL U.S.****Units = ug/m3**

Ref	8(a,o)	8(a,o)	8(a,o)	8(a,o)	8(a,o)	5(d)	13(o)	14(m)	14(ab)	15(s)
Site	San Jose CA	Honolulu	Winnemucca	Portland	Seattle	Albuquerque	Denver	Urban Denver	Non-urban Denver	Chicago
Dates	1980	1980	1980	1980	1980	12/84-3/85	1/11-30/82	11/87-1/88	11/87-1/88	7/94
Hours						7am-7pm-7am	6am-6pm-6a	9am-4pm-9am	9am-4pm-9am	0800-0800
Dur	24	24	24	24	24	12	12	7 & 17	7 & 17	24
Number	6	1	5	4	1		~ 26	~ 136	~ 150	16
Mass	30.40	25.80	55.74	80.38	25.30		35.73			14.97
OC										
EC										
Nitrate										
Sulfate							0.39			
Acidity										
Al	1.930	1.865	6.564	6.351	2.294		2.900			0.223
As				0.002	0.002					<0.0013
Ba							0.058			<0.038
Br	0.062	0.006	0.004	0.028	0.014		0.024			0.007
Ca	0.682	0.957	1.934	1.305	0.548		0.658			0.716
Cd							0.012			<0.012
Cl	0.430	0.938	0.176	0.176	0.228		1.235			0.036
Cr	0.006	0.005	0.006	0.010	0.003		<0.009			<0.0024
Cu	0.028	0.007	0.017	0.037	0.017		0.008			0.006
Fe	1.066	0.658	1.764	1.789	0.903		0.954			0.344
K	0.260	0.294	1.051	0.587	0.151		0.648			0.101
Mg										0.106
Mn	0.021	0.014	0.041	0.056	0.018		0.021			0.008
Mo										<0.0017
Na										<0.017
Ni	0.008	0.003	0.002	0.009	0.001		0.005			<0.0007
P	0.032			0.011			0.113			0.027
Pb	0.228	0.022	0.021	0.115	0.077		0.099			0.005
Rb							0.005			
S	0.257	0.258	0.215	0.427	0.121		<0.48			0.043
Sb										<0.017
Se										<0.0006
Si	5.214	3.766	11.903	12.128	4.332		7.460			0.739
Sn										<0.021
Sr							0.009			
Ti	0.086	0.067	0.164	0.186	0.091		0.090			0.019
V				0.004						<0.004
Zn	0.044	0.008	0.015	0.038	0.034		0.039			0.038

References are listed in Table 1 Appendix. Associated notes are explained in Table 1.

\* Values for this size fraction are calculated from the average measured values reported for the other two size fractions.

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6A-30

DRAFT-DO NOT QUOTE OR CITE

**COARSE COMPOSITION (24-hr AVG)****CENTRAL U.S.****Units = ug/m3**

Ref Site	16(o) Houston	6,7(o,p)* Harriman	17 Harriman	6,7(o,p)* Kingston	6,7(o,p)* Portage	6,7(o,p)* Topeka	8(a,o) El Paso	8(a,o) Inglenook	8(a,o) Braidwood	8(a,o) Kansas City KS
Dates	9/10-19/80	5/80-5/81	9/85-8/86	5/80-6/81	3/79-5/81	8/79-5/81	1980	1980	1980	1980
Hours		0000-0000		0000-0000	0000-0000	0000-0000				
Dur	12	24	24	24	24	24	24	24	24	24
Number	20	256	330	169	271	286	10	8	1	8
Mass	24.80	11.70	9.00	10.80	7.20	13.90	49.05	40.43	28.70	41.67
OC	3.10									
EC										
Nitrate	1.63									
Sulfate	0.91	3.04			0.48	0.55				
Acidity										
Al	1.093						2.748	2.426	1.931	2.284
As	<0.006						0.012		0.002	0.003
Ba	0.091									
Br	0.036	0.014		0.012	0.003	0.010	0.033	0.021	0.003	0.029
Ca	2.780	1.650		0.840	0.335	2.150	3.632	2.598	1.406	3.754
Cd	<0.006									
Cl	0.366	0.029		0.018	0.056	0.000	0.043			0.530
Cr	0.007						0.003	0.004	0.002	0.004
Cu	0.018						0.047	0.027	0.020	0.015
Fe	0.604	0.570		0.263	0.181	0.490	0.812	1.193	0.656	0.979
K	0.170						0.496	0.309	0.303	0.361
Mg										
Mn	0.021	0.021		0.018	0.006	0.016	0.023	0.041	0.017	0.025
Mo										
Na	<0.74									
Ni	0.004	0.001		BQL	0.001	0.001	0.001	0.002	0.001	0.002
P	<0.1							0.022	0.014	
Pb	0.124	0.057		0.040	0.013	0.040	0.191	0.079	0.013	0.109
Rb	<0.003									
S	<1.29	BQL		BQL	BQL	BQL	0.249	0.314	0.572	0.280
Sb	<0.009									
Se							0.001		0.001	
Si	2.990	1.880		1.700	0.905	2.310	5.377	6.312	5.767	4.809
Sn	<0.009									
Sr	<0.008									
Ti	0.036						0.077	0.116	0.083	0.074
V	<0.03									
Zn	0.058						0.057	0.055	0.012	0.040

References are listed in Table 1 Appendix. Associated notes are explained in Table 1.

\* Values for this size fraction are calculated from the average measured values reported for the other two size fractions.

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6A-31 DRAFT-DO NOT QUOTE OR CITE

COARSE COMPOSITION (24-hr AVG)					CENTRAL U.S.				Units = ug/m3		
Ref Site	8(a,o) Minneapolis	8(a,o) Kansas City MO	8(a,o) Akron	8(a,o) Cincinnati	8(a,o) Buffalo	8(a,o) Dallas	8(a,o) St. Louis	18(k,r) St. Louis	6,7(o,p)* St. Louis	17 St. Louis	6,7(o,p)* Steubenville
Dates	1980	1980	1980	1980	1980	1980	1980	8-9/76	9/79-6/81	9/85-8/86	4/79-4/81
Hours									0000-0000		0000-0000
Dur	24	24	24	24	24	24	24	6-12	24	24	24
Number	6	3	7	2	14	4	5		306	311	499
Mass	30.85	41.67	34.81	33.15	44.57	32.63	33.76	28.00	12.40	9.90	16.90
OC											
EC											
Nitrate											
Sulfate									3.04		4.80
Acidity											
Al	2.191	2.284	2.509	2.910	2.808	1.294	3.837	1.209			
As	0.001	0.003	0.003			0.006	0.001	0.001			
Ba								0.034			
Br	0.022	0.029	0.025	0.017	0.012	0.051	0.021	0.047	0.021		0.010
Ca	1.571	3.754	1.431	1.312	2.550	3.436	1.784	2.817	1.499		1.023
Cd								0.001			
Cl	0.293	0.530	0.572	0.103	0.728	0.029	0.053	0.257	0.093		0.211
Cr	0.002	0.004	0.014	0.002	0.015	0.005	0.001	0.009			
Cu	0.022	0.015	0.018	0.014	0.022	0.023	0.014	0.014			
Fe	0.744	0.979	1.640	0.883	2.040	0.720	0.587	1.218	0.580		1.610
K	0.310	0.361	0.324	0.363	0.206	0.210	0.291	0.392			
Mg											
Mn	0.026	0.025	0.044	0.021	0.078	0.020	0.017	0.035	0.019		0.039
Mo											
Na											
Ni	0.001	0.002	0.005	0.003	0.009	0.002	0.002	0.005	0.002		0.004
P				0.037				0.098			
Pb	0.098	0.109	0.097	0.099	0.108	0.252	0.095	0.189	0.088		0.043
Rb								0.002			
S	0.224	0.280	0.451	0.389	0.765	0.240	0.279	0.533	0.200		0.800
Sb								0.001			
Se								0.001			
Si	4.679	4.809	5.009	6.633	2.675	3.210	4.468	4.470	1.940		2.010
Sn								0.001			
Sr								0.007			
Ti	0.062	0.074	0.107	0.096	0.051	0.051	0.058	0.475			
V								0.004	BQL		0.002
Zn	0.027	0.040	0.069	0.148	0.043	0.030	0.021	0.074			

References are listed in Table 1 Appendix. Associated notes are explained in Table 1.

\* Values for this size fraction are calculated from the average measured values reported for the other two size fractions.

Table 6A-3

## Selected Ratios of Mass Components

	EAST		WEST		CENTRAL	
	Mean	N	Mean	N	Mean	N
FM/CM	2.59	8	0.89	11	1.06	25
FM/PM10	0.65	8	0.41	11	0.51	25
Tot Carbon/FM	0.25	7	0.54	5	0.64	5
NH42SO4/FM	0.47	12	0.15	13	0.39	28

N = number of studies contributing to the calculated means.

Tot Carbon = (OCx1.4 + EC).

Table 4a. Site-to-Site Variability of PM<sub>2.5</sub> Concentrations (ug/m<sup>3</sup>)

Study Area	Denver Metropolitan		Phoenix		Philadelphia		San Joaquin Valley	
No. of Sites	3,a		3,b		4,c		6,d	
Study Dates	11/2/87 - 1/31/88		10/13/89 - 1/17/90		7/25/94 - 8/14/94		6/14/88 - 6/9/89	
Reference	14		11		3		10	
	Mean	Spread	Mean	Spread	Mean	Spread	Mean	Spread
Fine Mass	19.67	2.89	29.38	3.49	32.18	2.17	29.89	10.02
OC	7.25	0.79	10.09	2.69	4.16	0.94	4.87	2.70
EC	4.41	0.78	7.49	1.71	0.69	0.21	3.24	2.58
Nitrate	3.96	0.93	3.60	0.37			8.17	2.27
Sulfate	1.55	0.16	1.33	0.24	13.43	0.33	3.00	1.33
Al	0.037	0.005	0.131	0.015	0.114	0.009	0.152	0.055
Br	0.018	0.006	0.011	0.003	0.009	0.005	0.010	0.006
Ca	0.058	0.001	0.167	0.033	0.058	0.014	0.096	0.050
Cl	0.141	0.013	0.366	0.356	0.026	0.007	0.094	0.070
Cr	0.003	0.002	0.003	0.001			0.003	0.002
Cu	0.017	0.008	0.015	0.003	0.007	0.001	0.096	0.036
Fe	0.111	0.023	0.216	0.035	0.127	0.037	0.180	0.060
K	0.077	0.009	0.209	0.020	0.060	0.008	0.188	0.080
Mn	0.012	0.003	0.023	0.010	0.003	0.000	0.006	0.003
Ni	0.002	0.002	0.003	0.001	0.007	0.002	0.016	0.030
Pb	0.075	0.017	0.039	0.009	0.019	0.010	0.029	0.021
S	0.642	0.077	0.436	0.038	3.251	0.081	1.242	0.565
Si	0.272	0.009	0.430	0.066	0.165	0.022	0.460	0.245
Ti	0.009	0.001					0.017	0.004
V					0.019	0.003	0.015	0.028
Zn	0.031	0.008	0.056	0.030	0.041	0.018	0.078	0.027

Mean = Mean over all sites of the average concentrations determined at each site for the sampling period.

Spread = ABS(Highest Mean Conc. - Lowest Mean Conc.)/2) for all the sites.

a. Federal, Auraria, and Welby sites in urban Denver.

b. Central Phoenix, Scottsdale, and Western Phoenix sites.

c. Broad Street, Castor Avenue, Roxboro, and Northeast Airport sites.

d. Stockton, Crow's Landing, Fresno, Kern, Fellows, and Bakersfield sites.



Table 4b. Site-to-Site Variability of PM10 Concentrations (ug/m3)

Study Area	San Jose		Phoenix		San Joaquin Valley	
No. of Sites	2,a		3,b		6,c	
Study Dates	12/16/91 - 2/24/92		10/13/89 - 1/17/90		6/14/88 - 6/9/89	
Reference	29		11		10	
	Mean	Spread	Mean	Spread	Mean	Spread
Fine Mass	64.95	1.65	62.47	7.06	62.92	17.28
OC	19.39	0.15	14.55	3.48	7.87	4.15
EC	9.02	0.42	8.33	1.78	3.51	2.76
Nitrate	10.90	0.60	4.46	0.45	9.44	3.02
Sulfate	2.24	0.09	1.70	0.29	3.57	1.46
Al	0.845	0.035	2.670	0.273	2.993	1.570
Br	0.012	0.001	0.014	0.003	0.012	0.005
Ca	0.670	0.048	2.096	0.317	0.950	0.390
Cl	0.728	0.032	0.559	0.349	0.388	0.225
Cr	0.003	0.001	0.011	0.002	0.009	0.003
Cu	0.029	0.002	0.036	0.009	0.084	0.046
Fe	0.834	0.027	1.475	0.170	1.413	0.445
K	0.823	0.021	0.878	0.083	0.720	0.220
Mn	0.014	0.001	0.054	0.014	0.030	0.011
Ni	0.003	0.000	0.006	0.002	0.019	0.032
Pb	0.035	0.004	0.062	0.013	0.039	0.027
S	1.147	0.091	0.615	0.041	1.472	0.605
Si	2.905	0.045	7.442	0.862	7.517	1.765
Ti	0.088	0.024	0.121	0.024	0.128	0.033
V	0.007	0.003			0.022	0.030
Zn	0.065	0.005	0.090	0.034	0.085	0.029

Mean = Mean over all sites of the average concentrations determined at each site for the sampling period.

Spread = ABS(Highest Mean Conc. - Lowest Mean Conc.)/2 for all the sites.

a. San Carlos St. and Fourth St. sites.

b. Central Phoenix, Scottsdale, and Western Phoenix Sites.

c. Stockton, Crow's Landing, Fresno, Kern, Fellows, and Bakersfield sites.

## 7. HUMAN EXPOSURE TO PARTICULATE MATTER AMBIENT AND INDOOR CONCENTRATIONS

### 7.1 INTRODUCTION

The 1982 United States Environmental Protection Agency (U.S. EPA) Air Quality Criteria Document for Particulate Matter and Sulfur Oxides (PM-SO<sub>x</sub> AQCD) thoroughly reviewed the PM exposure literature through 1981. The later 1986 "Second Addendum to Air Quality Criteria for Particulate Matter and Sulfur Oxides (1982)" added coverage of newly available health effects information with references up to 1986. Consequently, literature directly concerning human exposure to PM has only been previously reviewed thoroughly in an AQCD through 1981 and partially reviewed through 1986.

This new analysis first summarizes key points from the exposure section of the 1982 PM-SO<sub>x</sub> AQCD, and then reviews thoroughly the PM exposure literature from 1982 through 1993 and includes 1994 literature published and in press through approximately September 1994. Some additional literature available in 1994 and 1995 has also been included.

The U.S. Environmental Protection Agency regulatory authority for PM only extends to the ambient air, defined in 40CFR as that portion of the atmosphere, external to buildings, available to the general public. One major objective of this chapter is to examine the utility of centralized ambient PM monitoring data as a reasonable surrogate for the average of personal exposures to ambient PM of people in the surrounding community. A secondary objective is to quantify the contribution of ambient air to the personal exposure.

By the operative definition of ambient air, air inside a building or on private property is not regulated by the NAAQS. However, it is important to consider total personal exposures to PM both from the regulated ambient air and non-regulated air. This is because a variable fraction of ambient PM penetrates into different non-ambient settings where exposure to PM of ambient origin also takes place and, independently, toxic PM can be generated within a non-ambient setting (e.g. cigarette smoke).

Personal exposure to PM is important in itself, because it may give us clues as to which components of PM may be active or inactive biologically. In addition, personal exposure can act as a confounder in epidemiological studies which use an inferred community exposure

to ambient PM as a parameter to correlate with community health parameters. On the other hand, an individual's personal exposure to total PM is a critical parameter for analysis if that person is a member of a cohort whose health outcomes are being tracked individually. Therefore, the chapter examines not only personal exposures to ambient PM, but also community and individual exposures to PM, which include that portion of ambient PM which penetrates into indoor microenvironments ( $\mu$ Es). This is to aid in the interpretation of those acute and chronic epidemiology studies of Chapter 14, in which ambient PM concentrations are assumed to be an indicator or a surrogate for mean community exposure to PM or an individual exposure to ambient PM.

This chapter focuses on studies which include information on measurements of simultaneous personal PM exposures, indoor-residential PM concentrations and ambient PM concentrations. Because people spend an average of 21 h per day indoors (Robinson and Nelson, 1995) the indoor environment is the major exposure category. Therefore, studies on concentrations of PM indoors are discussed below in Section 7.6 on Indoor Air. The reason for this separation of indoor concentration from personal exposure is explained below in the general concepts Section 7.1.2.

### **7.1.1 Ambient PM Concentration as a Surrogate for PM Dosage**

The health effects of PM on an individual depend upon the mass and composition of those particles which are deposited within the various regions of the respiratory tract during the time interval of interest. The amount of this potential-dose (FR, Part VI, EPA, Guidelines for Exposure Assessment, May 29, 1992) will be the product of the concentration inhaled (e.g., the instantaneous personal exposure) times the ventilation rate (a function of activity and basal metabolism) times the fractional deposition, which is a function of ventilation rate and mode of breathing (e.g., oral or nasal). If all people had identical ventilation rates and deposition patterns, then the potential-dosage distribution could be linearly scaled to the personal exposure distribution which would serve as a suitable primary surrogate. The usage of ambient PM concentration in health studies as a surrogate for personal PM exposure, and thereby a secondary surrogate for the PM dosage, would be suitable if ambient concentration was also linearly related to the personal exposure (Mage, 1983).

1 The ventilation rate, which is at a minimum during the night while asleep ( $\approx 6$  L/m)  
2 and at a maximum during the day while awake ( $\approx 12$  L/m) is in phase with PM exposure  
3 which is also lower at night than during the day (Clayton et al., 1993). Consequently the  
4 product of the 24-h average exposure, the 24-h average ventilation rate, and the average  
5 deposition parameter for the average ventilation, would seriously underpredict the amount of  
6 particulate matter deposited in the respiratory tract (Mage, 1980).

7 In practice, when relating human health to pollution variables, one is forced to use  
8 ambient concentration as a surrogate for exposure and dosage because there are typically only  
9 fragmentary data on personal exposures in populations. Data are also limited on ventilation  
10 rates as a function of basal metabolism and physical activities. Furthermore, there are  
11 virtually no applicable data on the deposition rates of the particles which people are inhaling  
12 since the size distribution is unknown and deposition is influenced by individual physiological  
13 parameters which are unmeasured. According to Hodges and Moore (1977), "even when an  
14 explanatory variable (ambient PM concentration) can be measured with negligible error it  
15 may often be standing as a proxy for some other variable (dosage) which cannot be measured  
16 directly, and so it (dosage) is subject to measurement error". This measurement error can  
17 produce a negative bias on the relationship between health effects and PM dosage, which  
18 may be a partial explanation of why many previous studies have found a positive but not  
19 statistically significant relationship between health effects and ambient PM concentration  
20 (Pickles, 1982).

21 In the sections of this Chapter that follow, the relationships between ambient PM  
22 concentration, indoor PM concentrations and personal exposures to PM are discussed in  
23 detail. The reader should keep in mind the following two caveats while going through this  
24 chapter:

- 25  
26 1. Both ambient PM concentration and personal exposure to PM are surrogates for the  
27 amount of PM deposited in people's respiratory tracts. Even this quantity is a  
28 surrogate for the true (but unknown) species and/or fraction of total PM that is the  
29 specific etiological toxic agent(s) that act by an unknown mechanism. This  
30 unknown quantity should be the independent variable for developing the underlying  
31 relationship of ambient PM and PM exposure to the health indices used as the  
32 dependent variables.  
33
- 34 2. Virtually all analyses and discussions presented below are based upon the personal  
35 exposure to PM of non-smokers. Only Dockery and Spengler (1981) included 6

smokers out of 37 subjects. Smokers are often excluded from these studies because a personal exposure monitor (PEM) on a smoker will not capture the main-stream tobacco smoke that is directly inhaled. In Section 7.6 on indoor air pollution, it is shown that side-stream environmental tobacco smoke (ETS) is the largest identifiable indoor source of PM. For the average smoker, the amount of direct inhalation (several milligrams of PM per cigarette) can be two-to-three orders of magnitude greater than the microgram amounts of ETS which the PEM captures (Rexford and Lowery, 1980). The relationships presented below, of ambient PM to individual PM exposure, only apply to non-smokers.

### 7.1.2 General Concepts for Understanding PM Exposure and Microenvironments

PM represents a generic class of pollutants which requires a different interpretation of exposure in contrast to that for the other specific criteria gaseous 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 fireplace, a 1- $\mu$ m aerodynamic diameter (A.D.) particle emitted from the motor vehicle and a 1- $\mu$ m A.D. particle emitted from the fireplace can have different shape, different mass, different chemical composition, and different toxicity. A 1- $\mu$ m "particle" can be a single entity, or an agglomeration of smaller particles, such as a small Pb particle bound to a larger crustal particle. Furthermore, indoor sources of particles produce a wide variety of particles of varying size and composition that people will be exposed to, as shown in Figure 7-1 (Owen et al., 1992). Given that the health effects of inhalation of any particle can depend upon its mass and chemical composition, it would be of use to measure PM exposure in terms of mass and chemical composition as a function of size distribution (Mage, 1985).

The total exposure of an individual to PM during a period of time is composed of exposure to a variety of different particles from a variety of different sources in a variety of different microenvironments ( $\mu$ E). A  $\mu$ E was defined by Duan (1982) as "a chunk 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  $\mu$ E and its surrounding  $\mu$ Es.

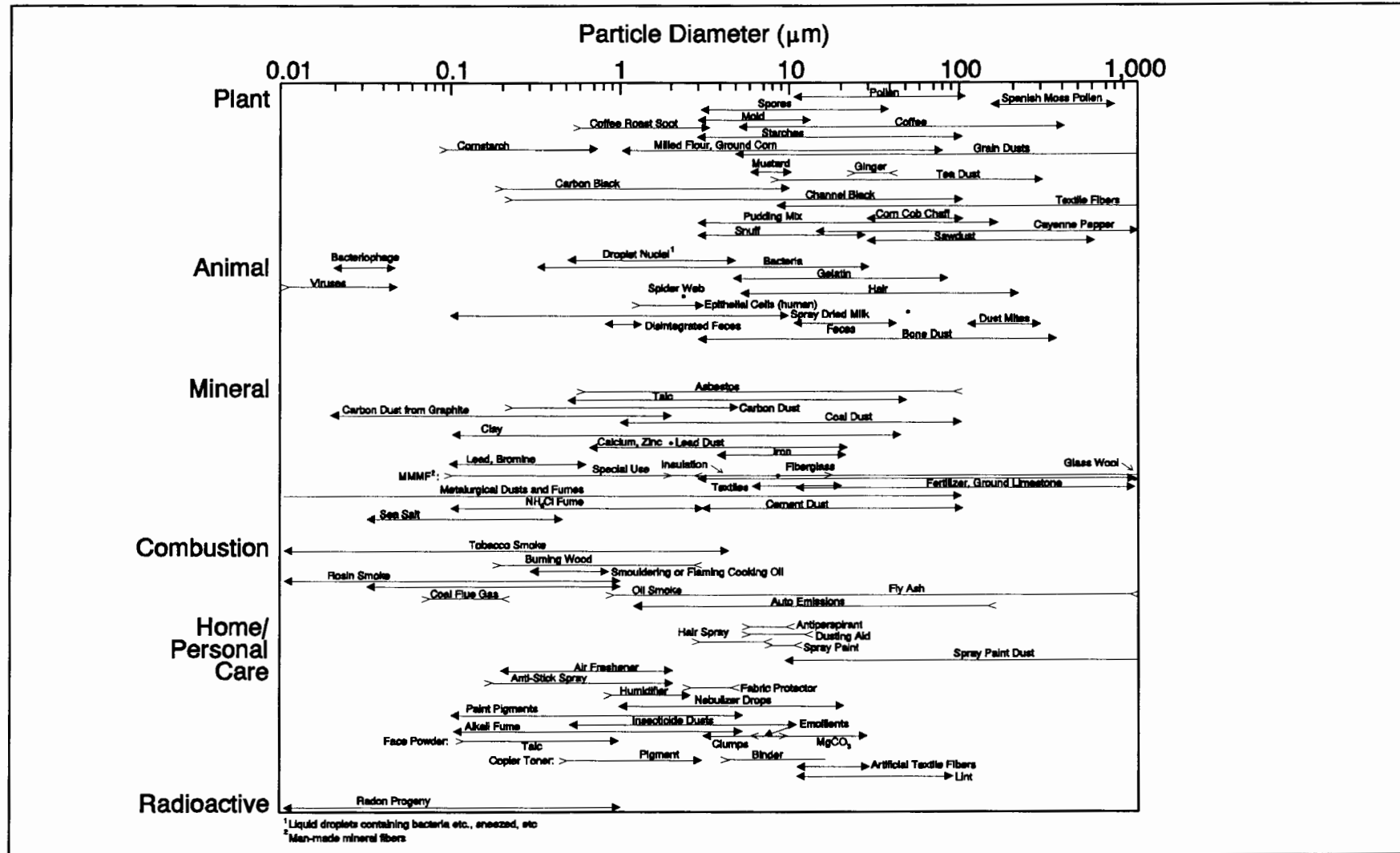


Figure 7-1. Sizes of indoor particles.

Source: Owen et al. (1992)

1 For example, a kitchen with a wood stove can constitute a single  $\mu$ E for total PM,  
2 when the stove is off, and all people in the kitchen would have similar PM exposures. When  
3 the stove is in operation, the kitchen could have a significant vertical PM concentration  
4 gradient and a child on the floor in a far corner and an adult standing at the stove could be  
5 exposed to significantly different PM concentrations.

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

12 In general, as a person moves through space and time, they pass through a series of  
13  $\mu$ Es and their average total exposure ( $X$   $\mu$ g/m<sup>3</sup>) PM for the day can be expressed by the  
14 following equation,

$$X = \sum X_i t_i / \sum t_i \quad (7-1)$$

17  
18 where  $X_i$  is the total exposure to PM in the  $i^{\text{th}}$   $\mu$ E, visited in sequence by the person for a  
19 time interval  $t_i$  (Mage, 1985). Individual human activity patterns determine the time-  
20 sequence in which these  $\mu$ Es may be visited and, therefore, the magnitude of the overall  
21 concentration to which a person is exposed. Let two people on a given day spend 1-h  
22 outdoors. If one person is outside from 7 to 8 a.m and the other is outside from 7 to 8 p.m.  
23 they can have significantly different PM exposures, neither of which would be characterized  
24 by the midnight-to-midnight 24-h average.

25 With appropriate averaging over sets of 4 classes of  $\mu$ Es (e.g. indoors, ambient-  
26 outdoors, occupational, and in-traffic we can simplify the Equation 7-1 as follows (Mage,  
27 1985):

$$X = (X_{\text{in}} t_{\text{in}} + X_{\text{out}} t_{\text{out}} + X_{\text{occ}} t_{\text{occ}} + X_{\text{tra}} t_{\text{tra}}) / T \quad (7-2)$$

1 where each value of X is the mean value of total PM concentration in the  $\mu$ E class while the  
2 subject is in it, time (t) is the total time the subject is in that  $\mu$ E during the day, and T is  
3 equal to the sum of all times (usually 1-day). Similar equations may be written for personal  
4 exposures to particles from specific sources (e.g. Diesel soot), for specific chemicals (e.g.  
5 Pb), or for specific size intervals ( $PM \leq 2.5\mu$  AD).

6 In reference to the situation cited above, of two people on the same day spending an  
7 identical 1-h as  $t_{out}$  at different times during the day, they would have to have two different  
8 values of  $X_{out}$  in their exposure calculation. This is in accordance with the precept of Ott  
9 (1982) that an air pollutant exposure requires the confluence of two variables - the  
10 concentration of PM  $X(x,y,z,t)$  at a location (x,y,z) and time t, and the position of an  
11 individual's breathing zone at x,y,z,t.

12 In the literature, many excellent studies have reported data on air quality concentrations  
13 in  $\mu$ E settings that do not meet a rigorous definition of an exposure, which requires  
14 occupancy by a person (Ott, 1982). Section 7.6 on Indoor Concentrations and Sources, cites  
15 Thatcher and Layton (1994) who report that "merely walking into a room increased the  
16 particle concentration by 100% (from 10 to 20  $\mu\text{g}/\text{m}^3$ )", perhaps by air currents reentraining  
17 PM. Consequently, a measurement of air quality in a space that includes time when it is  
18 unoccupied may not be a valid measure that can be used to estimate an exposure. If this  
19 measure includes the periods of time when the space was unoccupied it will tend to be biased  
20 low as a measure of the exposure within it during periods of occupancy.

21 In the context of exposure, it may be inappropriate to associate an average exposure to  
22 a person while cooking at a stove in a kitchen with a concentration measurement that is  
23 influenced by periods when people were not in the kitchen or when the stove was not in  
24 operation. It is therefore understood that an average concentration measured in an indoor  
25 setting - including periods when people are not present - may not have direct relevance for  
26 computing personal exposure because it is not necessarily the concentration during the  
27 portion of time that the subject was inside that  $\mu$ E.

28 The literature on 24-h average PM concentrations in indoor  $\mu$ Es, such as those in  
29 residential settings, are treated separately in Section 7.6, as is done for 24-h average ambient  
30 PM concentrations in Chapter 6. In the exposure portion of this chapter, specific reference  
31 will be made to some of those studies where simultaneous personal exposures and indoor



1 measurements have been made so that the relationship between indoor concentration and  
2 personal exposure can be examined.

3 In practice a cascade sampler can collect ambient PM samples by size fractionation for  
4 separate chemical analyses, but such a complete definition of personal exposure to PM by  
5 chemistry and size is impossible to obtain. Although some personal monitors can be  
6 equipped with a cyclone or impactor separator and two filters to capture two sizes (e.g.,  
7  $<2.5 \mu\text{m}$  and  $2.5$  to  $10 \mu\text{m}$ ), because of the current size of a two filter sampler and the low  
8 mass collected in the two fractions, one almost exclusively obtains a single integrated  
9 measurement of particle mass collected (e.g.,  $<2.5 \mu\text{m}$  or  $<10 \mu\text{m}$ ). Consequently, health  
10 studies on individuals are usually only able to develop associations between their observed  
11 health effects and their observed exposure expressed as an integral mass of PM collected and  
12 its average chemical composition.

13 Health studies on populations can make multiple measurements of ambient and indoor  
14 PM concentrations simultaneously (e.g.,  $\text{PM}_{2.5}$ ,  $\text{PM}_{10}$ , TSP) along with components of PM,  
15 such as polycyclic aromatic hydrocarbons (PAHs), to help understand the size distribution  
16 and chemistry of the particles in the ambient and indoor atmospheres. However, these data  
17 may be weakly correlated with simultaneous personal PM exposure measurements.

### 19 **7.1.3 Review of State-of-knowledge Recorded in the 1982 PM-SO<sub>x</sub> AQCD**

20 In 1982 it was known, from personal monitoring and indoor monitoring, that SO<sub>2</sub> is  
21 almost always lower indoors than outdoors because of the virtual absence of indoor sources  
22 for SO<sub>2</sub> and the presence of sinks for SO<sub>2</sub> in indoor settings (Exceptions can occur if high  
23 sulfur coal or kerosene are used as fuel in a poorly vented stove or space heater). However,  
24 this relationship does not hold for PM as the indoor and personal monitoring data show both  
25 higher- and lower-than ambient PM concentrations in indoor settings as a function of particle  
26 size and human activity patterns.

27 The largest coarse mode particles ( $>10 \mu\text{m}$ ), which are generally of nonanthropogenic  
28 origin (wind blown dust, etc.), require turbulence to provide vertical velocity components  
29 greater than their settling velocity to allow them to remain suspended in the air (Figure 7-1).  
30 Outdoor particles enter into an indoor setting either by bulk flow, as through an open  
31 window, in which all particles can enter at the inlet condition, or by pressure driven drafts

1 and diffusional flows through cracks and fissures in the barriers of the building envelope  
2 when all windows are closed. In the latter mode of entry, velocities are relatively lower,  
3 thereby settling out the largest coarse particles in the passage through the barriers.

4 Indoor settings are usually quiescent (Matthews et al., 1989), and the larger ambient  
5 particles that do enter indoors quickly settle out by gravity and electrostatic forces, leading to  
6 the presence of the familiar dust layers on horizontal surfaces and vertical TV screens that  
7 require constant cleaning (Raunemaa et al., 1989). However, human activity in indoor  
8 settings, such as smoking, dusting, vacuuming and cooking, does generate fine particles  
9 ( $<2.5 \mu\text{m}$ ) and coarse particles ( $>2.5 \mu\text{m}$ ), and resuspends particles that previously had  
10 settled out (Thatcher and Layton, 1994; Litzistorf et al., 1985).

11 There were only three studies of personal PM exposures, compared to ambient PM  
12 concentrations, that were referenced in the PM-SO<sub>x</sub> criteria document. Binder et al. (1976)  
13 reported that "outdoor air measurements do not accurately reflect the air pollution load  
14 experienced by individuals who live in the area of sampling", in a study in Ansonia, CT,  
15 where personal exposures to PM<sub>5</sub> were double the outdoor PM concentrations measured as  
16 TSP (PM<sub>27</sub>) (115 versus 58  $\mu\text{g}/\text{m}^3$ ). Spengler et al. (1980) was cited as reporting that "there  
17 was no correlation [ $R^2 = 0.04$ ] between the outdoor level [of respirable particles] and the  
18 personal exposure of individuals" in a study in Topeka, KS. Figure 7-2, from Repace et al.  
19 (1980), was presented as an example of the variability of PM exposures which show very  
20 little influence of ambient concentration. Consequently, at the time of writing the 1982 PM-  
21 SO<sub>x</sub> AQCD, two major factors were known to influence the relationship of ambient to indoor  
22 PM air quality. They were (1) the variability of indoor concentrations of PM compared to  
23 outdoor concentrations as a function of particle size (e.g., fine indoor  $\geq$  fine outdoor and  
24 coarse indoor  $<$  coarse outdoor) and (2) the variation of exposures of individuals related to  
25 the different activities that are involved with the local generation of particles in their  
26 immediate surroundings (smoking, traffic, dusting and vacuuming at home, etc.). This  
27 understanding was summarized as follows (pg. 5-136, PM AQCD, 1982):  
28  
29

- 30 • long term personal exposures to fine fraction PM ( $<2.5 \mu\text{m}$ ) of outdoor origin, may  
31 be estimated by ambient measurements of the  $<2.5 \mu\text{m}$  PM fraction.

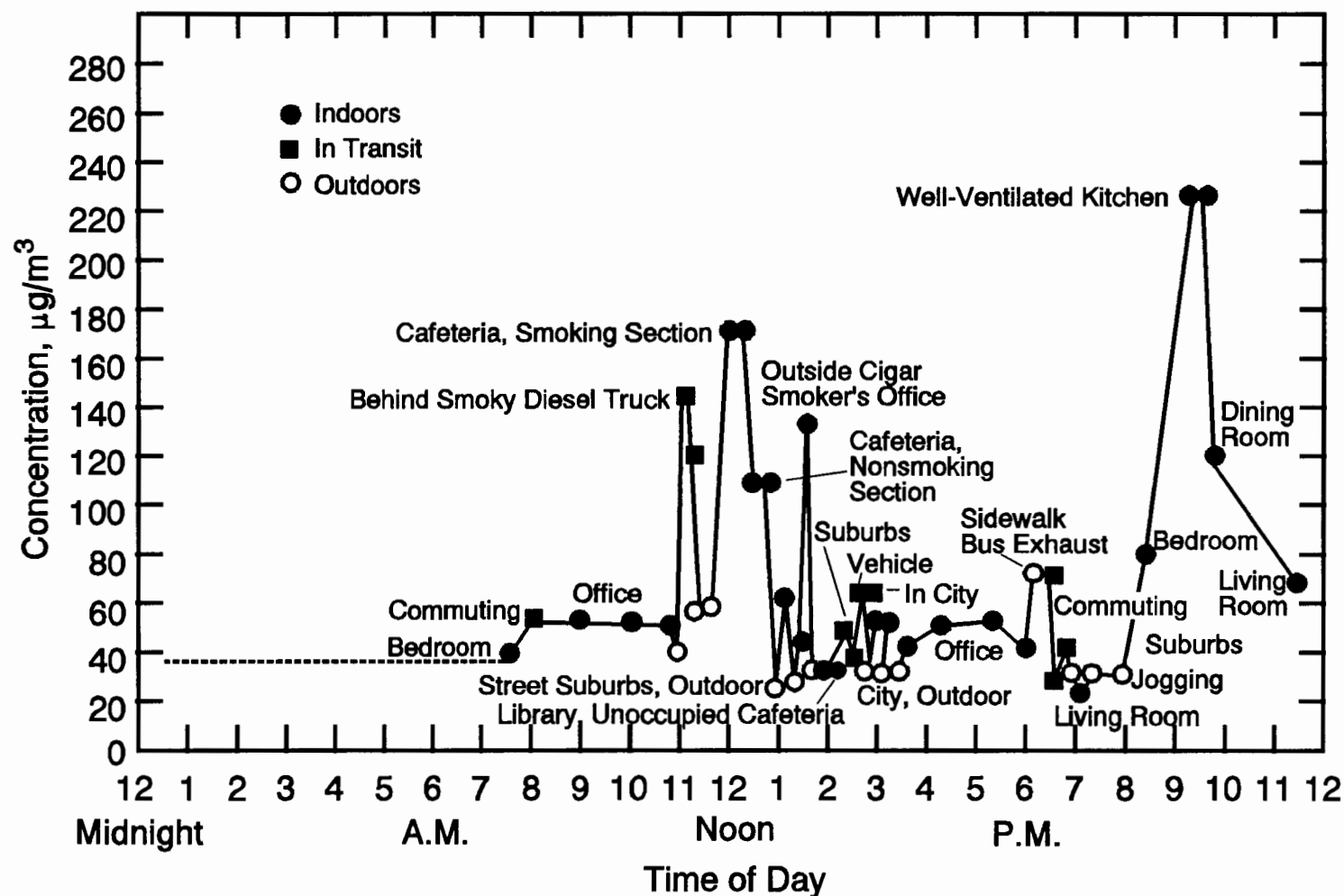


Figure 7-2. An example of personal exposure to respirable particles.

Source: Repace et al. (1980)

- Personal activities and indoor concentrations cause personal exposures to PM to vary substantially. Ambient measurements appear to be a poor predictor of personal exposure to PM.
- Tobacco smoke is an important contributor to indoor concentrations and personal exposures where smoking takes place.

## **7.2 DIRECT METHODS OF MEASUREMENT OF HUMAN EXPOSURE TO PM BY PERSONAL MONITORING**

Human exposure to air pollution can be measured by placing a personal exposure monitor (PEM) close to the breathing zone of an individual. However, the very act of studying the subjects can influence the measured value of their exposure and create an erroneous reading. These influences arise because the subjects become conscious of the study objectives from the indoctrination required to obtain their written informed consent to participate, and the presence of the PEM on their body is a constant reminder.

The physical location of the monitor inlet, as worn by the subject, can also influence the subject's PM exposure and the recorded PM. The movements of the subject's body and sampling flow rate can alter the air currents in the subjects breathing zone. "The presence of the body and its movement affect what a personal sampler collects" (Ogden, 1993). When in close proximity to a source actively emitting PM (within a meter) a small change in PEM position (e.g. from left side to right side) can vary the PM measurement.

These unquantifiable 'errors' in a PM PEM measurement may be greater than the filter weighing errors and flow rate measurement errors that can be quality controlled through calibration procedures. This may be important for interpretation of the PM PEM data in the literature because the expectation is that these errors inflate the variance of the measurements. In the following section, the individual error components that arise from the measurement process are discussed.

### **7.2.1 Personal Monitoring Artifacts**

#### **7.2.1.1 'The Hawthorne Effect'**

If subjects carry a personal exposure monitor (PEM) they may change their behavior, subconsciously or consciously, which is known as "The Hawthorne Effect" (Last, 1988).

1 The name derives from early studies of worker productivity at Western Electric's Hawthorne  
2 plant in Cicero, IL (Mayo, 1960). For instance a subject may choose not to go to the opera  
3 because the pump noise of the monitor would be disturbing to others. Even though the  
4 exposure measured in the alternative activity may be quite accurate, it would be an artifact in  
5 the context of exposure assessment, because the activity not performed (opera attendance)  
6 would have been the correct one to monitor.

#### 7 8 **7.2.1.2 The Monitor Effect**

9 The filtration of the breathing zone air by a PEM can reduce the PM concentration in  
10 the breathing zone by "self dilution" (Cohen et al., 1984). The placement of the personal  
11 monitor in the breathing zone, as well as its flow rate, can alter the air flow stream lines in  
12 the area of the nose or mouth that would exist in its absence. There may be an electrostatic  
13 charge on the plastic cassette filter holder which can possibly affect the collection of charged  
14 particles (Cohen et al., 1982).

#### 15 16 **7.2.1.3 Subject Effect**

17 A subject may contaminate the personal monitoring data by an inadvertent action, such  
18 as forgetting to put on the PEM upon awakening in the morning, or purposefully choosing  
19 either not to wear it when going to the opera (anti-'Hawthorne Effect') or placing it close to  
20 a source. If such actions are not recorded in a diary or reported to the investigator during a  
21 verbal debriefing, the exposure data, although valid per se as an actual concentration  
22 measurement, could be treated as a valid exposure of a subject in his/her daily life and  
23 related to an incorrect classification.

24 For example, Sexton et al (1984) reported that one male subject with a personal exposure  
25 mean of  $77 \mu\text{g}/\text{m}^3$  had a spouse with a simultaneous personal exposure of  $37 \mu\text{g}/\text{m}^3$ , with no  
26 recorded activity that could explain the higher exposure values.

#### 27 28 **7.2.1.4 Non-Response Error**

29 In performance of a personal monitoring study, people often refuse to participate. The  
30 refusal rate increases with the burden on the respondents due to the time required to  
31 complete questionnaires, diaries and the need to carry the personal monitor with them

1 throughout the study. If the cohort of people who refuse to participate have significantly  
2 different personal PM exposures than the participants, then the study will produce a biased  
3 estimate of the exposures of the total population.  
4

### 5 **7.2.2 Characterization of PM Collected by Personal Monitors**

6 The amount of PM collected by different types of personal monitors with the identical  
7 nominal cut-point can be variable. Small differences in the cut point (AD at 50% efficiency)  
8 and in other portions of the penetration curve can exist under calm wind conditions when the  
9 monitor is stationary, and these differences can also be a function of the air velocity relative  
10 to the monitor. Consequently, the difference between two PM measurements made by two  
11 nominally identical monitors of different design, can be a function of the wind speed and the  
12 size distribution of the PM in the air mass being sampled. Given the knowledge of the  
13 sampled size distribution (as collected) and the complete penetration curve, the concentration  
14 in the free atmosphere can be predicted (Mage, 1985). For example, if a sampler collects 1  
15  $\mu\text{g}/\text{m}^3$  of PM in a size interval that has an overall efficiency of  $\phi$ , then we can estimate that  
16 the atmosphere contained  $1/\phi$   $\mu\text{g}/\text{m}^3$  of PM of the same size range. A recent field  
17 comparison of different types of respirable dust samplers used in occupational settings where  
18 coarse mode particulate is predominating, by Groves et al. (1994), shows that there is a  
19 considerable difference between the mass collected by sets of paired cyclones sampling in a  
20 concentration range of 0.5 to 6.6  $\text{mg}/\text{m}^3$ , which is much higher than normally seen in non-  
21 occupational personal exposure studies. This type of comparison study has not been done for  
22 personal monitors used in nonoccupational studies at the ambient and indoor respirable  
23 concentrations on the order of 0.01 to 0.1  $\text{mg}/\text{m}^3$  where the fine mode is more important.  
24

### 25 **7.2.3 Microscale Variation and the Personal Cloud Effect**

26 The tendency for human activity in the home or at work to generate a 'personal activity  
27 cloud' of particles from clothing and other items (carpet, stuffed furniture, etc.), that will be  
28 intense in the breathing zone, and diluted near an area monitor located several meters away,  
29 has also been cited as a contributing factor to the discrepancy between personal measures of  
30 exposure and time weighted average (TWA) exposures using microenvironmental  
31 measurements (Martinelli et al., 1983; Cohen et al., 1984; Rodes et al., 1991). The

1 difference between sampling for PM at the nose, on the lapel or at a point several meters  
2 away from a person can be appreciable. The microscale variation in PM between a personal  
3 monitor sampling at the nose, versus an identical monitor sampling at the lapel, has been  
4 investigated by Cohen et al. (1982, 1984) who found no net bias resulted from sampling at  
5 either location in a concentration field of uniformly dispersed aerosol. However, they noted  
6 that spatial concentration variability and resuspended dust from clothing, and to a lesser  
7 extent electrostatic charges on plastic filter cassette holders (and plastic eyeglass frames),  
8 could lead to different exposure measurements in the facial region, with three times as much  
9 mass collected by a filter attached to the clothing as from the air sampled directly in the  
10 breathing zone.

11 Fletcher and Johnson (1988) also measured metal concentrations (measurement method  
12 and size unspecified) in an occupational exposure situation (metal spraying of spindles on a  
13 lathe) and found 50% higher concentrations measured from the left lapel compared to the  
14 right lapel, which reflected the orientation of the operator to the lathe. When a neutrally  
15 buoyant tracer gas mixture was released 0.5 m from an operator in a different work setting  
16 there was no variation between the left and right lapels, and the nose, as found by Cohen et  
17 al. (1982). However, when the experiment was performed with a heavier-than-air tracer gas  
18 mixture, the nose measurement was approximately 25% less than the lapel concentrations.  
19 This implies that if submicron particles, which behave like a gas, are emitted close to the  
20 subject in a buoyant plume, there may also be significant microscale variations in the  
21 breathing zone.

22 Parker et al. (1990) measured the aerosol distribution in a small test room resulting  
23 from a nozzle-jet injection, using a "heated phantom" (mannequin), and found larger  
24 discrepancies between chest mounted monitors and area monitors up to three meters away,  
25 by up to a factor of ten difference.

### 28 **7.3 NEW LITERATURE ON PARTICLE EXPOSURES SINCE 1981**

29 The following sections review studies that measured PEM PM in the general non-  
30 smoking population. In these studies, the subjects spent time at home and in other indoor  
31 environments that include time at work. In the USA, recent data indicate that on a daily

1 basis, an average US resident spends approximately 21 h indoors (87.2%), 100 minutes in  
2 (or near) a vehicle (7.2%), and 80 minutes outdoors (5.6%) [Robinson and Nelson, 1995].

3 The concentration of PM in residential and commercial indoor settings is thoroughly  
4 reviewed and presented in Section 7.6. However, the concentrations of PM and personal  
5 exposures to PM in 'indoor' industrial workplaces (e.g. coal mines) and the "dusty trades"  
6 (e.g. carpentry or machinist), which are covered by occupational standards for air quality,  
7 are not covered in this document.

8 Almost all the studies of PM exposure in the general public have been conducted on  
9 urban and suburban residents. These subjects are often working in occupations that do not  
10 require PM monitoring to assure that occupational standards are being met (e.g. in an  
11 office). However, PM monitoring in an industrial workplace by a subject - independently of  
12 an official corporate industrial hygiene program - can have legal or security implications for  
13 an employer. For example, in a study in Tennessee (Spengler et al., 1985) some potential  
14 subjects were unable to participate because their employer (Oak Ridge National Laboratory)  
15 would not allow them to wear PM monitors at work. Such exclusion of subjects from  
16 exposure studies can negatively bias measured exposure distributions if the reason for the  
17 exclusion is related to their potential for high PM exposure.

18 A further complication arises from the fact that industrial exposures tend to be  
19 dominated by a specific type of particle. Coal miners are exposed to coal dust, textile  
20 workers are exposed to cotton dust and welders are exposed to metal fumes. An additional  
21 chapter on personal exposures to industrial PM would be needed to describe the various  
22 industries and trades that have their own individual PM problems, and the usage pattern and  
23 efficiencies of respirators and masks that are required to be worn. Therefore, occupational  
24 PM studies are not presented, and only some selected studies are cited to illustrate a  
25 particular point that is applicable to exposure studies in general, such as microscale variation  
26 in PM when close to a source of PM.

27 It may be useful to keep in mind that the baseline exposure of nonsmoking workers in  
28 the "dusty trades" or industrial workplaces may be similar to that of other nonsmoking  
29 people in their communities. Their total working day exposure would then be approximated  
30 by that baseline exposure plus their incremental workplace exposure for 8 h, in a similar



manner to a smoking increment for smokers. On a day off from work, these worker's exposures may be similar to that of the general nonsmoking public.

### 7.3.1 Review of the Literature

#### 7.3.1.1 Results of U.S. Studies

Dockery and Spengler (1981) compared personal  $PM_{3.5}$  exposures and ambient  $PM_{3.5}$  concentrations in Watertown, MA, and in Steubenville, OH. In Watertown, 24-h personal samples were collected on a 1-in 6-day schedule, and in Steubenville, 12-h personal samples (8 a.m. to 8 p.m.) were collected on a Monday-Wednesday-Friday schedule. A correlation coefficient of 0.692 between the mean personal and the mean ambient concentration for 37 subjects, 18 in Watertown and 19 in Steubenville, was reported for the pooled data. However, this appears to be an artifact of two separate clusters formed by these data, each with considerably lower correlation. When these data are analyzed separately, the regression coefficient between personal and ambient for Watertown is  $R = 0.01$  and for Steubenville it is  $R = 0.43$ .

Sexton, Spengler and Treitman (1984) studied personal exposures to respirable particles ( $PM_{3.5}$ ) for 48 nonsmokers during a winter period in Vermont, where firewood was either the primary or secondary heating source for the subject. Their results showed that personal exposures were 45% higher than indoor averages ( $36 \mu g/m^3$  versus  $25 \mu g/m^3$ ) and indoor averages were 45% higher than outdoor averages ( $25 \mu g/m^3$  versus  $17 \mu g/m^3$ ). This relationship is consistent with those reported in the 1981 PM-SO<sub>x</sub> AQCD (Spengler et al., 1980). Ambient air pollution, measured by an identical stationary ambient monitor (SAM) outside each residence (a pump contained in a heated box was connected to an external cyclone and filter), had no correlation with the resident's personal exposures ( $R^2 = 0.00$ ) and 95% of the subjects had personal exposures greater than the median outdoor concentration. This would not contradict the first conclusion cited from the 1982 PM-SO<sub>x</sub> AQCD if there were sources of  $PM_{3.5}$  indoors.

Spengler et al. (1985) reported a study of  $PM_{3.5}$  exposures in the non-industrial cities of Kingston and Harriman, Tennessee, during the winter months of February through March, 1981. A large TVA coal burning power plant (Watts Bar) with very tall stacks in the immediate area was not a local source of particulate pollution. In this study, two

Harvard/EPRI PM<sub>3.5</sub> monitors were used for each person. One stationary indoor monitor (SIM) remained indoors in the home, in the open air of a first floor activity room, and the second monitor (PEM) was carried for 24-h to obtain the personal exposure. In each community, identical Harvard/EPRI samplers (SAM) were placed at a central site to represent ambient PM<sub>3.5</sub> concentrations. The results of the study are shown in Table 7-1. In both communities, 95% of the subjects had personal exposures to PM<sub>3.5</sub> greater than the average ambient concentrations. The mean personal exposure and indoor concentrations ( $44 \pm 3 \mu\text{g}/\text{m}^3$  and  $42 \pm 3 \mu\text{g}/\text{m}^3$ ) were more than 100% greater than the mean ambient average of  $18 \pm 2 \mu\text{g}/\text{m}^3$  sampled on the same days.

**TABLE 7-1. QUANTILE DESCRIPTION OF PERSONAL, INDOOR, AND OUTDOOR PM<sub>3.5</sub> CONCENTRATIONS (in  $\mu\text{g}/\text{m}^3$ ), BY LOCATION IN TWO TENNESSEE COMMUNITIES**

City	Group	N	95%	75%	50%	25%	5%	Mean	S.E.
Kingston	Personal	133	99	47	34	26	19	42	2.5
	Indoor	138	110	47	31	20	10	42	3.5
	Outdoor	40	28	22	16	12	6	17	2.7
Harriman	Personal	93	122	54	35	24	15	47	4.8
	Indoor	106	129	45	27	18	10	42	4.1
	Outdoor	21	34	23	15	13	9	18	4.0
Total K&H <sup>a</sup>	Personal	249	113	48	34	26	17	44	2.8
	Indoor	266	119	46	29	20	10	42	2.6
	Outdoor	71	33	23	17	13	7	18	2.1

<sup>a</sup>Includes samples from 13 subjects living outside Kingston and Harriman town limits and from four field personnel residing in these communities.

N = number of samples.

S.E. = Standard error.

Source: Spengler et al. (1985).

For the complete cohort, the correlation between PM PEM and PM SAM was  $r = 0.07$  ( $p = 0.30$ ), and between PM PEM and PM SIM was  $r = 0.70$  ( $p = 0.0001$ ). The correlation between simultaneous PM PEM and PM SAM was  $r = 0.15$  for 162 nonsmoke

1 exposed individual observations ( $p = 0.06$ ). For 63 observations on smoke exposed  
2 individuals, the correlation  $r = 0.16$  was not significant ( $p = 0.16$ ).

3 An important finding was that in nonsmoking households, the PM PEM is always  
4 higher than SIM and SAM. "This implies that individuals encounter elevated concentrations  
5 away from home, and/or that home concentrations are elevated while they are at home and  
6 reduced while they are away". This observation is supported by the findings of Thatcher and  
7 Layton (1994), reported in Section 7.6 - merely walking into a room can raise the  
8 concentrations of PM by 100% (from 10 to 20  $\mu\text{g}/\text{m}^3$ ).

9 This study is relevant to the analyses by Dockery et al. (1992) of PM mortality in St.  
10 Louis, MO, and in Eastern Tennessee counties surrounding the cities of Kingston and  
11 Harriman, which are discussed in Chapter 12 on epidemiology. Although the Spengler et al.  
12 (1985) and Dockery et al. (1992) studies are not directly comparable, because different years  
13 of data were used (1981 versus 1985/1986), this might call into question the meaning of the  
14 correlation of ambient PM and mortality, if individual PEM data are uncorrelated with the  
15 SAM data. One possible explanation may be that even though individual PEM of non-  
16 smokers as a group are not well correlated with SAM data ( $r = 0.15$ ,  $p = 0.06$ ) the mean  
17 PEM of the nonsmoking population may be better correlated with the mean SAM on any  
18 given day as discussed in Section 7.5.2 (Mage and Buckley, 1995).

19 Morandi et al. (1988) investigated the relationship between personal exposures to PM  
20 and indoor and outdoor PM concentrations, using a TSI Model 3500 piezobalance that  
21 measures respirable particles in the range  $<3.5 \mu\text{m}$ . For the group of 30 asthmatics in  
22 Houston, TX, that were studied, outdoor concentrations averaged 22  $\mu\text{g}/\text{m}^3$ , indoor  
23 concentrations averaged 22% higher than outdoor (27  $\mu\text{g}/\text{m}^3$ ) and, in motor vehicles, the  
24 average concentration of particles was 60% higher than the average outdoors (35  $\mu\text{g}/\text{m}^3$ ). As  
25 for correlations between the various measurement categories, personal 12-h (7 a.m. to  
26 7 p.m.) daytime exposures to PM were not predicted as well by fixed site dichotomous  
27 sampler ambient monitors ( $R^2 = 0.34$ ) as by the indoor exposures ( $R^2 = 0.57$ ). However,  
28 for 1-h exposures, they found no correlation ( $R^2 = 0.00$ ) between the personal exposures to  
29  $\text{PM}_{10}$  and the indoor exposures measured with a TSI model 5000 stationary continuous  
30 piezobalance located in the 'den' area of the home. The authors noted that use of home air  
31 conditioning and recirculation tended to increase the PM exposures, and that misclassification

1 of human activities and microenvironments likely explained the inability to predict personal  
2 exposures from microenvironmental data.

3 Lioy et al. (1990) reported a study done during the winter (January 1988) in the  
4 industrial community of Phillipsburg, NJ, where personal PM<sub>10</sub> was monitored along with  
5 indoor and outdoor PM<sub>10</sub>. They collected PM<sub>10</sub> (fine plus coarse particles on a single filter).  
6 In this study of eight residences of 14 nonsmoking nonsmoke-exposed individuals, the  
7 geometric mean 24-h concentrations were 68, 48 and 42  $\mu\text{g}/\text{m}^3$  for personal, outdoor and  
8 indoor sites, respectively. The arithmetic mean personal PM exposure of 86  $\mu\text{g}/\text{m}^3$  was 45 %  
9 higher than the mean ambient concentration of 60  $\mu\text{g}/\text{m}^3$ . The higher ambient than indoor  
10 concentrations in this study, a reversal of the relationships found in the Sexton et al. (1984),  
11 Spengler et al. (1985) and Morandi et al. (1988) studies, may be caused by the local  
12 industrial source of coarse particles in that community and the absence of cigarette smokers  
13 in the residences sampled. This difference also may be partially explained by the 10  $\mu\text{m}$   
14 particle sizes in the NJ study and the 3.5  $\mu\text{m}$  particle sizes in the other studies, which would  
15 suggest that the NJ homes had less influence from the locally generated coarse particles that  
16 tend to settle out in the home. The regression coefficient between personal and ambient  
17 PM<sub>10</sub> for all 14 people on the 14 days of the study (n = 191 valid personal values) was 0.19  
18 ( $R^2 = 0.037$ , p = 0.008). With three personal exposure extreme values removed (n = 188  
19 personal values), the coefficient was 0.50 ( $R^2 = 0.25$ , p = 0.007).

20 In all five studies, the personal PM was measured to be higher than either the indoor or  
21 the outdoor PM measurements. This relationship has also been found in the two PTEAM  
22 studies (Perritt et al., 1991; Clayton et al., 1993) described in detail later in Section 7.3.3.  
23 For these PTEAM studies during the day (7 a.m. to 7 p.m.) average personal PM<sub>10</sub> exposure  
24 data (150  $\mu\text{g}/\text{m}^3$ ) were 57% higher than the average indoor and outdoor concentrations,  
25 which were virtually equal (95  $\mu\text{g}/\text{m}^3$ ). At night (7 p.m. to 7 a.m.) average PM<sub>10</sub> personal  
26 exposures (77  $\mu\text{g}/\text{m}^3$ ) were higher than the average indoor concentrations (63  $\mu\text{g}/\text{m}^3$ ) but  
27 lower than the average outdoor concentration (86  $\mu\text{g}/\text{m}^3$ ). Consequently, considering that the  
28 PTEAM subjects were overwhelmingly mostly indoors at night, a time-weighted-average  
29 (TWA) of the indoor and outdoor PM concentrations appears to always underestimate the  
30 personal exposures to PM.

1 It has been proposed (WHO, 1982a; Spengler et al., 1985; Mage, 1985) that such a  
2 discrepancy between the TWA and the personal monitoring measurements may be caused by  
3 two factors described as follows: (1) Human exposure to PM at work and in traffic are only  
4 partially accounted for in a TWA of indoor and outdoor ambient PM values; and (2) Indoor  
5 and outdoor averages reflect periods of low concentration during which the subject is not  
6 present.

7 With regard to the first factor, the PM of occupational exposures, and exposures in  
8 traffic that also reflect the vehicular emissions of PM plus the resuspension of roadway dust  
9 from the turbulence of the vehicles, are not well represented by ambient PM measurements.  
10 Ambient PM monitors are usually sited several meters above ground level, at a location  
11 uninfluenced by a single local source, so that the data recorded can represent an average  
12 community type concentration (Mage, 1983). The complexity of the situation is exemplified  
13 by the PTEAM study reported by Clayton et al. (1993). People who were employed had  
14 lower daytime exposures to PM than nonemployed people ( $n = 59, 127 \mu\text{g}/\text{m}^3$  versus  
15  $n = 111, 162 \mu\text{g}/\text{m}^3$ ), and people who had time in traffic had lower PM exposures than  
16 those who stayed at home ( $n = 31, 97 \mu\text{g}/\text{m}^3$  versus  $n = 121, 163 \mu\text{g}/\text{m}^3$ ). A possible  
17 explanation may be that people who stay home generate PM by doing housework and people  
18 who go off to work may be driving to a location where the indoor PM and ambient PM are  
19 lower than at their home.

20 With regard to the second factor, the PM pollution generating activities in a home  
21 usually occur only when a person is at home, as discussed in Section 7.1.2. Therefore, the  
22 PM in a home will be higher when a person is present than when the home is unoccupied. A  
23 24-h average of the indoor concentration thereby underestimates the average exposure of a  
24 person while in that home.

25 Ambient PM is also higher during the day (when industry and traffic are active, and  
26 wind speeds are high) than at night when PM generating activities are at a minimum and the  
27 air is still. Consequently, a 24-h average ambient PM value generally underpredicts the  
28 concentrations during the daylight hours and the exposures of people going outdoors during  
29 that period.

30 Therefore, a 24-h TWA personal exposure will always tend to be underpredicted by a  
31 simple TWA of 24-h residential-indoor and ambient-outdoor PM concentration data that fails

to account for occupational exposures, in-traffic exposures, and the intensity of personal exposures during human activity that cannot be recorded by area monitors several meters away from the subject.

### 7.3.2 Personal Exposures in International Studies

The Global Environment Monitoring System (GEMS) of the World Health Organization/United Nations Environment Programme (WHO/UNEP) commissioned a series of four pilot studies of personal exposure to PM in Zagreb (WHO, 1982a), Toronto (WHO, 1982b), Bombay (WHO, 1984) and Beijing (WHO, 1985). In these studies, people who worked in the participating scientific institutes were recruited to carry a PM sampler and their exposures were matched to the ambient concentrations measured outside their home or in their communities. The results of these studies of PM, expressed as mean personal exposure (PEM) and mean ambient (SAM), and the regression  $R^2$  between them are presented in Table 7-2.

In addition to the institute personnel, the Toronto study also measured exposures of asthmatics to  $PM_{2.5}$  and obtained  $R^2$  values of 0.07 and 0.00 in the summer and winter respectively. The net result of these international studies is that they confirm the lack of a consistent relationship between individual personal PM exposures and ambient concentrations as found in the U.S. studies. The results of the Beijing study are of importance because of (a) the recent paper by Xu et al. (1994), which reports a correlation between mortality in Beijing and ambient TSP and  $SO_2$  and (b) the very low correlations between personal exposure to PM and ambient PM concentrations (not statistically different from zero) found in the WHO study ( $R^2 = 0.03$  and  $0.07$ ). The major fuel in Beijing is coal, and in the winter the ambient  $PM_{2.7}$  (TSP) averages up to  $500 \mu g/m^3$  (WHO/UNEP, 1992). During the GEMS PM exposure study of 1985, the 24-h ambient concentrations of  $PM_{3.5}$  measured outside the subjects homes averaged  $420 \mu g/m^3$ , the indoor concentrations in the homes averaged  $364 \mu g/m^3$ , and the personal exposures averaged  $191 \mu g/m^3$ . The subjects who were workers at the institute conducting the study spent little time outdoors and their days were spent at the institute. The lower relative values of their exposure appear to be caused by lower values at home during the evenings. Meals are usually prepared during the day when the workers are not there and the indoor exposures during cooking can be quite high.

**TABLE 7-2. SUMMARY OF WHO/UNEP GEMS/HEAL PM, PERSONAL EXPOSURE PILOT STUDY RESULTS**

Location Season	PM $\mu\text{m}$	n	m	Time	PEM Mean $\pm$ SE	SAM Mean $\pm$ SE	R <sup>2</sup> PEM vs SAM	p
Toronto	25	13		8-h				
winter			72		122 $\pm$ 9	68 $\pm$ 9	0.15	NS
summer			78		124 $\pm$ 4	78 $\pm$ 4	0.10	NS
Zagreb	5	12		1-wk				
summer			12		114 $\pm$ ?	55 $\pm$ ?	0.00	NS
winter			12		187 $\pm$ ?	193 $\pm$ ?	0.50	NR
Bombay	3.5	15		24-h				
winter			105		127 $\pm$ 6	117 $\pm$ 5	0.26	NR
summer			102		67 $\pm$ 3	65 $\pm$ 3	0.20	NR
monsoon			101		58 $\pm$ 3	51 $\pm$ 2	0.02	NS
Beijing	3.5	20						
winter			71	24-h	177 $\pm$ ?	421 $\pm$ ?	0.07	NS
summer			40	1-wk	66 $\pm$ ?	192 $\pm$ ?	0.03	NS

n = number of subjects carrying PEM.

m = total number of observations.

NR = Not Reported, but listed as significant.

NS = Not significantly different from 0.

? = Not reported.

\*25  $\mu\text{m}$  A.D. computed from flow rate and open filter design.

Smith et al. (1994) reported the cooking exposures to PM<sub>10</sub> listed in Table 7-3 for Beijing, Bangkok and Pune. In Beijing, personal exposures of the cooks during cooking were 4 to 20 times higher than the 24-h outdoor values on the days that cooking took place. The presence of high levels of coarse particles in the ambient air, which do not readily penetrate into the institute and the homes, may contribute to the significantly higher ambient values that are uncorrelated with the personal exposures.

### 7.3.3 The Particle TEAM (PTEAM) Study

In 1986, the U. S. Congress mandated that EPA's Office of Research and Development "carry out a TEAM Study of human exposure to particles." EPA's Atmospheric Research and Exposure Assessment Laboratory (AREAL) joined with California's Air Resources Board (CARB) to sponsor a study in the Los Angeles Basin. The study was carried out primarily by the Research Triangle Institute and the Harvard School of Public Health, with

**TABLE 7-3. SUMMARY OF DAILY INDOOR, OUTDOOR, AND PERSONAL EXPOSURES TO PM<sub>10</sub> DURING COOKING AS A FUNCTION OF FUEL TYPE IN THREE CITIES IN ASIA**

City	Cooking Fuel	Indoor ( $\mu\text{g}/\text{m}^3$ )	Outdoor ( $\mu\text{g}/\text{m}^3$ )	Personal Cooking Only ( $\mu\text{g}/\text{m}^3$ )
Beijing, PRC	Coal (vented)	550	550	1900
	Gas	400	430	5000
	LPG	370	410	3300
	Coal Gas	420	440	9100
	Natural Gas	410	440	1600
Pune, India	Agric. Residue	2800	2600	900
	Wood	2000	920	1100
	Biomass	2100	1000	1100
	Kerosene	480	340	530
	LPG	250	250	420
Bangkok Thailand	Charcoal	330	330	550
	LPG near traffic	390	450	850
	LPG far from traffic	300	285	3900

Source: Smith et al. (1994).

additional support from Lawrence Berkeley Laboratory, Acurex, and AREAL. The main goal of the study was to estimate the frequency distribution of exposures to particles for nonsmoking Riverside residents. Another goal was to determine particle concentrations in the participants' homes and immediately outside the homes.

### 7.3.3.1 Pilot Study

#### 7.3.3.1.1 Study design

A pilot study was undertaken in nine homes in Azusa, CA in March of 1989 to test the sampling equipment (Özkaynak, et al., 1990). Newly-designed personal exposure monitors (PEMs) were equipped with inhalable (PM<sub>10</sub>) and fine (PM<sub>2.5</sub>) particle inlets. The PEMs



1 were impactors with 4-Lpm Casella pumps (Wiener, 1988). Two persons in each household  
2 wore the PEMs for two consecutive 12-h periods (night and day). Each day they alternated  
3 inlet nozzles. The first five households were monitored concurrently for seven consecutive  
4 days (March 6 to 13, 1989); the last four households were then monitored concurrently for  
5 four consecutive days (March 16 to 20, 1989). This resulted in approximately 100 PEM  
6 samples for each size fraction.

7 Indoor and outdoor particle concentrations were monitored using microenvironmental  
8 exposure monitors (MEMs). These monitors were the Harvard "black boxes" (Wiener,  
9 1989) employing a 10 Lpm pump. Several indoor MEMs were placed in different rooms in  
10 each house to determine the magnitude of room-to-room variation. These monitors were  
11 capable of monitoring both fine and inhalable particles simultaneously.

12 A central site with a PEM, MEM, and two EPA reference methods (dichotomous  
13 samplers and high-volume samplers with a 10  $\mu\text{m}$  size-selective inlet) was also operated  
14 throughout the 11 days (22 12-h periods) of the study.

#### 15 **7.3.3.1.2 Results**

16 Side-by-side comparisons indicated good agreement of all four monitors (Table 7-4).  
17 Good agreement was also noted between outdoor concentrations at the homes and at the  
18 central site (Wiener et al., 1990). Room-to-room variation of particle levels was generally  
19 less than 10%. Therefore the several indoor MEM values in a particular house were  
20 averaged to provide a single mean indoor value to compare to the corresponding outdoor  
21 value (Table 7-5). It was decided that this finding would justify using only one indoor  
22 monitor in the subsequent full-scale study (Clayton et al., 1991).

23 The personal exposures were about twice as great as the indoor or outdoor  
24 concentrations for both  $\text{PM}_{10}$  (Table 7-6a) and  $\text{PM}_{2.5}$  (Table 7-6b). Considerable effort was  
25 expended to determine whether this was a sampling artifact, due for example to the constant  
26 motion of the sampler; however, no evidence could be found for an artifactual effect.  
27 Nonetheless, to reduce chances for an artifactual finding in the main study, it was decided to  
28 use identical PEMs for both the personal and fixed (indoor-outdoor) samples in the main  
29 study.

**TABLE 7-4. PTEAM PREPILOT STUDY: MEAN OUTDOOR PARTICLE CONCENTRATIONS ( $\mu\text{g}/\text{m}^3$ )**

	Central Site PM-10				Mean SD		Residential	
	MEM	PEM	DICOT	HIVOL			MEM	SD
Mean	56.9	59.1	61.7	56.6	58.4	5.7	61.4	7.4
SD	28.8	25.2	27.6	31.5	28.8	3.3	26.0	4.4

	Central Site PM-2.5			Mean SD		Residential	
	MEM	PEM	DICOT			MEM	SD
Mean	39.4	46.0	41.8	41.4	6.2	41.7	7.1
SD	23.3	23.7	20.6	22.9	4.6	21.6	5.8

Each sampler collected 22 12-h samples over 11 days.  
MEM: Microenvironmental monitor: 10 Lpm impactor.  
PEM: Personal exposure monitor: 4 Lpm impactor.  
DICOT: Dichotomous sampler: 16.67 Lpm virtual impactor.  
HIVOL: High-volume (1130 Lpm) impactor.

**TABLE 7-5. PTEAM PREPILOT STUDY: TWENTY FOUR-HOUR (24-h) PARTICLE CONCENTRATIONS ( $\mu\text{g}/\text{m}^3$ )**

	PM-10		PM-2.5	
	Indoor	Outdoor	Indoor	Outdoor
Mean	58.7	62.6	36.3	42.6
SD	24.6	24.9	18.6	21.6
SE	3.4	3.5	2.6	3.0

Regressions of outdoor on indoor concentrations showed low  $R^2$  values (1 to 30%) for both  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  size fractions, as did regressions of daytime indoor on personal concentrations ( $R^2 = 0$  to 18%). Overnight indoor concentrations had somewhat better ability to explain personal exposures ( $R^2 = 14$  to 58%), as might be expected from the fact that the personal monitor was placed on the bedside table during the sleeping period. Personal exposures were essentially uncorrelated with outdoor concentrations ( $R^2 = 0$  to 2%) (Özkaynak et al., 1993).

**TABLE 7-6a. PTEAM PREPILOT STUDY: TWENTY FOUR HOUR (24-h) PM-10 CONCENTRATIONS ( $\mu\text{g}/\text{m}^3$ )**

House	Day	Person 1	Person 2	Indoors	Outdoors
1	1	102	86	54	132
1	3	142	125	38	49
1	5	158	150	49	70
1	7	92	127	34	49
2	1	109	158	122	112
2	3	99	140	37	48
2	5	131	87	41	70
2	7	62	56	32	46
3	1	98	107	86	115
3	3	100	141	39	45
3	5	143	132	71	79
3	7	76	103	36	44
4	2	109	92	77	102
4	4	90	77	34	47
4	6	99	122	36	37
5	2	80	104	76	99
5	4	70	77	62	65
5	6	80	78	54	50
6	8	130	152	114	39
6	10	150	102	106	51
7	9	209	126	46	72
7	11	80	71	29	39
8	9	135	178	73	59
8	11	97	151	38	28
9	8	136	102	63	43
9	10	273	91	121	48
Mean		117.2	112.9	60.3	63.0
SD		44.9	30.8	28.5	27.1
SE		8.8	6.0	5.6	5.3

**TABLE 7-6b. PTEAM PREPILOT STUDY: TWENTY-FOUR HOUR (24-h) PM-2.5 CONCENTRATIONS ( $\mu\text{g}/\text{m}^3$ )**

House	Day	Person 1	Person 2	Indoors	Outdoors
1	2	44	96	22	67
1	4	55	88	25	39
1	6	55	382	21	33
2	2	58	53	31	52
2	4	46	100	27	43
2	6	51	50	28	40
3	2	53	66	48	58
3	4	62	94	30	35
3	6	109	88	39	39
4	1	75	61	33	71
4	3	46	43	19	29
4	5	118	94	31	46
4	7	40	40	17	26
5	1	65	69	62	96
5	3	59	70	35	38
5	5	40	56	42	55
5	7	34	53	25	28
6	9	71	81	56	33
6	11	77	75	53	18
7	8	64	135	17	27
7	10	111	67	32	35
8	8	53	100	27	27
8	10	110	1453	35	35
9	9	178	48	70	40
9	11	105	58	42	28
Mean		71.2	140.8	34.7	41.6
SD		32.7	275.5	13.7	16.8
SE		6.5	55.1	2.7	3.4

1 **7.3.3.2 Main Study**

2 **7.3.3.2.1 Study design**

3 A three-stage probability sampling procedure was adopted (Pellizzari et al., 1993a).

4 Ultimately 178 residents of Riverside, CA took part in the study in the fall of 1990.

Respondents represented 139,000  $\pm$  16,000 (S.E.) nonsmoking Riverside residents aged ten and above. Their homes represented about 60,000 Riverside homes.

Each participant wore the PEM for two consecutive 12-h periods. Concurrent PM<sub>10</sub> and PM<sub>2.5</sub> samples were collected by the stationary indoor monitor (SIM) and stationary ambient monitor (SAM) at each home. The SIM and SAM were identical to the PEM except for the pump, which was a Medo pump operated off line current. A total of ten particle samples were collected for each household (day and night samples from the PEM<sub>10</sub>, SIM<sub>10</sub>, SIM<sub>2.5</sub>, SAM<sub>10</sub>, and SAM<sub>2.5</sub>). Air exchange rates were also determined for each 12-h period. Participants were asked to note activities that might involve exposures to increased particle levels (nearby smoking, cooking, gardening, etc.). Following each of the two 12-h monitoring periods, they answered an interviewer-administered questionnaire concerning their activities and locations during that time.

Up to four participants per day could be monitored, requiring 48 days in the field. A central outdoor site was maintained over the entire period (September 22, 1990 through November 9, 1990). The site had two high-volume samplers (Wedding & Assoc.) with 10- $\mu$ m inlets (actual cutpoint about 9.0  $\mu$ m), two dichotomous PM<sub>10</sub> and PM<sub>2.5</sub> samplers (Sierra-Andersen) (actual cutpoint about 9.5  $\mu$ m), one PEM, one PM<sub>10</sub> SAM, and one PM<sub>2.5</sub> SAM.

#### **7.3.3.2.2 Results**

Of 632 permanent residences contacted, 443 (70%) completed the screening interview. Of these, 257 were asked to participate and 178 (69%) agreed.

#### **7.3.3.2.3 Quality of the Data**

More than 2,750 particle samples were collected, about 96% of those attempted. All filters were analyzed by X-ray fluorescence (XRF) for a suite of 40 metals. More than 1,000 12-h average air exchange rate measurements were made. A complete discussion of the quality of the data is found in Pellizzari et al., 1993b, and in Thomas et al., 1993. Blank PEM and SIM/SAM filters (N = 51) taken to the field increased in mass by an average of 9.5  $\mu$ g; this value was subtracted from each field sample. Limits of detection (LODs), based on three times the standard deviation of the blanks, were on the order of 7 to 10  $\mu$ g/m<sup>3</sup>. All

field samples exceeded the LOD. Duplicate samples (N = 363) showed excellent precision for all types of particle samplers at all locations, with median relative standard deviations ranging from 2 to 4%.

The collocated particle samplers at the central site showed good agreement, with correlations ranging from 0.96 to 0.99. The central-site PEMs collected about 12% more mass than the dichotomous samplers, which in turn collected about 7% more than the modified Wedding hi-vol samplers. These relative relationships had also been noted in the pre-pilot study in Azusa. It was noted that the Wedding samplers collected about the same mass as the dichotomous samplers during the day, but about 13% less mass at night. Multivariate tests indicated that the Wedding samplers appeared to have a temperature dependency, amounting to an increase of about 1% per °F (Özkaynak et al., 1993, Appendix A).

#### **7.3.3.2.4 Concentrations**

Concentrations of particles and elements have been reported (Clayton et al., 1993; Özkaynak et al., 1993; Pellizzari et al., 1993; Wallace et al., 1993). Population-weighted daytime personal PM<sub>10</sub> concentrations averaged about 150 µg/m<sup>3</sup>, compared to concurrent indoor and outdoor mean concentrations of about 95 µg/m<sup>3</sup> (Table 7-7). The overnight personal PM<sub>10</sub> mean was much lower (77 µg/m<sup>3</sup>) and more similar to the indoor (63 µg/m<sup>3</sup>) and outdoor (86 µg/m<sup>3</sup>) means. About 25% of the population was estimated to have exceeded the 24-h National Ambient Air Quality Standard for PM<sub>10</sub> of 150 µg/m<sup>3</sup>. Over 90% of the population exceeded the California Ambient Air Quality Standard of 50 µg/m<sup>3</sup>.

#### **7.3.3.2.5 Correlations**

The central site appeared to be a moderately good estimator of outdoor particle concentrations throughout the city. Spearman correlations of the central-site concentrations measured by all three methods (PEM-SAM, dichot, Wedding) with outdoor near-home concentrations as measured by the SAMs ranged from 0.8 to 0.85 (p < 0.00001). Linear regressions indicated that the central-site 12-h readings could explain 57% of the variance observed in the near-home 12-h outdoor concentrations (Figure 7-3).

**TABLE 7-7. POPULATION-WEIGHTED<sup>a</sup> CONCENTRATIONS AND  
STANDARD ERRORS ( $\mu\text{g}/\text{m}^3$ )**

Sample type	N	Geom. Mean	GSD	Arith. Mean + SE	Percentile	
					90% + SE	98%
<b>Daytime PM<sub>10</sub></b>						
Personal	171	129	1.75	150 + 9	260 + 12	380
Indoor	169	78	1.88	95 + 6	180 + 11	240
Outdoor	165	83	1.68	94 + 6	160 + 7	240
<b>Overnight PM<sub>10</sub></b>						
Personal	168	68	1.64	77 + 4	140 + 10	190
Indoor	163	53	1.78	63 + 3	120 + 5	160
Outdoor	162	74	1.74	87 + 4	170 + 5	210
<b>Daytime PM<sub>2.5</sub></b>						
Indoor	173	35	2.25	48 + 4	100 + 7	170
Outdoor	167	38	2.07	49 + 3	100 + 6	170
<b>Overnight PM<sub>2.5</sub></b>						
Indoor	166	27	2.21	36 + 2	83 + 6	120
Outdoor	161	37	2.23	51 + 4	120 + 5	160

<sup>a</sup>Personal samples weighted to represent nonsmoking population of 139,000 Riverside residents aged 10 or above. Indoor-outdoor samples weighted to represent 61,500 homes with at least one nonsmoker aged 10 or above.

Outdoor 12-h concentrations of PM<sub>10</sub> could explain about 25 to 30% of the variance observed in indoor concentrations of PM<sub>10</sub>, but only about 16% of the variance in 12-h personal exposures to PM<sub>10</sub> (Figure 7-4). This is understandable in view of the importance of indoor activities such as smoking, cooking, dusting, and vacuuming on exposures to particles. The higher daytime exposures were even less well represented by the outdoor concentrations.

Indoor concentrations accounted for about half of the variance in personal exposures. However, neither the indoor concentrations alone, nor the outdoor concentrations alone, nor time-weighted averages of indoor and outdoor concentrations could do more than explain

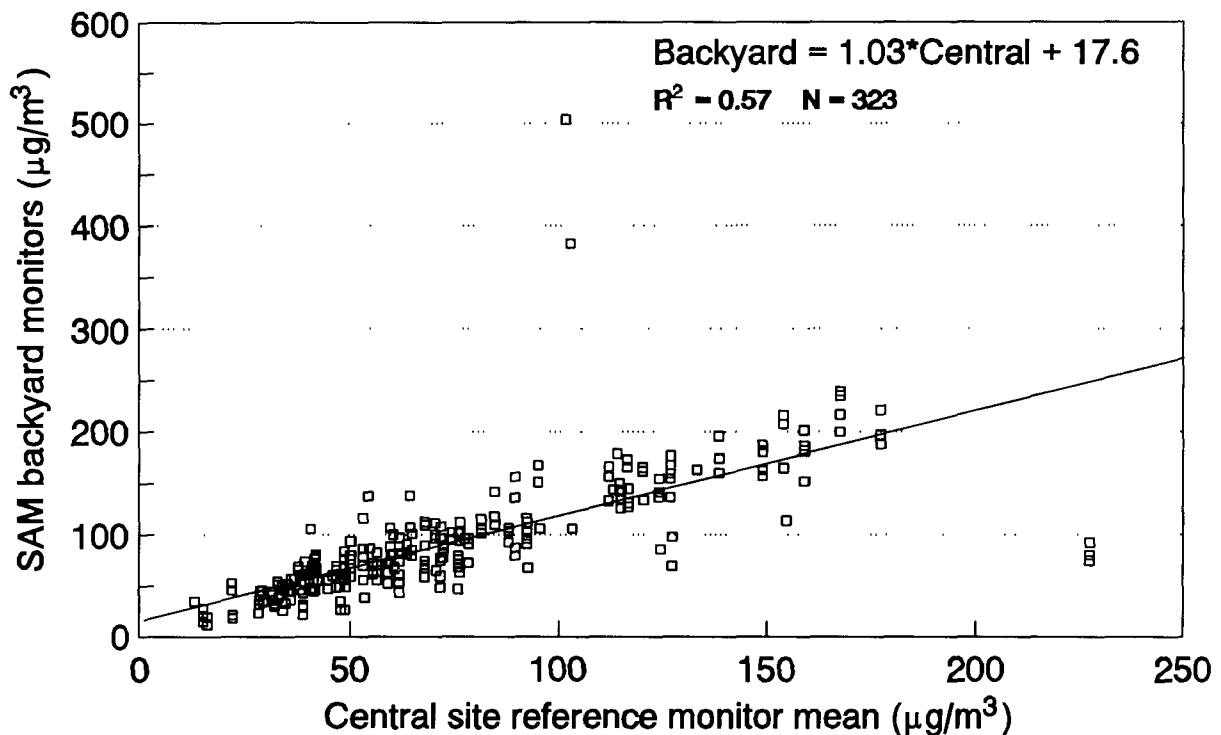


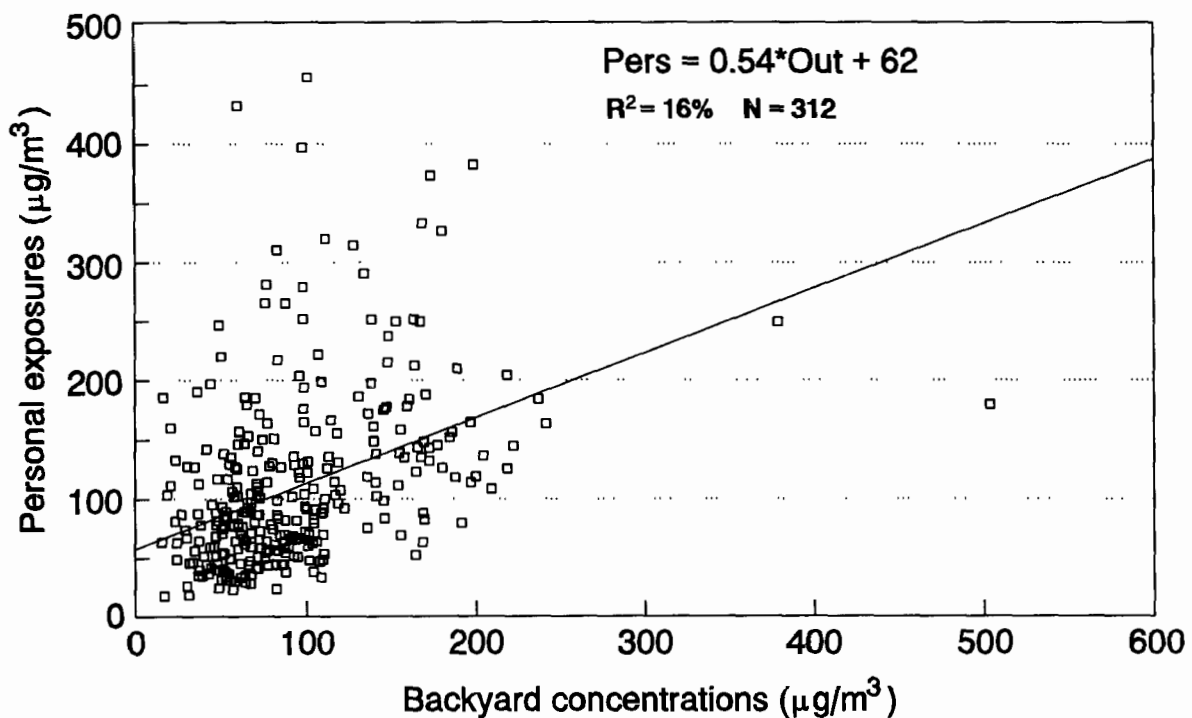
Figure 7-3. Central-site mean of two dichotomous samplers versus residential outdoor monitors.  $R^2 = 57\%$ .

about two-thirds of the observed variance in personal exposures. The remaining portion of personal exposure is assumed to arise from personal activities or unmeasured microenvironments that are not well represented by fixed indoor or outdoor monitors.

#### 7.3.3.2.6 Discussion

The more than 50% increase in daytime personal exposures compared to concurrent indoor or outdoor concentrations suggested that personal activities were important determinants of exposure. However, the nature of this "personal cloud" of particles has not yet been determined. Scanning electron microscopy was undertaken on 138 personal filters (Mamane, 1992). Skin flakes were common on many filters. A preliminary analysis suggested that the average number of skin flakes per filter was 120,000 to 150,000. The mass of a small number of personal filters may have been considerably increased by unusually large numbers of skin flakes. However, attempts to calculate the mass of skin

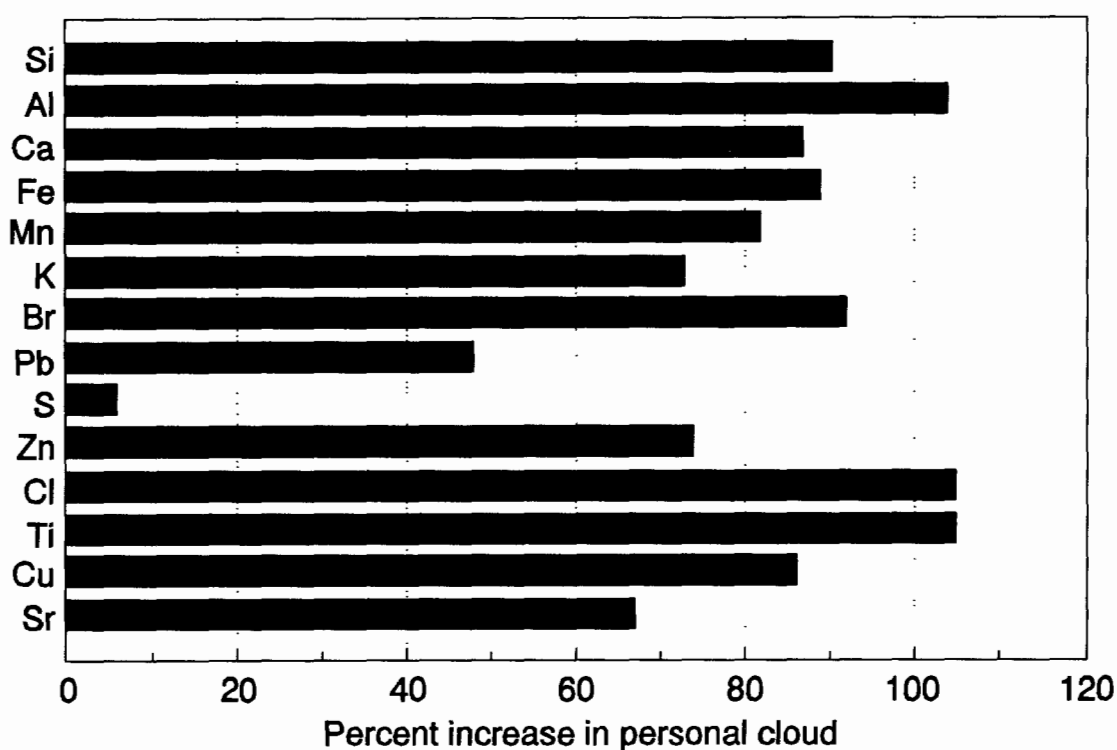




**Figure 7-4. Personal exposures versus residential (back yard) outdoor PM<sub>10</sub> concentrations.  $R^2 = 16\%$ .**

flakes from estimates of their volume and density suggest an average contribution to the mass of only about  $4 \mu\text{g}/\text{m}^3$ , less than 10% of the mass of the average personal cloud.

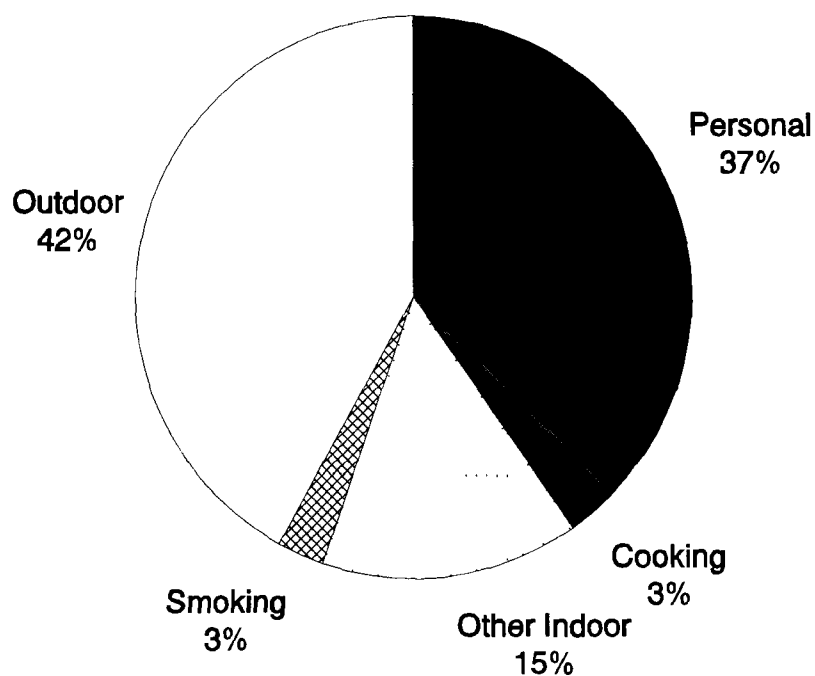
Another approach to the composition of the personal cloud is elemental analysis, using X-ray fluorescence. Analysis of all personal and indoor filters showed that 14 of 15 elements were elevated by values of 50 to 100% in the personal filters compared to the indoor filters (Figure 7-5). This observation suggests that a component of the personal cloud is an aerosol of the same general composition as the indoor aerosol. This could be particles created by activities (e.g., cooking) or re-entrained household dust from motion (walking across carpets, sitting on upholstered furniture). House dust is a mixture of airborne outdoor aerosols, tracked-in soil and road dust, and aerosols produced by indoor sources. As such, it should contain crustal elements from soil, lead and bromine from automobiles, and other elements from combustion sources. This would be consistent with the observation that nearly all elements were elevated in personal samples. The fact that personal overnight samples showed smaller mass increases than the personal daytime samples is also consistent with the



**Figure 7-5. Increased concentrations of elements in the personal versus the indoor samples.**

fact that the participants were sleeping for much of the 12-h overnight monitoring period, and were thus not engaging in these particle-generating or reentraining activities.

A source apportionment of the personal  $\text{PM}_{10}$  mass during the daytime period is shown on Figure 7-6. This chart is derived by subtracting the average SIM and SAM ( $95 \mu\text{g}/\text{m}^3$ ) from the mean PEM ( $150 \mu\text{g}/\text{m}^3$ ) given on Table 7-7. The  $55 \mu\text{g}/\text{m}^3$  difference is shown as the 37% fraction of the total of  $150 \mu\text{g}/\text{m}^3$  labelled Personal 37%. The source of this 'personal cloud' is indeterminable from the SIM, SAM and PEM data. As discussed previously, it is likely to consist primarily of resuspended dust that would have a composition of a mixture of all the other sources. The 15% other-indoor PM represents the indoor mass that could not be assigned to ETS, cooking or ambient PM. It is likely that the 52% of other-indoor plus personal-cloud categories contains an appreciable amount of ambient PM that came indoors over a long period of time and is resuspended by activity. If so, then the PEM would be at least 50% of ambient origin.



N = 166 Samples

**Figure 7-6. Source apportionment of PTEAM PM-10 Personal Monitoring (PEM) Data. ‘Other indoor’ represents PM found by the indoor monitor (SIM) for which the source is unknown. ‘Personal PM’ represents the excess PM captured by the PEM which cannot be attributed to either indoor (SIM) or outdoor (SAM).**

Source: Clayton et al. (1993).

1 The PTEAM Study and the 13 PEM studies discussed in this chapter so far are  
 2 summarized in Table 7-8. This table shows that many of the early studies reported no  
 3 statistically significant correlation between PEM and SAM. However, these early studies  
 4 were all characterized by a non-probability sample and a relatively small sample size. The  
 5 PTEAM study in Riverside was a probability sample (Clayton et al., 1993) and the Lioy et  
 6 al. (1991) study in Phillipsburg, which was not a probability sample, have large sample sizes  
 7 and achieved significance. The other studies, such as WHO/UNEP (1982a,b) or Morandi et  
 8 al. (1988) are equivocal. Consequently it is not clear yet what the general pattern is and  
 9 why. In the following sections, PEM/SAM comparisons of some constituents and two means  
 10 of visualizing the complex relationships of SAM and PEM are discussed.

**TABLE 7-8. COMPARISON OF PEM EXPOSURE OF INDIVIDUALS TO THE SIMULTANEOUS AMBIENT (SAM) PM CONCENTRATION IN TEN U.S. CITIES AND FOUR FOREIGN CITIES**

Reference	Year	Location	PM $\mu\text{m}$	n	Time	Mean PEM	Mean SAM	R <sup>2</sup> PEM vs SAM	p
Binder et al.	1973	Ansonia	5	20	24-h	115	59	NS	NS
Dockery & Spengler	1975	Watertown	3.5	18	24-h	35	17	0.00	NS
Dockery & Spengler	1976	Steubenville	3.5	19	12-h	57	64	0.19	NR
Spengler et al.	1979	Topeka	3.5	46	12-h	30	13	0.04	NS
WHO/UNEP	1981	Toronto	25						
	Winter	non-asthmatic		13	8-h	122	68	0.15	NS
	Winter	non-asthmatic		13	8-h	124	78	0.10	NS
	Summer	asthmatic		13	8-h	91	54	0.00	NS
	Summer	asthmatic		13	8-h	124	80	0.07	NS
Spengler et al.	1981	Kingston/ Harriman	3.5	97	24-h	44	18	0.00	NS
WHO/UNEP	1982	Zagreb	5	12	1-wk				
	Summer					114	55	0.00	NS
	Winter					187	193	0.50	NR
Sexton & Spengler	1982	Waterbury	3.5	48	24-h	36	17	0.00	NS
WHO/UNEP	1982	Bombay	3.5	15	24-h				
	Winter					127	117	0.26	NR
	Summer					67	65	0.20	NR
	Monsoon					58	51	0.02	NS
WHO/UNEP	1985	Beijing	3.5	20					
	Winter				24-h	177	421	0.07	.09
	Summer				1-wk	66	192	0.03	NS
Morandi et al.	1988	Houston	3.5	30	12-h	27	16	0.34	< .05
Lioy et al.	1988	Phillipsburg	10	14#	24-h	86	60	0.04	.008
				14*	24-h	76	60	0.25	.001
Perritt et al.	1989	Azusa	2.5	9	24-h	79	43	0.01	NS
			10	9	24-h	115	62	0.01	NS
Clayton et al.	1990	Riverside	10	141	24-h	113	84	0.23	NR

n = Number of individuals carrying personal monitors

NS = Not statistically significant from 0

NR = p Value not reported, but mentioned as significant

# = 14 subjects carried PEMS for 14 days for 191 valid measurements

\* = Three outliers are removed and regression is for 188 measurements

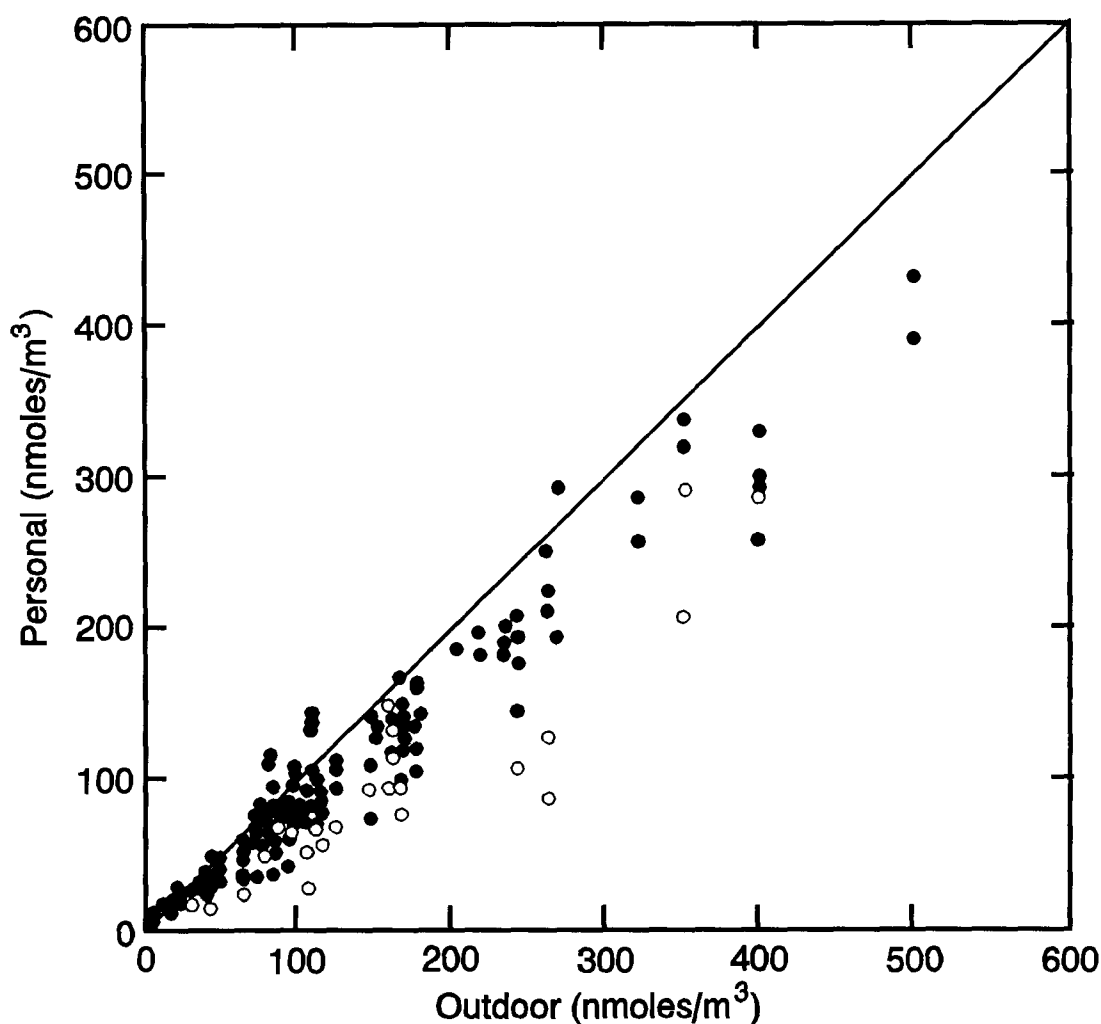
Year = year study was performed

#### 7.3.4 Personal Exposures to Constituents of PM

The absence of an apparent correlation between ambient PM concentrations and personal exposures to PM found in most early US and international studies does not necessarily hold for specific chemical constituents of the PM that have predominantly outdoor sources. Suh et al. (1993) measured personal exposures to sulfate ( $\text{SO}_4^{2-}$ ) and acidity ( $\text{H}^+$ ), and ambient and indoor concentrations in State College, PA, summer 1991. The correlations between personal and ambient values of sulfate and acidity were  $R^2 = 0.92$  and  $0.38$  respectively, which is in marked contrast to the  $R^2 \approx 0$  between earlier reported ambient PM and personal PM (Sexton et al., 1984, Spengler et al., 1985; Morandi et al., 1988).

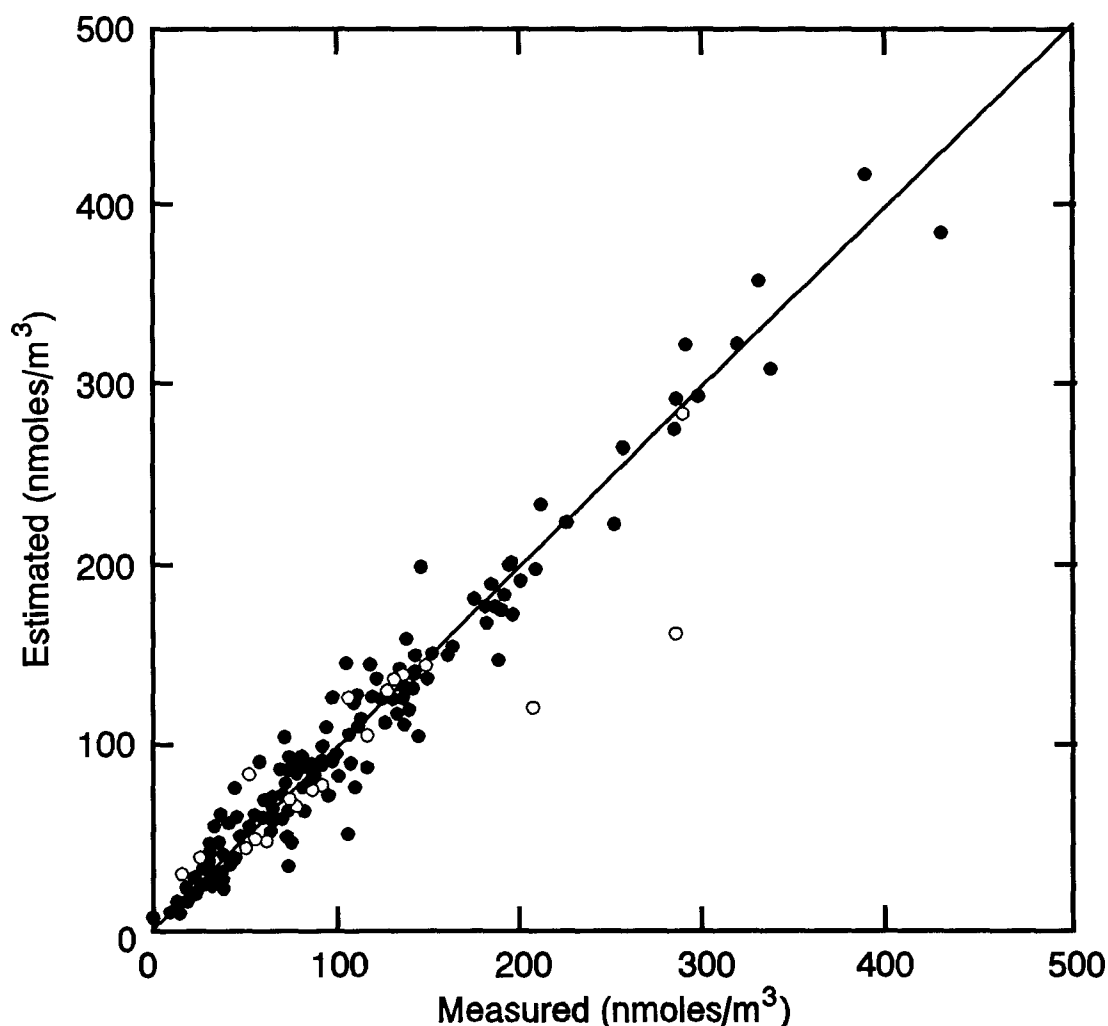
Figure 7-7 shows the consistent relation between ambient and personal sulfate measurements (slope =  $0.78 \pm 0.02$ ), and Figure 7-8 shows the improvement in prediction by using the TWA with a correction factor (estimated personal sulfate =  $0.885 \times \text{TWA}$ ,  $R^2 = 0.95$  with slope =  $0.96 \pm 0.02$ ). Personal acidity was also computed by the same equation with a correction for personal ammonia ( $\text{NH}_3$ ) exposure that gave an  $R^2 = 0.63$ . As opposed to PM which has both indoor and outdoor sources, the sulfate and acidity are virtually all of outdoor origin. Consequently, the characteristics of the indoor environment, such as air conditioning and ammonia sources, modify the personal exposures indoors.

Another important consideration in estimating personal exposures, from the indoor and outdoor environmental measurements, is that the chemical composition of the excess in personal exposure compared to the TWA exposure calculation may be significantly different than that predicted from the indoor and ambient data alone. For example, the excess personal PM found by Morandi et al. (1988) appeared to be related to in-traffic exposures which would have a different chemical composition compared to either the average ambient or average indoor compositions. Exposures to particles in vehicles are quite variable, perhaps as a function of traffic density, and do not constitute a simple microenvironment for estimation purposes. For example, Roemmelt et al. (1993) reported an average in-bus concentration of  $570 \mu\text{g}/\text{m}^3$  of TSP (open filter collection at  $1 \text{ m}^3/\text{h}$ ), with a minute value peak-to-mean ratio of 3:1 using a MINIRAM monitor ( $\approx \text{PM}_5$ ), during an 8.5-h period on 16 March 1993 in downtown Munich. Simultaneous ambient TSP data were not reported.



**Figure 7-7. Personal versus outdoor  $\text{SO}_4^{=}$ . Open circles represent children living in air conditioned homes; the solid line is the 1:1 line.**

In addition to the two factors cited just above, a microscale ‘personal cloud’ can be generated by the person’s activities which complicates the exposure measurement process. This effect is most important in occupational settings where personal exposures are not readily comparable to weighted area sampling measurements. For example, Lehmann et al. (1990) measured workers exposure to diesel engine exhaust by personal monitoring of  $\text{PM}_{10}$  with a range of 0.13 to 1.2  $\text{mg}/\text{m}^3$ , compared to an area estimate range of 0.02 to 0.80  $\text{mg}/\text{m}^3$ . MMWR (1988) reports the exposures of nurses and respiratory therapists to the aerosols of ribavirin during treatment of patients by ribavirin aerosols administered inside an oxygen tent. Bedside area monitors averaged 317  $\mu\text{g}/\text{m}^3$  while personal exposures ranged



**Figure 7-8. Estimated ("best fit" model) versus measured personal  $\text{SO}_4^{=}$ . Model includes indoor and outdoor concentration and activity data. Open circles are air conditioned homes; the solid line is the 1:1 line.**

from 69 to 316  $\mu\text{g}/\text{m}^3$  with an average of 161  $\mu\text{g}/\text{m}^3$ . The implications of these differences in exposure with position relative to a source are discussed in previous Section 7.2.3.

Environmental Tobacco Smoke (ETS) is a category of PM that is found in many indoor settings where smoking is taking place or recently had occurred. As stated in the Indoor Air Section 7.6, ETS is the major indoor source of PM where smoking occurs. Because of the depth of the discussion and coverage of ETS in Section 7.6, no further discussion will be made here other than to note that ETS adds on the order of 25 - 30  $\mu\text{g}/\text{m}^3$  to 24-h average

1 personal exposures and residential indoor environments where smoking takes place  
2 (Holcomb, 1993; Spengler et al., 1985).

3 ETS represents an appreciable contribution to the personal PM exposure of the  
4 nonsmoker which is uncorrelated to the ambient PM concentration. In many of the PM PEM  
5 studies, smoking status and exposure to ETS was self-identified by the subjects in their  
6 questionnaires and diary responses. In the absence of an independent verification by a  
7 measure of nicotine or cotinine, a subject could be misclassified (Leaderer and Hammond,  
8 1991). For example, smoking of a non-tobacco product may not be reported. In the  
9 USEPA Denver and Washington CO exposure studies (Wallace et al., 1988) there were  
10 several subjects who had high breath CO but their diary and CO PEM record gave no  
11 evidence of an equivalent exposure to CO or methylene chloride (which metabolizes to CO).  
12 A biological measure of cotinine or nicotine could indicate whether the excessive breath CO  
13 was from nonreported smoking or endogenously produced.

14 The random ETS increment will tend to reduce the correlation between PEM and SAM.  
15 If one were able to subtract out the ETS from the PEM PM data, the correlation of SAM  
16 with the non-ETS PEM PM might be improved (Dockery and Spengler, 1981).

17 As stated as a *caveat* in the introductory section 7.1, the inhalation of main-stream  
18 tobacco smoke will be a major additive exposure to PM for the smokers, which dwarfs the  
19 nonsmoker's PEM PM. Therefore the results presented so far apply only to nonsmokers,  
20 and a major proportion of the US population (e.g. smokers) has a total exposure to PM that  
21 is at least one order of magnitude greater than that of the nonsmokers.

## 22 **7.4 INDIRECT MEASURES OF EXPOSURE**

23 The early air pollution literature related health to ambient particulate matter (TSP)  
24 concentrations as a surrogate for personal exposures to PM. Although this relationship has  
25 been shown to be highly questionable for specific individuals, it still is used in studies such  
26 as Pengelly et al. (1987) who estimated TSP exposures of school children in Hamilton,  
27 Ontario, by interpolation of ambient TSP concentrations to the school locations.

28 The first usage of a time-weighted-average (TWA) of environmental exposures to  
29 estimate total human personal exposure to an air pollutant (Pb) was by Fugas et al. (1973).



1 In theory, a human exposure to PM could be estimated by use of Equation 7-2 and  
2 knowledge of the average PM concentration in each microenvironment ( $\mu$ E) that a person  
3 experiences and the duration of the exposure in each such  $\mu$ E (Duan, 1982; Mage, 1985).  
4 For a room with no source in operation, the whole room could be treated as a single  $\mu$ E.  
5 However, when a PM source is in operation and gradients exist, that very same room may  
6 need to be described by multiple  $\mu$ Es. These  $\mu$ Es could have dimensions of an order of a  
7 few centimeters close to the source, and dimensions of an order of several meters, farther  
8 away from the source.

9 Under research conditions, the complete spatial variation of a gaseous tracer  
10 concentration in a test chamber can be mapped (Yost et al., 1994) and measurements at  
11 multiple fixed points can be made (Baughman et al., 1994). Baughman et al., 1994,  
12 proposed that a  $\mu$ E could be considered to have a uniform concentration if the coefficient of  
13 concentration variation within it was less than 10% (standard deviation/mean). In the  
14 presence of a source of PM, these data indicate that tens of such  $\mu$ Es would have to be  
15 defined when a subject is moving about in its immediate vicinity. A simultaneous video  
16 recording of an individual's exact position and activity, while measuring the instantaneous  
17 concentration, can be used to visualize a concentration field (O'Brien et al., 1989; Gray  
18 et al., 1992) and could be used to measure the concentration field distortion that occurs from  
19 the presence of the person. These new techniques establish the variability of concentration  
20 over small distances and their relations to human activity. It is clearly impossible to use  
21 these research techniques routinely in an exposure survey or to maintain multiple area  
22 monitors throughout a normal setting of daily activity while recording human activity in their  
23 vicinities.

24 Ogden et al. (1993) compared exposures from personal sampling and static area  
25 sampling data for cotton dust exposures. The British cotton dust standard specifies static  
26 sampling, because the 1960 dose-response study used to set the standard used static sampling  
27 data to compute worker exposure and dosage. Ogden et al. (1993) found median personal  
28 exposures of 2.2 mg/m<sup>3</sup> corresponding to a mean static background concentration of  
29 0.5 mg/m<sup>3</sup>. They concluded that "The presence of the body and its movement affect what a  
30 personal sampler collects, so static comparisons cannot be used to infer anything about the  
31 relationship of the (static) method with personal sampling." Ingham and Yan (1994)

confirmed this finding by modelling the human body as a cylinder and showing that unless the personal monitor length/diameter ratio was greater than four, the aspiration efficiency (the fraction of particles sampled that would be sampled in the absence of the body) could be greatly affected.

Rodes et al., 1991, compared the literature relationships of personal exposure monitoring (PEM) to  $\mu$ E area monitoring (MEM) for PM, as shown in Figure 7-9, to which Ogden et al., 1993 is added as a single point. The authors found that PEM/MEM ratios ranged from 3 to 10 in occupational settings, and from 1.2 to 3.3 in residential settings. These combined data show that approximately 50% of all measured PEM PM values are more than 100% greater than the estimated simultaneous MEM values using the TWA approach. Their explanation points to this excess PM as due to the spatial gradient about indoor sources of PM which are usually well away from area monitors which thus fail to capture the high exposures individuals may get when in close proximity to a source. They suggest that clothing lint and skin dander could only add, at most, a few percent to the total PM mass collected by a personal exposure monitor.

#### **7.4.1 Personal Exposure Models Using Time-Weighted-Averages (TWA) of Indoor and Outdoor Concentrations**

Several studies have used the relationship of Equation 7-2 to compute the time-weighted-average (TWA) exposure of subjects. The procedure calls for a time-activity diary to be kept so that the time at-home, outdoors, at-work, in-traffic, etc., can be defined. By use of  $\mu$ E monitoring data from the study itself (or literature values of PM concentrations in similar  $\mu$ Es) and concurrent ambient monitoring, one can predict the concentration that would be measured if the subject had carried a PEM.

Because people in the USA spend 21 h indoors each day (Robinson and Nelson, 1995), the concentration in indoor  $\mu$ Es is a most important quantity for usage within a TWA PM model. The important articles on indoor air quality for PM have been reviewed extensively in Section 7.6. Many of these articles, such as Quackenboss et al. (1991), estimated TWA PM<sub>10</sub> exposures from SIM and SAM measured at subject's homes without collecting simultaneous PEM for validation of the TWA model.

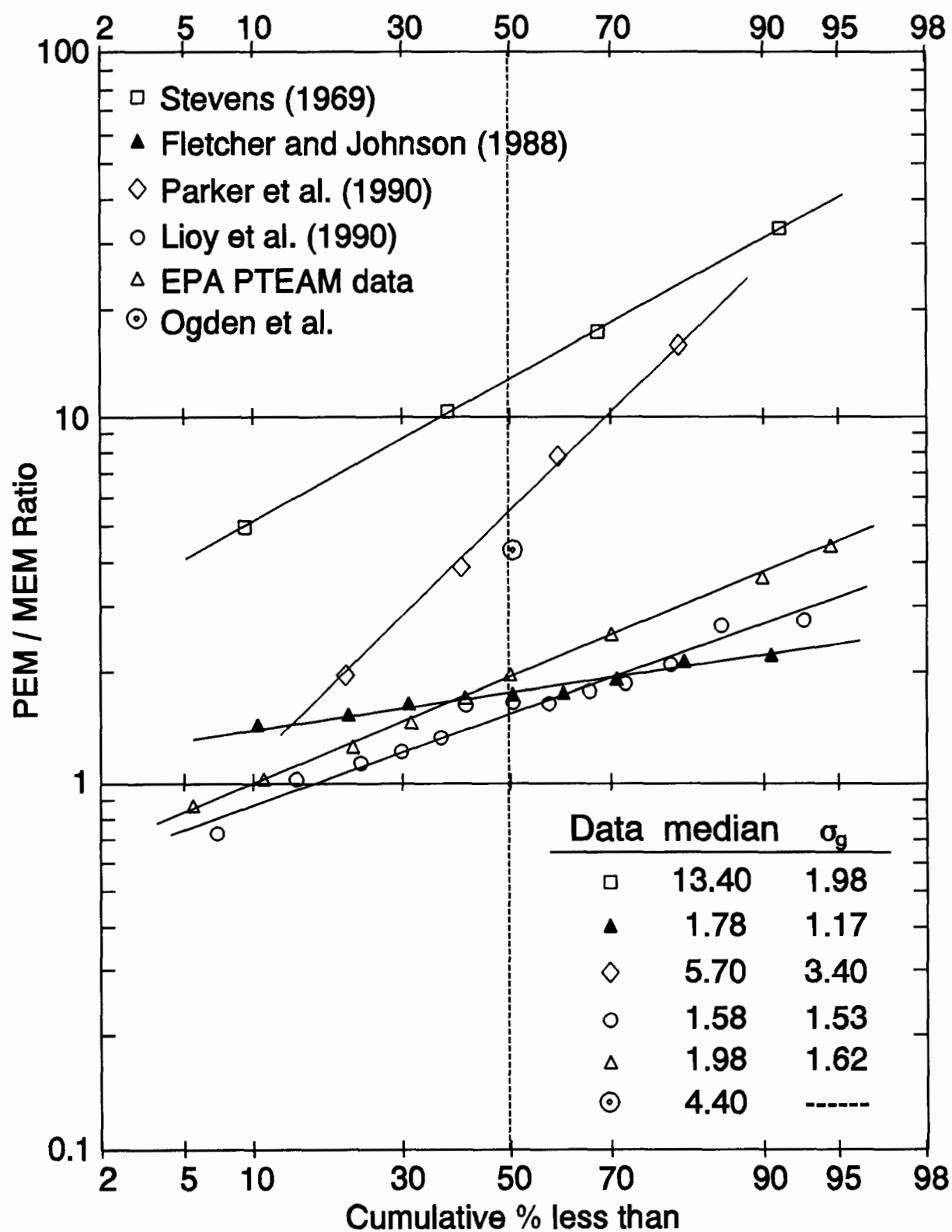


Figure 7-9. Personal activity cloud and exposure.

Source: Rodes et al. 1991

1 The articles that are discussed here predict PM exposures of non-smokers that include  
2 ETS, and most provide PEM data for comparison. This may also be interpreted as the  
3 exposure of smokers minus their exposure to direct main-stream smoke and incompletely  
4 diluted side-stream smoke.

5 As opposed to the gaseous pollutants for which continuous hour-to-hour time series of  
6 SAM data are available, PM SAM monitoring data have been often only available as a time  
7 series of 24-h SAM measurements. Consequently, in much of the early PM TWA  
8 literature, the modelers assumed, by necessity, the same ambient PM in the morning and  
9 evening, which might not be accurate (Dockery and Spengler, 1981).

10 Spengler et al. (1980) in a study of PEM, SAM and SIM in Topeka, Kansas, found the  
11 averages of  $PEM = 30 \mu g/m^3$ ,  $SIM = 24 \mu g/m^3$  and  $SAM = 13 \mu g/m^3$ . They note "It  
12 suggests that somewhere in an individual's daily activities, they are being exposed to PM at  
13 concentrations higher than what is measured either indoors or outdoors". This relationship  
14 has been found in almost all other studies, such as PTEAM (Clayton et al., 1993) where  
15 daytime PEM averaged  $150 \mu g/m^3$  and SIM and SAM averaged just under  $100 \mu g/m^3$ .  
16 Spengler et al.(1985) measured 24-h PEM, SIM and SAM. The resulting relationship based  
17 on Equation 1 was:  $PEM = 17.7 \mu g/m^3 + 0.9 TWA$ . The authors noted, in addition to the  
18 previous suggestion, that the excess of PEM over TWA may be due to an incorrect  
19 assumption that the indoor and outdoor are constant during the 24-h sampling period.

20 Morandi et al., (1988) compared  $PM_{3.5}$  PEM with simultaneous SIM and SAM data.  
21 They found that their TWA model overestimated PEM below  $27 \mu g/m^3$  SAM and  
22 underestimated PEM above  $27 \mu g/m^3$  SAM. The authors concluded that "this result indicates  
23 that there were differences between PM mean concentrations in  $\mu Es$  with similar  
24 characteristics ... The implication for air pollution health effect studies is that, for  
25 contaminants with significant indoor sources, PEM may be the only adequate measure of  
26 exposure when using short-term averaging times".

27 Koutrakis et al. (1992), in a study discussed in Section 7.6 on Indoor Air report that  
28 their source-apportionment mass-balance model predicts penetration from outdoors to  
29 indoors of order 85-90% for Pb and sulfur compounds. The authors claim that:

1 "We can satisfactorily predict indoor fine aerosol mass and elemental concentrations  
2 using the respective outdoor concentrations, source type and usage, house volume and  
3 air exchange rate."

4 The authors note that this may be a cost-effective approach to estimating peoples'  
5 exposure while indoors since the necessary ambient data may be available and the housing  
6 profile may be collected with a simple interview. This technique could possibly correct the  
7 shortcomings noted above by Morandi et al. (1988).

8 Colome et al. (1992) measured indoor and outdoor PM-10 at homes of asthmatics in  
9 California. Their personal monitoring data, limited to three individuals, confirmed that  
10 "some protection from higher outdoor concentration is afforded by shelter if smokers and  
11 other particulate sources are not present". This observation may be important for estimating  
12 the exposure of elderly and infirm people who are assumed to be the susceptible cohort.

13 Klepeis et al. (1994) present an up-to-date TWA PM Model that uses, as an input, real-  
14 time hourly PM SAM data and a mass balance equation to predict exposures of nonsmokers  
15 in various indoor settings based on ambient PM data, presence of PM sources such as  
16 smokers, and other variables relating to air exchange rates. The addition of the additive  
17 terms that allow for sources, such as cooking and presence of smokers adds to the TWA of  
18 Equation 7-2, which in effect is a correction for the underprediction of the  $\mu\text{E}$  concentration.

19  
20 In summary, as described by several authors, the PM PEM exposure of individuals who  
21 are not smoke exposed has been shown to be higher than their corresponding TWA of SIM  
22 and SAM. The exact reason for this excess in PM, sometimes called a 'personal cloud', is  
23 not known (Rodes et al., 1991). It has been thought to reflect the fact that the person's  
24 presence itself can stir up loosely settled-dust by induced air motion and vibration (Ogden,  
25 1993). Thatcher and Layton (1994) gave an example where merely walking into a room  
26 raised the total suspended dust from 10 to 20  $\mu\text{g}/\text{m}^3$ . A study by Litzistorf et al. (1985) of  
27 asbestos type fibers in a classroom showed how fibers (f) were stirred up when it was  
28 occupied. The levels rose from below the detectable level of 10000 f/ $\text{m}^3$  to 80000 f/ $\text{m}^3$   
29 when occupied, and they returned to below detectable levels within 1 h after the end of the  
30 class. Millette and Hays (1994) present a detailed discussion of the general topic of  
31 resuspended dust in their text on settled asbestos dust.

1 It may not be a proper procedure to use a 24-h average concentration in a physical  
2 setting, such as a kitchen, to estimate a person's exposure while in the kitchen. As described  
3 previously in the discussion of the definition of a microenvironment, the same kitchen can  
4 constitute one or more  $\mu$ Es depending on the source operation pattern. In many studies, such  
5 as Spengler et al. (1985), the SIM sampled the indoor residential setting for 24-h in phase  
6 with the PEM. The resulting average SIM will often underestimate the person's exposure  
7 while they are at home and may contribute to the difference between a TWA exposure and  
8 the PEM.

9 In a similar manner, a person's workplace exposure may be more or less than that in  
10 their home. In the PTEAM study (Clayton et al., 1993), there was a general decrease in  
11 exposure for those who were employed outside their home. However, employment in a  
12 "dusty trade", such as welding, may increase their PM PEM. Liroy et al. (1990) give an  
13 example of a subject with a hobby involving welding which led to a 24-h PEM reading of  
14  $971 \mu\text{g}/\text{m}^3$ . The variables influencing the contribution to PEM PM from industrial  
15 exposures have not been discussed in this chapter because of their complexity. The reader  
16 should bear in mind that application of a TWA model to a subject with such an exposure  
17 may create a high TWA estimate with a large uncertainty.

18 Another exposure category that is important for TWA analysis is that within a vehicle  
19 in transit (Rudolf, 1994). In California, people spend approximately 100 minutes per day in  
20 or near a vehicle (Jenkins et al., 1992). In vehicles people are exposed to auto exhaust, road  
21 dust resuspended from vehicle turbulence, and PM generated within the vehicle as ETS or  
22 exhaust leakage. Roemelt et al. (1993) reported a range of TSP in an urban bus up to  $1500 \mu\text{g}/\text{m}^3$   
23 with a mean of  $570 \mu\text{g}/\text{m}^3$  as measured with an optical monitor during an 8.5-h  
24 daytime period.

25 Indirect estimation of a person's time-weighted-average (TWA) PM exposure may be a  
26 cost-effective alternative to direct PEM PM measurement. Mage (1992) compared the  
27 advantages and disadvantages of the TWA indirect method compared to the direct PEM  
28 method. The primary advantages of the indirect method are the low cost and low burden on  
29 the subject, because it uses only a time-activity diary and no PM PEM is required; the  
30 disadvantage is the low accuracy. The primary advantage of the PEM PM method is that it  
31 is a high accuracy direct measurement; the disadvantage is the high cost and high burden on

the subject (see Section 7.2.1.4). Mage (1992) proposed a combined study design in which direct measurements on a subset of subjects can be used to calibrate the TWA estimates of the other subjects. Duan and Mage (1995) present an expression for that includes: the optimum fraction of subjects to carry the PEM as a function of the relative cost of the PM PEM to the TWA PM estimate and the correlation coefficient between the PEM and the TWA.

## 7.5 DISCUSSION

### 7.5.1. Relation of Individual Exposures to Ambient Concentration

The previous sections discussed the individual PM PEM vs PM SAM relationships of 14 studies listed in Table 7-8. In many of the PM studies there is no statistically significant linear relationship between PEM and SAM, and in other studies the relationship is positive and statistically significant. This section discusses these data in terms of understanding the complex relationship between the SAM concentrations and the individual PEM exposures. In the following section, the relationship of the SAM to the mean PEM in the community surrounding the SAM will be presented.

The principle of superposition is offered as a basis for visualization of the process involved in creating a total exposure. A linear system will exist for respirable-PM PEM exposures if the expected PEM response to a source emitting 2 mg/min of PM is exactly twice the PEM response to that identical source emitting 1 mg/min of identical PM. If superposition applies, then we can construct the total exposure by adding all the increments of exposures from the various source classes and activities that a subject performs on a given day.

Let the SAM be representative of the macroscale ambient PM concentration in the community as shown on Figure 7-10a. This is the exposure that would be measured for a homeless person if they spent 24-h per day outdoors near the SAM site. Neglecting local microscale variation (e.g. backyard barbecue or leaf burning), while people are outdoors they are exposed to 100% of the SAM value (Figure 7-10b). Assume that this exposure is also the baseline PM for a location in traffic which occurs outdoors. The increment produced by the local traffic is considered later.

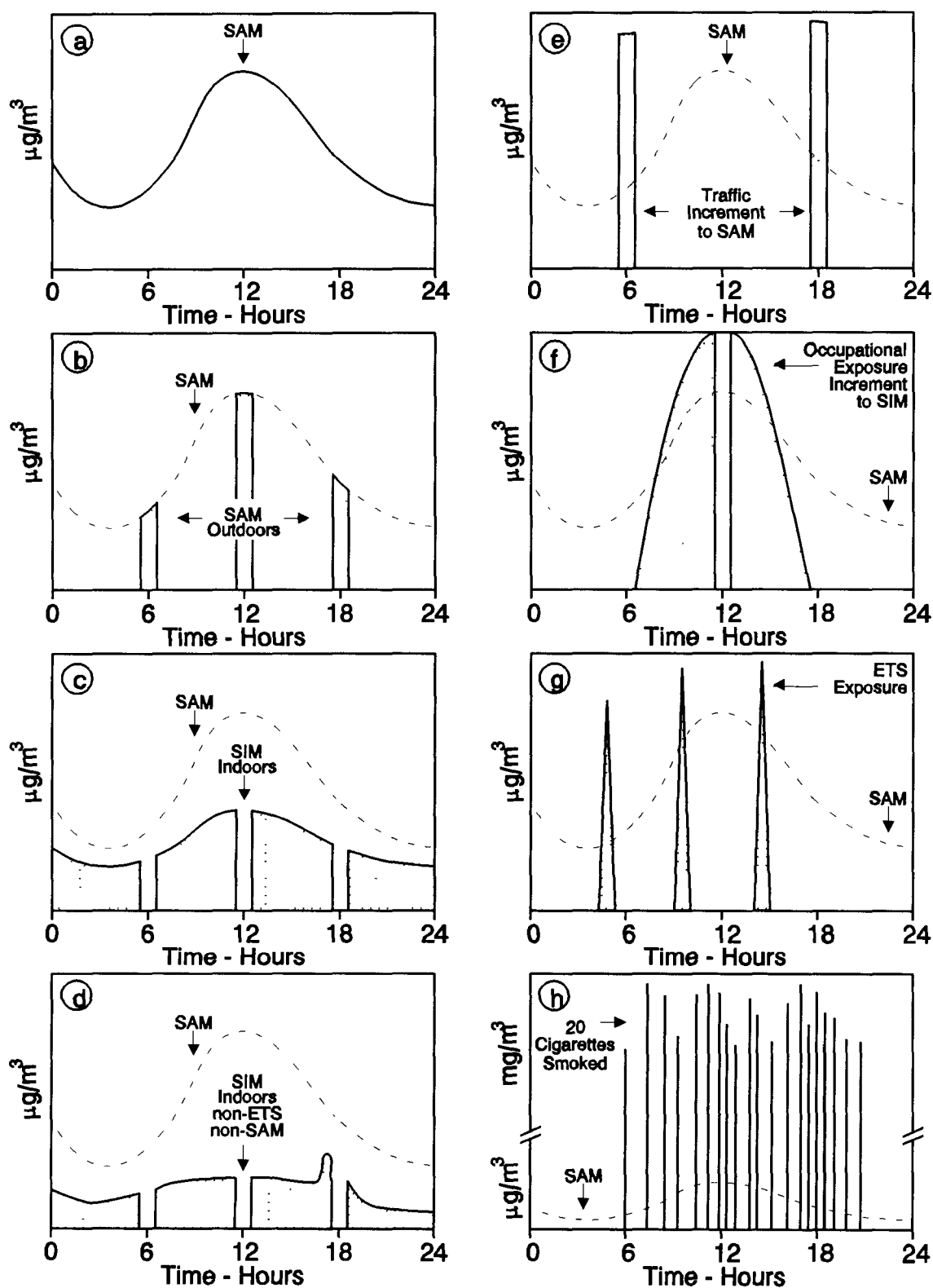


Figure 10a-h. Components of personal exposure.



1 While people are indoors, they are exposed to a variable fraction of time-lagged SAM  
2 PM. This constitutes an amount of (1) the fresh PM which depends on recent SAM and the  
3 air exchange rate between indoors and outdoors, and the PM deposition sinks (filtration of  
4 recirculated air, surfaces, etc.), and (2) PM from outdoor sources that had been deposited in  
5 the past but is resuspended due to human activity and air currents. PTEAM (Clayton et al.,  
6 1993), as cited in Section 7.6, found that outdoor air was the major source of indoor  
7 particles, accounting for 75% of the fine fraction ( $<2.5 \mu\text{m AD}$ ) and 67% of the coarse  
8 fraction ( $2.5 \mu\text{m AD}$  to  $10 \mu\text{m AD}$ ) in indoor air. It is noted that these average fractions  
9 will be lower in communities with lower average SAM values. Lewis (1991) reported an  
10 apportionment of indoor air PM in 10 homes within a wood burning community in Boise,  
11 Idaho. The results showed that 50% of the fine PM was of outdoor origin (SAM), and in 9  
12 of 10 homes, 90% of the sulfur was from outdoors (one home had an anomolous sulfate  
13 injection from a humidifier using tap water). This is consistent with indoor sources varying  
14 independently of the SAM in a stationary manner (constant mean and variance), so that the  
15 relative contribution of indoor sources to indoor exposures decreases as SAM increases.  
16 Figure 7-10c represents the increment to PEM from outdoor sources of SAM while the  
17 subjects are indoors at home and at work. The SAM value is shown as the dotted line for  
18 reference in this and all the following Figures 7-10c and 7-10h.

19 While people are indoors, at home and at work, they are also exposed to PM emitted  
20 by indoor sources - other than ETS from passive smoking and specific occupational sources.  
21 These sources, such as cooking, lint from clothing and furnishings, mold, insects, etc.,  
22 create PM that agglomerates and deposits as visible dust that can be continuously  
23 resuspended, which constitutes an additional PEM increment. Figure 7-10d shows the  
24 additive effect of this source.

25 In traffic, or near vehicles in a parking garage or parking lot, people are exposed to an  
26 increment of PM over and above the SAM value for that location. Figure 7-10e shows the  
27 additive PM for this setting that would be added to Figure 7-10b for the local vehicular  
28 emissions.

29 In an indoor setting, in the presence of a smoker or the wake of a smoker, a PEM will  
30 record an increment of ETS associated with the act of smoking. Figure 7-10f shows the  
31 added PM increment for this source.

1 At work in a 'dusty trade' such as welder, mechanic, or miner, there will be an  
2 increment of exposure associated with these occupational activities that generate PM.  
3 Figure 7-10g represents the additive PM for these activities which are assumed to take place  
4 'indoors'.

5 Last, but not least, is the physical act of smoking itself. As described previously, the  
6 main stream smoke from a cigarette, cigar, or pipe, bypasses the PM monitor and is inhaled  
7 directly. The mass of PM inhaled from smoking one-pack-per-day of the lowest Tar 'king  
8 soft pack' cigarettes, rated as delivering "1 mg 'tar' per cigarette by FTC method" is 20 mg  
9 per day (Woman's Day, 14 March, 1995). If this were distributed into a nominal 20 m<sup>3</sup> of  
10 air inhaled per day, it would be an additive increment on the order of 1 mg/m<sup>3</sup> to a 24-h  
11 PEM reading. Other cigarettes advertised in the same popular magazine are rated at "16 mg  
12 'tar' per cigarette by FTC method". Therefore one-pack-per-day smokers can have a PM  
13 exposure standard deviation that is much larger than the mean exposure to PM of non-  
14 smokers, simply from choice of brand. Figure 7-10h represents the act of smoking as  
15 creating exposures represented by the vertical spikes with an integral area  $\geq 1$  mg-day/m<sup>3</sup>  
16 per day.

17 For all subjects, by the principle of superposition, the sum of the areas in Figures 7-  
18 10b and 7-10c represents the exposure of an individual to the PM constituents that are  
19 characterized by a SAM PM concentration. The additional exposure categories that are  
20 independent of the SAM concentration (Figures 7-10d through 7-10g) and are appropriate for  
21 that subject would represent the portion of 24-h PEM PM that is not associated with SAM.  
22 Variance of SAM should explain much of the variance in the SAM related PEM fraction as  
23 defined by Figures 7-10b and 7-10c. The summation over a full day for all categories 7-10b  
24 to 7-10g would be the PEM for any subject, such as is shown in Figure 7-2 (Rpace and  
25 Lowery, 1980).

26 Although there are no data for PEM PM exposures of individuals living in homes  
27 without any indoor sources of PM, there are data for PEM sulfate as discussed previously in  
28 Section 7.3.4. Given that there are negligible sources of sulfur (S) that originate in the home  
29 (matches, low-grade kerosine, humidifiers using tap water) the high correlation of PEM S  
30 and SAM S ( $R^2 = 0.92$ ) of Figure 7-7 reported by Suh et al. (1993) where no appreciable  
31 sources of S were present, is an indication that the same relationship should hold for all

1 SAM PM of that size range. The data of Anuszewski et al. (1992) show that light scattering  
2 particles measured by nephelometry have very high correlation between indoor and outdoor  
3 concentrations ( $R^2 > 0.9$ ). Lewis (1991) and Cupitt et al. (1994) report that  $PM_{10}$  appears  
4 to penetrate with an average factor of 0.5 in Boise homes without woodburning. The factor  
5 goes up to 0.7 with woodburning, and the authors assume that the factor would go up to 0.9  
6 in the summer when homes are less tightly sealed.

7 If the variance of the PEM PM portion which is uncorrelated to SAM (10d to 10g) is  
8 very large, the percentage of the variance of the PEM PM that can be explained by the  
9 variance of SAM PM will be very small.

10 It may be possible that the 14 different populations sampled, cited in the 14 studies of  
11 Table 7-8, have widely different home characteristics, occupations, mode of commuting, and  
12 smoking exposures that contribute to the different PEM vs SAM relationships. In some of  
13 the cleaner communities, such as Watertown MA, Topeka KS, Waterbury VT, and Kingston  
14 and Harriman TN, SAM averaged less than  $20 \mu g/m^3$ . The non-SAM increments to PEM  
15 exposure in these locales were greater than the SAM and may have been so variable that the  
16 PEM PM became insignificantly correlated with the SAM PM data. The exception is  
17 Houston, with a SAM =  $16 \mu g/m^3$  and a significant  $R^2 = 0.34$  ( $0.005 < p < 0.05$ ).  
18 However, Morandi et al. (1988) note that deletion of 2 outlier observations would reduce  $R^2$   
19 and make it nonsignificantly different from 0 ( $p > 0.2$ ). This is in contrast to the two large  
20 studies in communities with high SAM levels (Clayton et al., 1993, Liroy et al, 1990), where  
21 the relations between PEM and SAM were significant.

22 All discussions above relate to nonsmokers. As for the smoker, the exposure from  
23 Figure 7-10h would outweigh the sum of all the other exposures, 7-10b through 7-10g. This  
24 smoking increment may have an important implication for interpretation of epidemiology  
25 studies that relate a surrogate of PEM PM to mortality.

26 In the epidemiology studies of PM and mortality of Chapter 12, the death counts are  
27 usually culled to remove suicides and trauma victims. This is because the SAM PM is not  
28 considered to have been a possibly contributing cause to the accident, violence or voluntary  
29 act that resulted in death. Consequently, smokers and nonsmokers alike are in the residual  
30 mortality counts that are regressed against SAM and weather related variables. The  
31 community SAM data are representative of the exposure to PM of outdoor origin expressed

by Figures 7-10b and 7-10c. For non-smokers this reflects about 50 - 75% of their exposure, which is an appreciable amount. However, for one-pack-per-day smokers, if their smoking exposure is more than an order of magnitude higher, the SAM may reflect less than 5.0 - 7.5% of their daily exposure to PM.

## **7.5.2 Relation of Community Exposures to Ambient Concentrations**

Studies of the relationship between ambient PM and mortality/morbidity implicitly assume that the PM concentration at an ambient monitoring station (SAM) is a surrogate for the mean PM exposure of people in the local community. It can be shown that if individuals' probability of mortality from PM exposure is linearly proportional to their PM exposure, then the expectation of total PM-related mortality in the community is proportional to the mean personal exposure to PM in the community. Therefore, it may be appropriate to ask the question, "how well does SAM PM characterize the mean PEM PM in the community?"

If all N people in a community carried a PEM, the mean PEM value is obtained by summing all PM PEM values and dividing by N. If indoor and outdoor PM are equally toxic on a  $\mu\text{g}$  basis, then no further information would be contained in PM SAM. The mean of a random sample of PEM PM measurements on subjects in the community would be an unbiased estimator of the actual community mean PEM PM, and such a mean may be more appropriate for use than a SAM measurement. Mage and Buckley (1995) tested the relationship of the mean PEM PM exposure to the SAM in several locations, and their results are given in the following section.

Figures 7-11a, 7-12a, 7-13a, and 7-14a show the individual personal PEM PM and the corresponding ambient SAM PM from four (4) studies cited in Table 7-8 for which individual data were available. For example, Figure 7-11a (Lioy et al, 1990) shows a set of PEM samples obtained from 14 nonsmoke exposed individuals on 14 consecutive days. Because these 14 subjects were not selected as a probability sample from the community of Phillipsburg, NJ, we consider their exposures as a biased sample from the exposure distribution that we would measure, had every person in the community carried a PM PEM. The outdoor average is estimated as the mean of four (4) ambient SAM PM values obtained on each day the people carried the PEM for  $\text{PM}_{10}$ .

Phillipsburg, NJ (Winter 1988)  
(all data included, n=191)

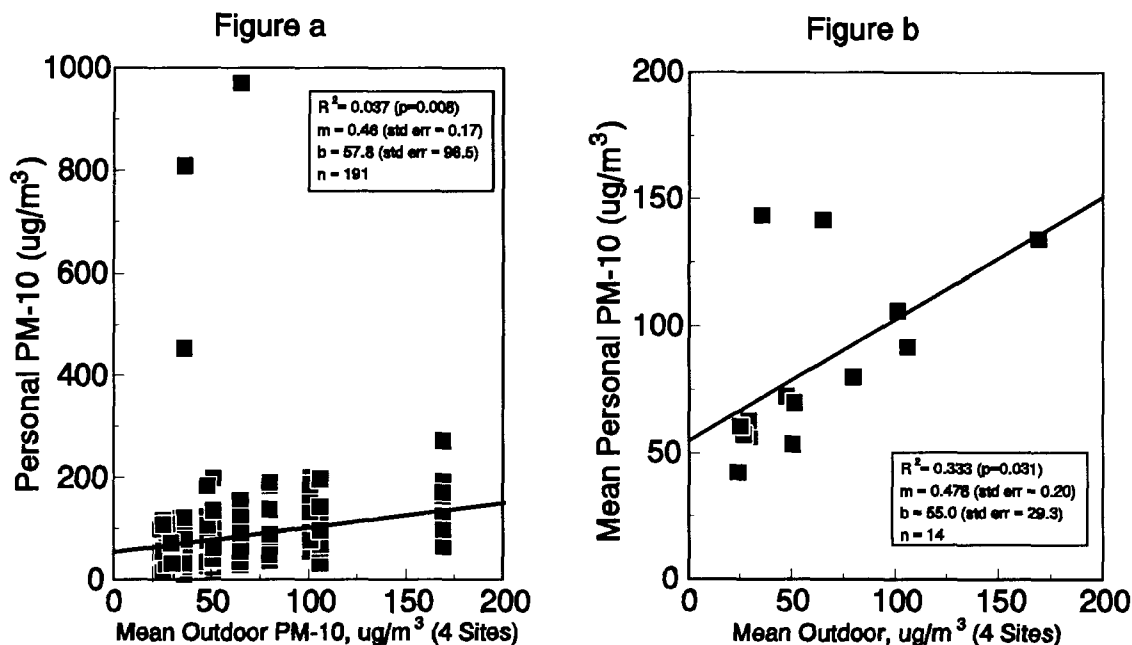


Figure 7-11a,b. Personal exposure to PM in Phillipsburg, NJ (Winter, 1988)

Source: Liroy et al. (1990).

The data plot is a vertical profile corresponding to up-to-14 valid PEM values obtained on that day. In the regression, each point is weighted equally, and the  $R^2$  value of 0.037 ( $p = 0.008$ ) would be significant if the sample were unbiased. The bias of a nonrandom sample has an expectation of zero and a finite variance if the choice of subjects is not based on factors related to exposure to PM. In Figure 7-11b, the mean of the daily PEM values is plotted. The  $R^2$  now has increased from 0.037 to 0.333 ( $p=0.031$ ). The interpretation is that, on the average, variation in SAM only explains on the order of 4% of the variation in an arbitrary individuals PEM, but that same variation in SAM explains 33% of the variation in their mean exposure.

Because both these PEM and SAM values are measured with error, an orthogonal regression may be more appropriate, with inverse variance weighting for each of the PEM

# Beijing, PRC (Winter 1985)

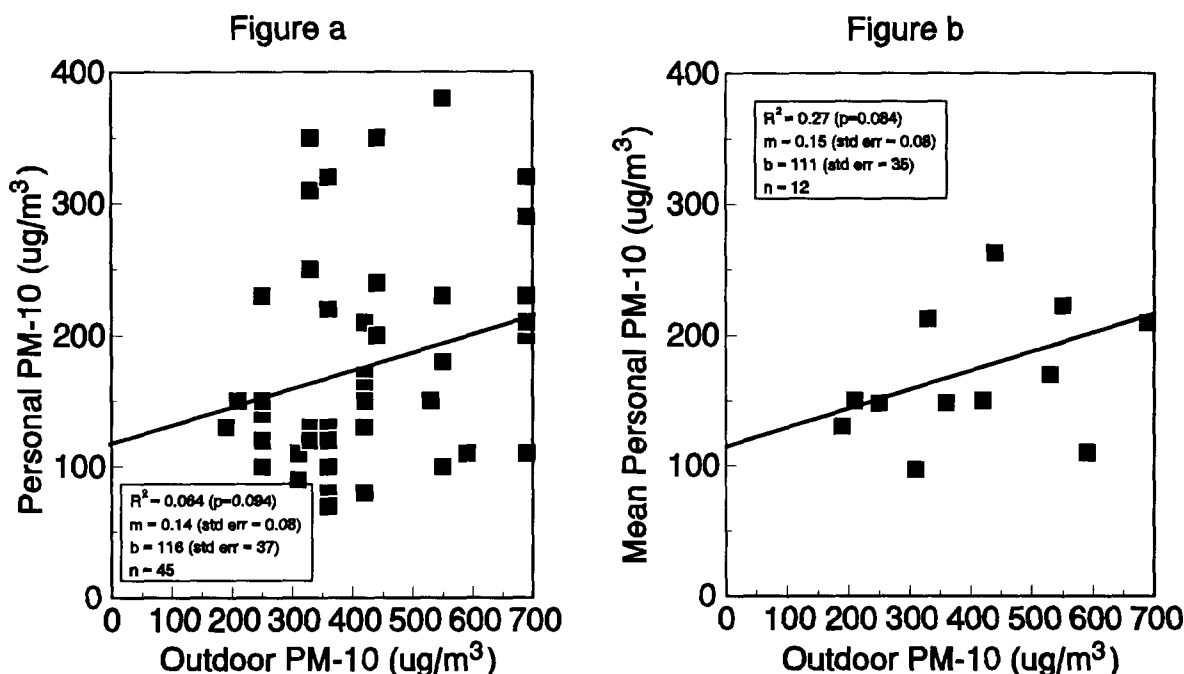


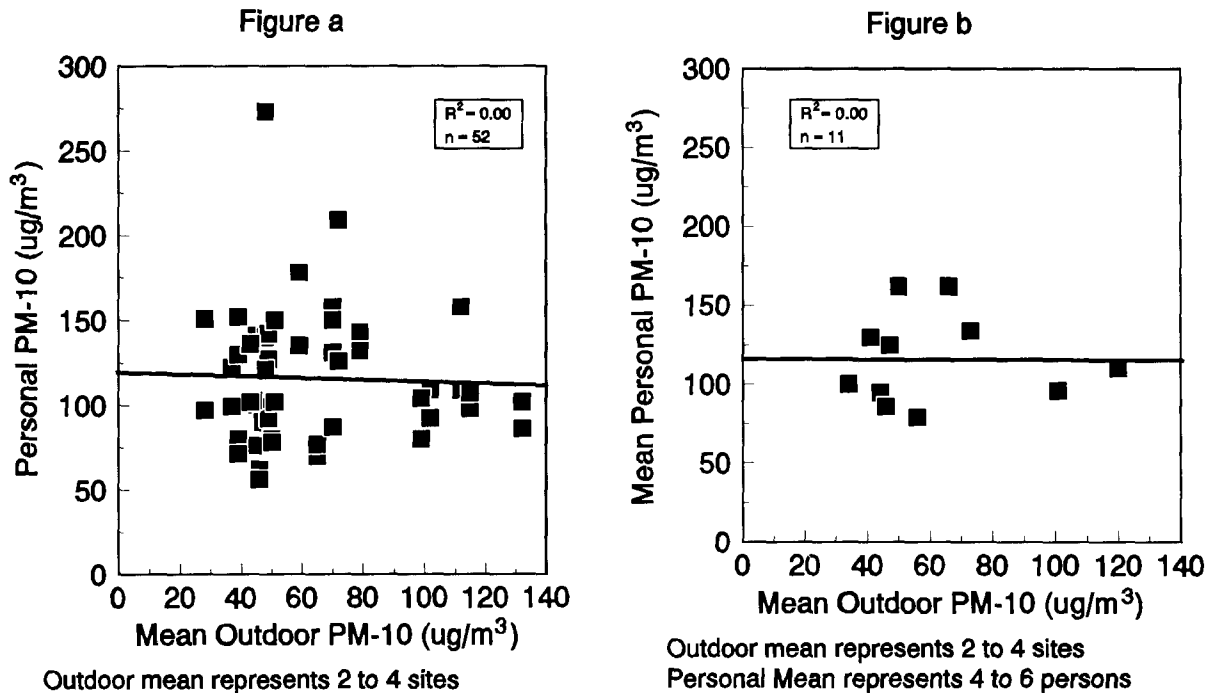
Figure 7-12a,b. Personal exposure to PM in Beijing, China (Winter, 1985).

1 and SAM means. This would be expected to change the regression slightly but not the  
 2 general conclusion that there is much more influence of SAM variation on the variation in  
 3 the mean community exposure.

4 In Beijing (Figure 7-12a,b) with a nonprobability sample of 20, the slope remains  
 5 relatively constant at 0.14 as the  $R^2$  value increases from 0.064 to 0.23 with the usage of  
 6 mean PM PEM exposure.

7 Figure 7-13a,b for Azusa, California, with a nonprobability sample of 9, the correlation  
 8 between PM PEM and PM SAM is negative (-0.01) and  $R^2$  is 0.0001. In this case, taking the  
 9 mean of personal exposures shows no significant improvement in the  $R^2$  value. Such a low  
 10 value of  $R^2$ , as in several of the studies cited in Table 7-8, may be caused by several factors,  
 11 such as sampling error (too few observations), a biased (nonprobability) sample, very strong  
 12 indoor sources of PM, or commuting of the people during the day to locations with  
 13 significantly different ambient pollution than in their home community.

# AZUSA, CA (Spring 1989)



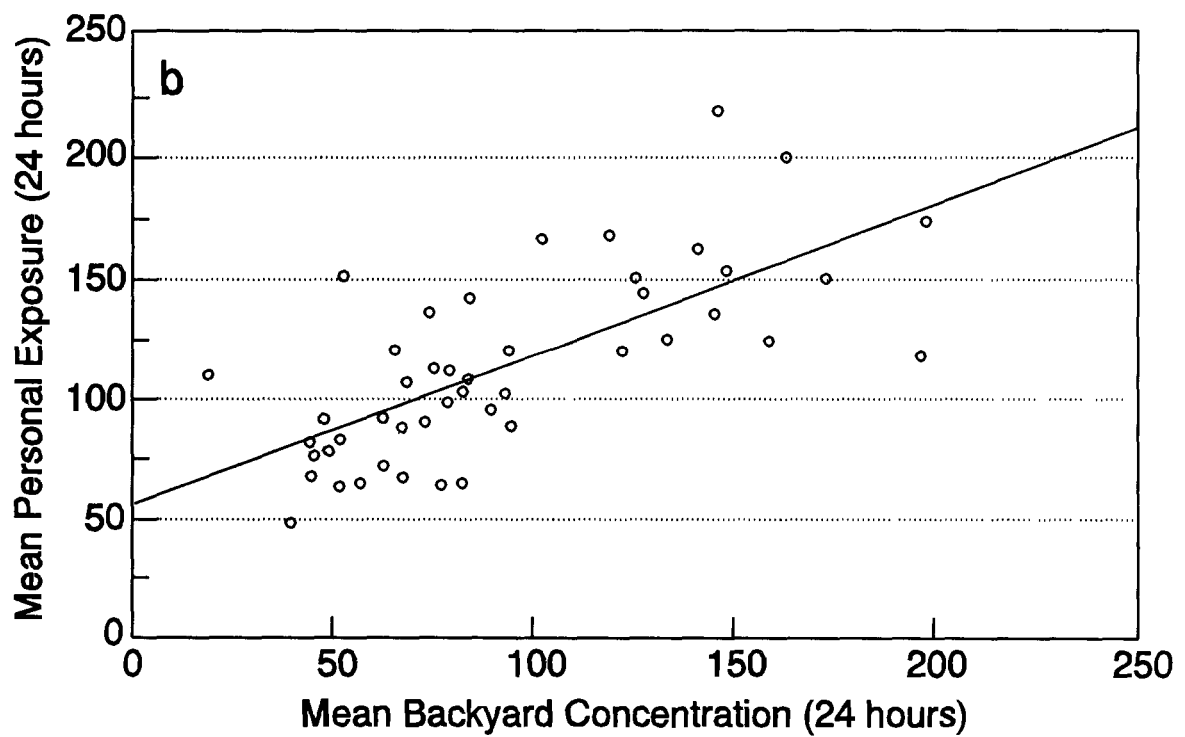
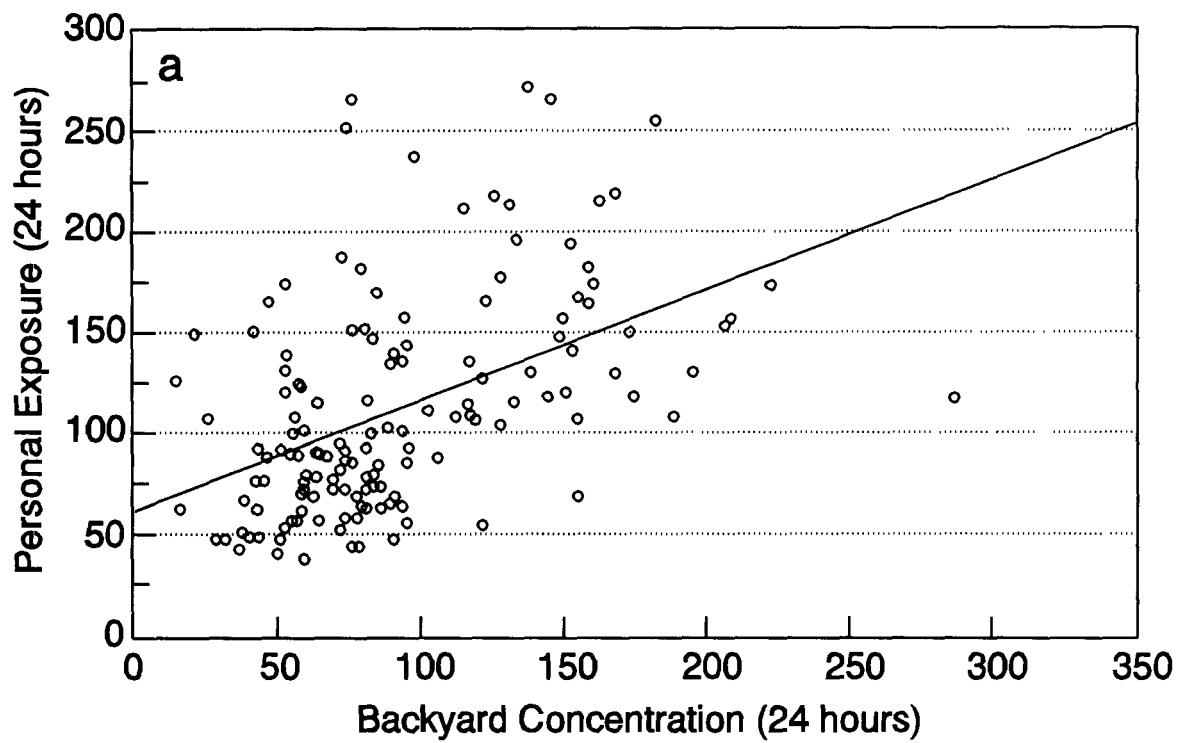
**Figure 7-13a,b. Personal exposure to PM in Azusa, CA (Spring, 1989).**

Source: Perritt et al. (1991).

In Figure 7-14a,b, Riverside, California, with a probability sample of 178 people, the  $R^2$  values are significant, and they improved by a factor of three, from 0.16 to 0.49, while the regression equation remained essentially the same.

The Riverside CA study and the Phillipsburg NJ study differ in three important aspects. In Phillipsburg, NJ, 14 nonsmoke-exposed at-home people carried a PEM for 14 days; in Riverside, CA, each day up to four different people, some of them who were smoke-exposed at-home, carried a PEM for one day over the 48-day study period.

1. The Phillipsburg NJ data have a (potentially) 2-fold more precise estimate of the mean given by 14 PEM measurements as compared to 4 in Riverside, CA ( $1/\sqrt{13} = 0.28$ ,  $< 1/\sqrt{3} = 0.57$ ).



1 Figure 7-14a,b. Personal exposure to PM in Riverside, CA.



2. The lack of smoke exposure to the subjects in NJ would reduce the variance of the PEM measurements, and
3. The use of a nonprobability sample in NJ (and all other studies in which nonprobability sampling occurs) limits the statistical applicability of the results.

The improvement in the regression  $R^2$  value by taking the mean of the PEM PM data is not an important finding of itself. This improvement in the regression coefficient is predictable from the Central Limit Theorem and the process of regression to the mean of the observations - as when random measurement errors are removed. The higher correlation of categorical exposure assignments has been noted in epidemiological studies.

The value of the improvement of the mean PEM relationship to SAM is that it provides a better visualization that helps in understanding how mean PEM varies with SAM. It thus provides a measure of the validity of the use of a daily PM SAM as a surrogate for the mean PM PEM in the community. It is clear that the uncertainty in predicting mean personal exposure PM is much smaller than the uncertainty in predicting the personal exposure PM for an individual when we note that the means have a much smaller variability about the line as shown in Figures 7-11b, 7-12b, 7-13b, and 7-14b.

There appears to be two distinct categories of exposure studies that are examined:

In the first type of study, such as Liroy et al. (1990) and Clayton et al. (1993), there is a significant  $R^2$  between individual PM PEM and PM SAM. In this category, there is an appreciable improvement in correlation between the mean PEM and SAM. It has been suggested that these cases with high correlation of PEM PM and SAM PM may arise where the fine portion of the ambient PM ( $PM_{2.5}$ ) is highly variable from day-to-day, and the ambient coarse fraction is relatively constant. In some locations, the fine portion of the ambient PM ( $PM_{2.5}$ ) is more variable from day-to-day than that of the ambient coarse fraction. In an urban area, the fine particle composition and the fine particle concentration are highly correlated from site-to-site on any given day. This is due, in part, to the homogeneous gas phase reactions of  $SO_x$  and  $NO_x$  to produce sulfates and nitrates, and aerosol droplet formation with the condensation nuclei, such as metals, which are emitted from ubiquitous sources, such as automobiles.

On the other hand, ambient coarse particles are generated locally, and they have higher deposition velocities than the fine particles. Their impact may then be limited by fallout to a

locality downwind of their emission point, as they are not readily transported across an urban area. Therefore, during an air pollution episode, people living in an urban area may be exposed to fine PM of similar chemical composition and concentrations, whereas they will be exposed to coarse PM with a chemical composition that can depend on the location of the exposure. Because PM<sub>2.5</sub> could penetrate readily into a nonambient setting, the correlation between the mean PM PEM and PM SAM would be high because all the people would have similar exposure to the ambient fine PM - plus exposure to indoor generated PM and ambient coarse PM which may have less fluctuation.

In the second type of study, such as Sexton et al. (1982) and Spengler et al. (1985), there is negligible correlation between individual PEM PM and SAM PM, and consequently there will be little correlation between their mean PEM and the SAM. In these cases, if the fine fraction is not an appreciable portion of the total PM, or there are significant indoor sources, then the correlations between mean PM PEM and PM SAM may not be as impressive as for the other case.

### **7.5.3 Implications for PM and Mortality Modeling**

PM related mortality may be specific to the most highly susceptible portion of the population. Such a cohort may be the elderly people with the most serious chronic obstructive lung disease (COLD) and cardiac insufficiency. Smithard (1954) relates the findings of Dr. Arthur Davies (Lewisham coroner) who autopsied 44 people who died suddenly during the 1952 London Fog:

"The great majority of deaths occurred in people who had pre-existing heart and lung trouble, that is to say they were chronic bronchitic and emphysematous people with consequent commencing myocardial damage. The suddenness of the deaths, Dr. Davies thought, was due to a combination of anoxia and myocardial degeneration resulting in acute right ventricular dilation"

Mage and Buckley (1995) hypothesize that these people with compromised cardio-pulmonary systems may be relatively inactive, while selecting to live in homes or institutional settings without sources of indoor pollution. If their time is spent in clean settings (e.g. where smoking is prohibited), then they would have little exposure to PM other than from the ambient pollution that intrudes into their living quarters. The exposure to PM of this cohort

would be highly correlated with PM SAM, and so would be their mortality, if this PM was indeed highly reactive in their pulmonary tracts. However, there have been no exposure studies done with people who correspond to the Lewisham mortality cohort. Individual PM PEM of people outside this cohort, who could be relatively insensitive to PM, might not be significantly correlated with PM SAM, as reported in most of the 14 studies cited in Table 7-8. This suggests a model to relate PM and mortality as follows. Let any person (j) on a given day have a probability of mortality,  $p(m) = k_j X_j$ , where  $k_j$  is the unit probability of mortality per  $\mu\text{g}/\text{m}^3$  of PM per day,  $X_j$  is the daily average exposure to PM,  $\mu\text{g}/\text{m}^3$ , independent of  $k_j$ . Let us assume that each individual (j) has their own personal value of  $k_j$  that can vary from day-to-day.

The expectation of total mortality (M) in a community of size N can be shown to be the summation of  $k_j X_j$  over all individuals ( $j = 1$  to  $N$ ) as follows:

$$M = \sum k_j X_j \quad (7-3)$$

If  $k_j$  is independent of  $X_j$ , then we can define  $K$  as  $(1/N) \sum k_j$ , and the mean community exposure  $\bar{X}$  as  $(1/N) \sum X_j$ , and it follows

$$M = N K \bar{X} \quad (7-4)$$

This implies that, given a linear relationship of mortality with PM PEM exposure (X), the expected mortality is proportional to the mean community personal exposure to PM. The individual in the community, on any given day, with the highest probability of dying from a PM exposure related condition is that individual with the highest product  $k_j X_j$ , not necessarily the highest exposed individual with the maximum value of  $X_j$ .

The Phillipsburg, NJ, data set is a case in point. In this study, three subjects had excessively high PEM PM (shown by the three maxima on Figure 7-11a). These values were caused by a hobby involving welding in a detached garage ( $971 \mu\text{g}/\text{m}^3$ ), a home remodeling activity ( $809 \mu\text{g}/\text{m}^3$ ) and usage of an unvented kerosine heater ( $453 \mu\text{g}/\text{m}^3$ ). Excessive PM generating activities are not expected of elderly people who may have compromised pulmonary systems. In fact, the elderly and infirm husband of the remodeler had a personal exposure of  $45 \mu\text{g}/\text{m}^3$  on the day of the remodeling activity. The indoor

monitors in the homes of the welder and remodeler only recorded  $55 \mu\text{g}/\text{m}^3$  and  $19 \mu\text{g}/\text{m}^3$ , respectively, during those events, indicating the specificity of the high exposure to only the individual involved. If we remove these three 'outliers', as being unrepresentative of the magnitude of exposures of those nonsmoke-exposed people most at risk from high values of  $k_j$ , as defined by Smithard (1954), then as shown on Figures 7-15a,b the correlation  $R^2$  improves markedly, from 0.250 to 0.914.

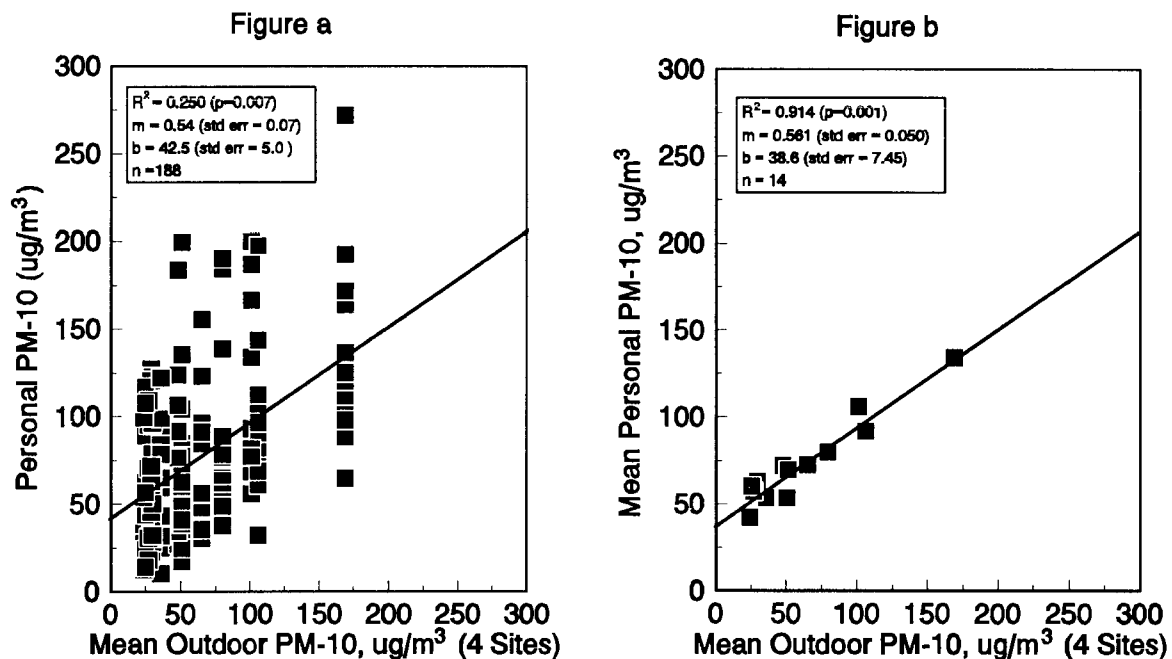
It is this relation of the PM PEM exposure to PM SAM concentration, as shown in Figures 7-15a,b that may be a better representation of the true situation underlying the PM vs mortality relationships because of the "healthy worker" effect. Chronically ill people who are sensitive to PM might change their behavior to minimize their exposure to irritants. Consequently, healthy people with high PEM PM measures in occupations and indoor settings can cause the regression  $R^2$  between PEM and SAM to be low, but they may not be the individuals at highest risk of the acute effects of PM exposure.

#### **7.5.4 Relative Toxicity of Ambient PM and Indoor PM**

In the previous sections the SAM PM was evaluated as a predictor of PEM PM on the implied basis that the health effects of PM were only mass dependent, and independent of chemical composition. It was shown in Table 7-8 that many early PM studies of PEM had a low correlation between PEM and SAM on an individual basis that was often not significantly different from zero. But, in the later studies (Clayton et al., 1993; Liou et al., 1990), a significant relationship was observed between PEM and SAM. Further analysis showed that on a daily basis, SAM would appear to be a good predictor of mean community PEM from the results of the Riverside, CA, and Phillipsburg, NJ studies.

However, there may be a significant difference in toxicity of PM per unit mass, as a function of source type and composition, such that some of the PM of indoor origin is less toxic than the ambient PM. If so, then the SAM might be a better choice of surrogate for the toxicity of an individual's exposure than the PEM which may be influenced by less toxic materials. There is some indication that on a unit mass basis, combustion products of fossil fuels (coal and oil) may be more acutely toxic to the pulmonary system than combustion products of biomass origin (tobacco, wood). Furthermore, soil constituents and other

Phillipsburg, NJ (Winter 1988)  
Three 'outliers' removed (971,809, & 453)

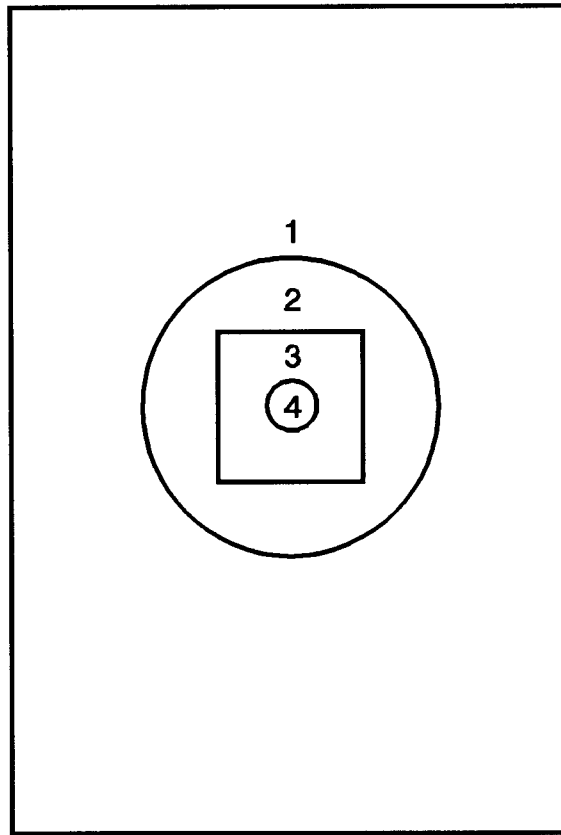


**Figure 7-15a,b. Personal exposure to PM in Phillipsburg, NJ with concentration outliers removed.**

Source: Lioy et al. (1990).

1 nonanthropogenic materials (iron oxide, alumina, Mt. St. Helens volcanic ash) also appear to  
 2 be less toxic than combustion products in general. See Chapter 11 regarding comparative  
 3 toxicity aspects.

4 In summary, there is evidence that not all PM constituents have the same  
 5 toxicity per unit mass. These differences are due to differences in aerodynamic diameter and  
 6 chemical composition. As shown on a Venn diagram [Figure 7-16, Mage (1985)], the  
 7 focusing of the description of a PM exposure increases the ability to estimate the potential  
 8 toxicity of the exposure. In the sequential description given below, the uncertainty in the  
 9 toxicity of the mixture is decreased as more information is provided.



**Figure 7-16. Venn diagram (Mage, 1985) showing focusing of information to more completely specify toxicity of a given PM mixture: (1) universe of all possible mixtures of PM with concentration of  $2 \mu\text{g}/\text{m}^3$ ; (2) subuniverse of all combinations of PM with concentration of  $2 \mu\text{g}/\text{m}^3$  in size interval 2.0 to  $2.5 \mu\text{m}$ ; (3) subuniverse of all combinations of PM with concentration of  $2 \mu\text{g}/\text{m}^3$  in size interval 2.0 to  $2.5 \mu\text{m}$  AD with 50% of automotive origin and 50% from indoor sources; and (4) subuniverse of all combinations of PM with concentration of  $2 \mu\text{g}/\text{m}^3$  in size interval 2.0 to  $2.5 \mu\text{m}$  AD with 50% of automotive origin and 50% from indoor sources; 25% Pb, 25% BaP and 50% unspecified inorganic materials.**

1.  $2 \mu\text{g}/\text{m}^3$  of TSP.
2.  $2 \mu\text{g}/\text{m}^3$  of TSP in the size interval 2 to  $2.5 \mu\text{m}$ .
3.  $2 \mu\text{g}/\text{m}^3$  of TSP in the size interval 2 to  $2.5 \mu\text{m}$ , 50% of automotive origin and 50% of indoor source origin.
4.  $2 \mu\text{g}/\text{m}^3$  of TSP in the size interval 2 to  $2.5 \mu\text{m}$ , 50% of automotive origin and 50% of indoor source origin,  $0.5 \mu\text{g}/\text{m}^3$  of Pb,  $0.5 \mu\text{g}/\text{m}^3$  of BaP and  $1 \mu\text{g}/\text{m}^3$  of unspecified inorganic material.

As applied to human exposure to PM, this concept of differential toxicity suggests that data collections might benefit by providing data that would allow the toxicity of a PM exposure to be evaluated in terms of information, in addition to the mass collected per unit volume.

#### 7.5.5 Conclusions

- (1) For any air pollutant, the total exposure of an individual consists of a variety of sequential exposures to a variety of microenvironments. They are typically, outdoor, indoors at-home, at-work, in-traffic and many other indoor microenvironments. The principle of superposition is a useful mechanism to visualize the summation process.
- (2) For any identified air pollutant, the ambient environment is one source of indoor pollution due to air exchange and infiltration. Whether the ambient is a significant or dominant source of indoor pollution depends on the relative strength of indoor sources and sinks.
- (3) For PM, studies have detected a 'personal cloud' related to the activities of an individual which may generate significant levels of airborne PM in his/her vicinity which may not be picked up by an indoor PM monitor at a distance.
- (4) For PM, some studies have identified significant sources in the home, e.g. due to cooking and smoking.
- (5) For PM of size fractions that include coarse particles, some studies have identified statistically significant relationships between personal exposures and other studies have not, probably due to overwhelming effects of indoor sources, 'personal clouds' and other individual activities.
- (6) For PM of a fine size fraction - such as sulfates, there seems to be more of a relationship between ambient concentration and personal exposure, than for coarser PM, perhaps because of the ability of fine PM to penetrate into indoor settings.
- (7) For a study population in which there is a detectable 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 personal exposure of an individual.
- (8) For fine PM constituents, such as sulfates, high correlations between ambient concentration and personal exposures have been identified.

- (9) For Riverside, CA, where 25% of the population was estimated to have personal exposures exceeding the 24-h National Ambient Air Quality Standard for PM<sub>10</sub> of 150 µg/m<sup>3</sup>, at least 50% of this mass is of ambient origin.

## **7.6 INDOOR CONCENTRATIONS AND SOURCES OF PARTICULATE MATTER**

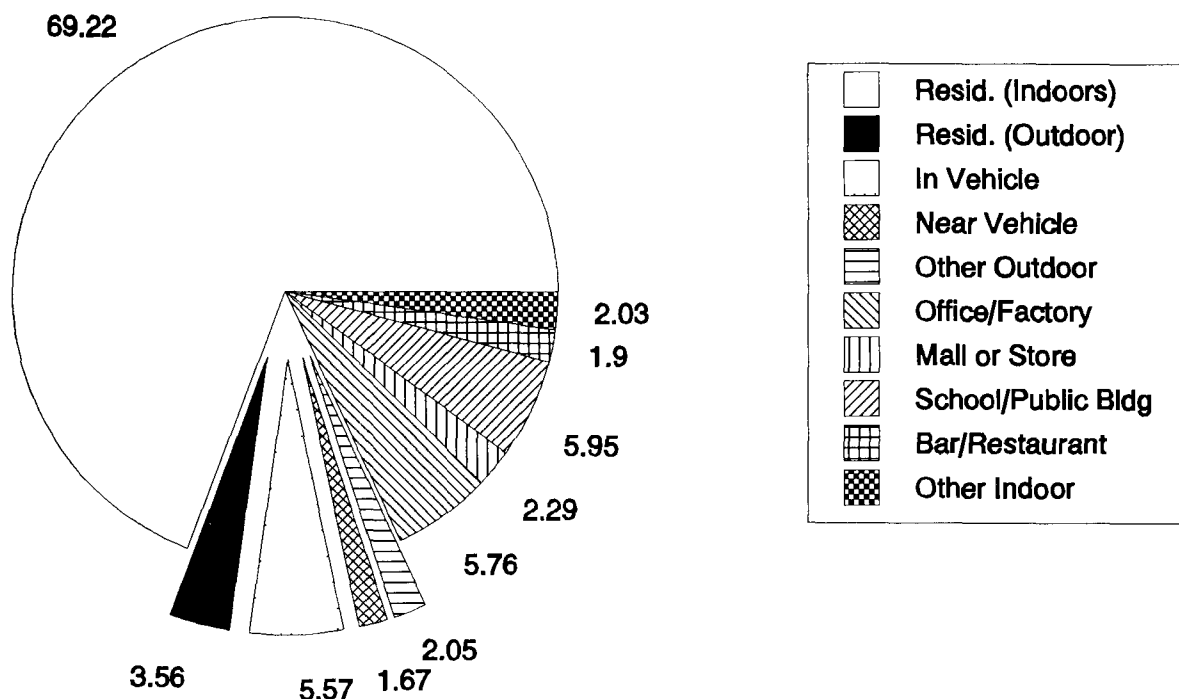
### **7.6.1 Introduction**

Although EPA regulates particles in outdoor air, not indoors, it is still important to consider indoor air. For one thing, most people spend most of their time indoors. The most recent nationwide study of time budgets (Robinson and Nelson, 1995), based on interviews with 9,386 respondents in 1993 to 1994, indicates that U.S. residents spend 87.2% of their time indoors, 7.2% in or near a vehicle, and only 5.6% outdoors (Figure 7-17). Secondly, we need to understand how outdoor particles are affected as they cross building envelopes. For a home with no indoor sources, how much protection is offered against particles of various size ranges? How do parameters such as the volume of the house, the air exchange rate, cleaning frequency and methods, and materials in the home affect particle concentrations? Indoor air studies have grappled with these topics and have the potential to answer these and other important questions ultimately affecting the health of the general public.

This section has two parts. The first part deals with field studies of particles indoors and outdoors, concentrating particularly on large-scale surveys of many homes and buildings. Besides presenting the observed indoor and outdoor particle concentrations, contributions of these studies toward understanding important parameters such as air exchange rates, source emission rates, and decay rates are also reported. This section will also discuss a few studies dealing with inorganic and organic constituents of particles (e.g., elements and PAHs) as well as other important considerations such as mutagenicity and the role of house dust in exposure to metals and pesticides. However, each of these topics is an entire field of study in itself, and can only be touched on in this section.

The second part of the chapter deals with indoor air quality models and the experiments and chamber studies performed to validate them. A crucial parameter for particle studies is the decay rate on surfaces, and a series of recent studies that have given information on this





**Figure 7-17. Percentage of time spent in different microenvironments by U.S. residents.**

Source: Robinson and Nelson (1995).

point are reviewed. Since major modeling efforts have been aimed specifically at cigarette smoking, a special section is devoted to these models.

In keeping with EPA's regulatory responsibilities, we omit the many studies in industrial workplaces and the "dusty trades". We also omit studies whose main focus is lead in indoor locations, since lead is a separate criteria pollutant and such studies are reviewed in the lead criteria document. Finally, although particle concentrations indoors are of crucial importance in determining the impact of radon daughters on health (smokers are at much higher risk from radon than nonsmokers), we omit studies focused on radon due to the fact that a different branch of EPA has regulatory authority over radon.

### 7.6.2 Concentrations of particles in homes and buildings

At least six major reviews of field studies of indoor particles have been published since 1980. However, all of these reviews, three of which were sponsored by tobacco companies,

were concerned with particles mainly as they relate to environmental tobacco smoke (ETS). Sterling et al. (1982) reviewed studies of ETS byproducts. The National Academy of Sciences (National Research Council, 1986) reviewed 16 ETS-related studies, including 8 in residences and 5 in offices or buildings. Repace (1987) reviewed 13 ETS-related studies, including three in residences and three in offices or hospitals. Guerin et al. (1992) reported on 21 field studies of particles worldwide, including 10 in residences and 10 in offices and public buildings. The U.S. Environmental Protection Agency (1992) reviewed 27 ETS-related studies (24 published since 1980) including 10 in residences and 5 in offices. Holcomb (1993) updated Sterling's review, including 41 studies published in the U.S. or Canada since 1980, with 14 studies in homes and 20 in offices or public buildings.

Since the last of these reviews, several important studies have been completed, including EPA's major probability-based PTEAM Study. Other large studies were not included in the earlier reviews for unknown reasons. And some studies, such as the Harvard 6-City study, have had very recent summaries of all the data, heretofore scattered in a number of publications. Therefore it is appropriate to provide a new review of all major studies at this time.

Since the two environments where people spend the most time are home (68 to 70%: Chapin 1974; Szalai et al., 1972; Robinson and Nelson, 1995) and work or school (17 to 20%), we will summarize the studies in these environments in turn.

#### **7.6.2.1 Concentrations in homes**

There have been three large-scale studies (greater than 150 homes) of airborne particles inside U.S. homes. In chronological order, these are:

1. The Harvard 6-City study, carried out by the Harvard School of Public Health beginning in 1979 and continuing through 1988, with measurements taken in 1,273 homes;
2. The New York State ERDA study, carried out by Research Triangle Institute in 433 homes in two New York State counties in 1986;
3. The EPA Particle TEAM (PTEAM) Study, carried out by Research Triangle Institute and Harvard University School of Public Health in 178 homes in Riverside, California in 1990.

We shall discuss the findings of each in some detail, since these studies present the most complete investigations to date of indoor and outdoor concentrations of particles.

### *The Harvard 6-City Study*

The Harvard 6-city study is a prospective epidemiological study of the health effects of particles and sulfur oxides. Focused on children, it has included pulmonary function measurements on more than 20,000 persons in the 6 cities, chosen to represent low (Portage, WI and Topeka, KN), medium (Watertown, MA and Kingston-Harriman, TN), and high (St. Louis, MO and Steubenville, OH) outdoor particle and sulfate concentrations.

The study took place in two measurement phases. The first phase involved monitoring about 10 homes in each city for respirable particles ( $PM_{3.5}$ ). The homes were measured every sixth day (24-h samples) for one to two years. In the second phase, a larger sample of 200 to 300 homes was selected from each city, with week-long  $PM_{2.5}$  samples collected both indoors and outdoors. Two weeks of sampling in summer and in winter were provided. Ultimately over 1,200 homes were monitored in this way.

Spengler et al. (1981) described the first 5 years of the Harvard 6-city study. During that Phase I period, pulmonary function measurements were administered to 9,000 adults and 11,000 children in grades 1 through 6. A questionnaire asks about living conditions, type of fuel and heating systems, occupation, and smoking habits of parents. Homes were selected on a volunteer basis, so that no extrapolations to a wider community are warranted. In each home a 24-h sample (beginning at midnight) was collected every sixth day. The cyclone sampler has a cut point of about  $3.5 \mu m$  at a flow rate of 1.7l Lpm. About 10 sites in each city were kept in operation for two years. The annual mean indoor and outdoor RSP concentrations are provided in Figure 7-18. As can be seen, the indoor concentrations exceeded the outdoor levels in all cities except Steubenville, where the outdoor levels of about  $46 \mu g/m^3$  slightly exceeded the indoor mean of about  $43 \mu g/m^3$ . The authors noted that the major source of indoor particles is cigarette smoke, and categorized their data by the number of smokers in the home (Table 7-9).

Dockery and Spengler (1981a) provided additional data analysis drawn from the same 6-city study but including data from 68 homes compared to the 55 reported on in Spengler et al. (1981). Annual (every sixth day) mean indoor  $PM_{3.5}$  concentrations (in  $\mu g/m^3$ ) were

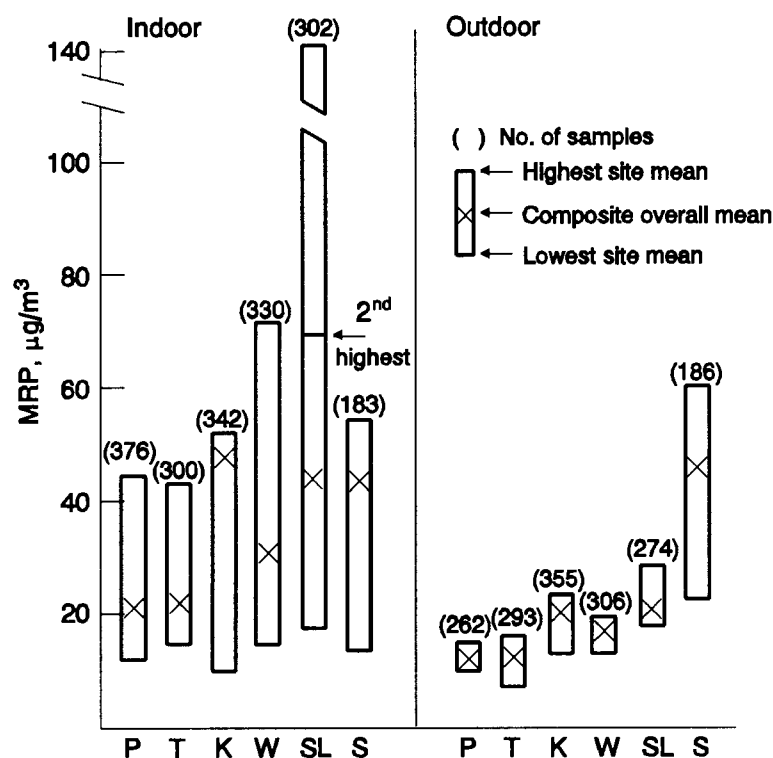


Figure 7-18. The annual mean concentration of respirable particles (MRP) for the highest and lowest site from the network of indoor and outdoor monitors in each city. (P-Portage, T-Topeka, K-Kingston/Harriman, W-Watertown, SL-St. Louis, S-Steubenville). Overall composite mean and the number of samples are also shown.

TABLE 7-9. CONCENTRATIONS OF PARTICLES (PM<sub>2.5</sub>) IN HOMES OF CHILDREN PARTICIPATING IN THE HARVARD SIX-CITY STUDY

Location	No. of homes	No. of samples	Mean (SD) (µg/m <sup>3</sup> )
<b>Indoors</b>			
No smokers	35	1,186	24.4 (11.6)
One smoker	15	494	36.5 (14.5)
Two or more	5	153	70.4 (42.9)
<b>Outdoors</b>	55	1,676	21.1 (11.9)

Source: Spengler et al. (1981).

- 1 20 and 23 in the two "clean" locations (Portage and Topeka); 31 and 36 in the two
- 2 "medium" locations (Watertown and Kingston-Harriman); and 39 and 47 in the two "dirty"
- 3 locations (Steubenville and St. Louis). Outdoor PM<sub>10</sub> concentrations (µg/m<sup>3</sup>) measured by

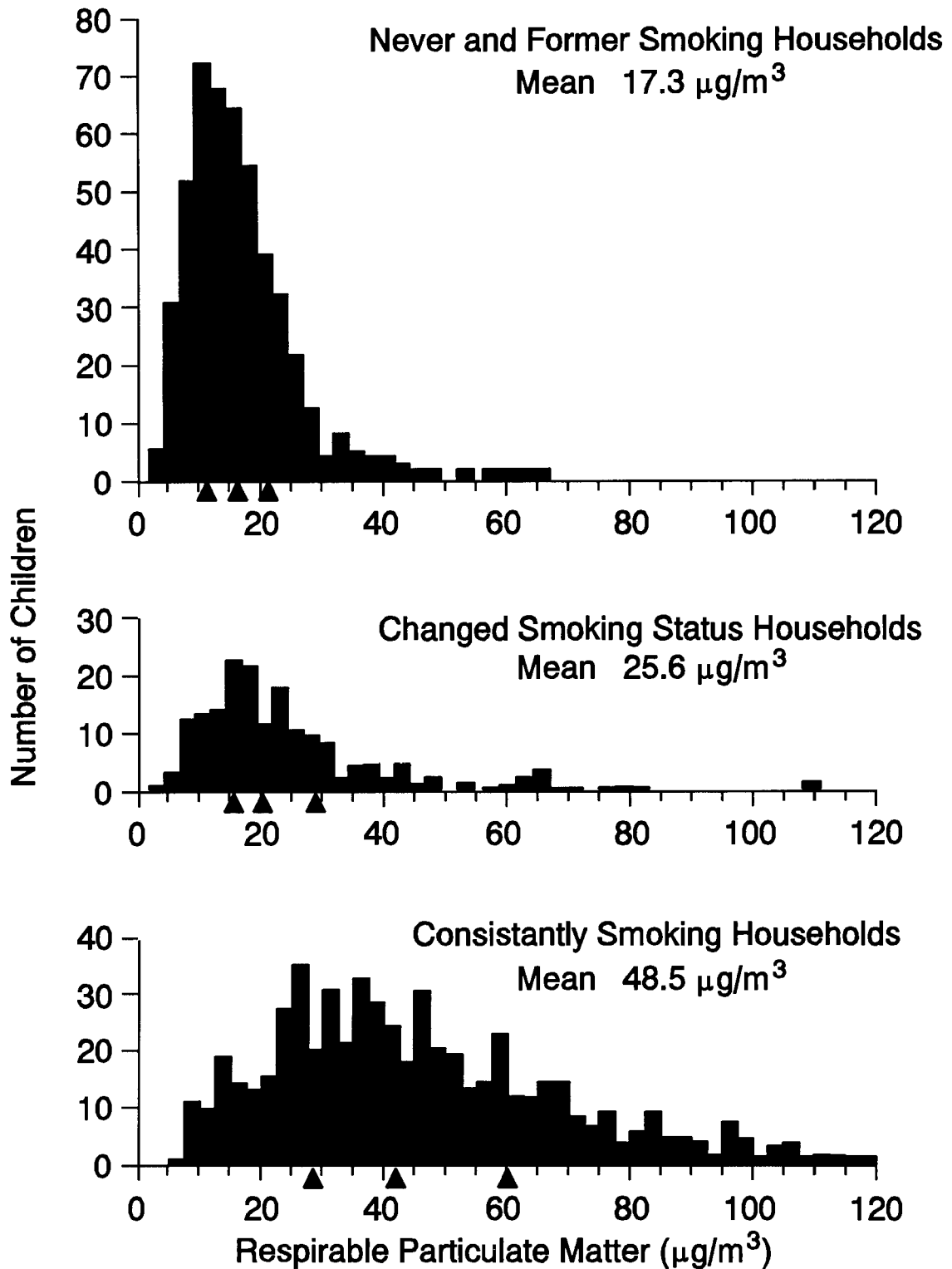
dichotomous samplers running every other day in the cities were  $20.1 \pm 0.6$  (SE) in Portage,  $31.9 \pm 1.1$  in Topeka,  $35.4 \pm 1.2$  in Kingston,  $41.1 \pm 1.0$  in Harriman,  $25.8 \pm 0.7$  in Watertown,  $37.4 \pm 1.0$  in St. Louis, and  $56.6 \pm 1.7$  in Steubenville (Spengler and Thurston, 1983). Corresponding outdoor  $PM_{2.5}$  concentrations were  $12.5 \pm 0.4$ ,  $12.9 \pm 0.4$ ,  $24.6 \pm 0.8$ ,  $24.3 \pm 0.7$ ,  $17.3 \pm 0.5$ ,  $20.5 \pm 0.5$ , and  $36.1 \pm 1.2$ . A mass balance model allowed estimation of the impact of cigarette smoking on indoor particles. Long-term mean infiltration of outdoor  $PM_{3.5}$  was estimated to be 70% for homes without air conditioners, but only 30% for homes with air conditioners. An estimate of  $0.88 \mu g/m^3$  per cigarette (24-h average) was made for homes without air conditioning, while in homes with air conditioning the estimate increased to  $1.23 \mu g/m^3$  per cigarette. A residual amount of  $15 \mu g/m^3$  not explained by the model was attributed to indoor sources such as cooking, vacuuming and dusting.

Letz et al. (1984) developed a model of personal exposure to particles based on 88 participants who wore personal monitors in the Kingston-Harriman portion of the 6-city study. From the 1 to 2 years of indoor-outdoor data on 57 homes in the 6 cities, they developed an equation relating indoor particle concentrations to those measured outdoors:

$$C_{in} = 0.385 C_{out} + 29.4 (\text{Smoking}) + 13.8.$$

Thus homes with smokers had a  $PM_{3.5}$  ETS component of  $29.4 \mu g/m^3$ . The residual of  $13.8 \mu g/m^3$  was assumed to be due to other household activities.

Neas et al. (1995) presented summary results for the entire second phase of the 6-city Study (1983 to 1988). In Phase 2, a total of 1,237 homes containing white never-smoking children 7 to 11 years old at enrollment completed three questionnaires and completed two weeks of summer and winter monitoring indoors and outdoors for  $PM_{2.5}$  using the Harvard impactor. At the beginning of the indoor monitoring study, 55% of the children were exposed to ETS in the home, and 32% were exposed to two or more smokers. Household smoking status changed for 173 children, (13% of smoking households ceased to smoke, 15% of the nonsmoking households became smoking households.) The annual (winter and summer) household  $PM_{2.5}$  mean concentration for the 580 children living in consistently smoking households was  $48.5 \pm 1.4$  (SE)  $\mu g/m^3$  compared to  $17.3 \pm 0.5 \mu g/m^3$  for the 470 children in consistently nonsmoking households (Figure 7-19). Among the 614 exposed



**Figure 7-19. Distribution of numbers of children living in households with varying respirable particulate matter ( $\text{PM}_{2.5}$ ) as a function of parental smoking status.**

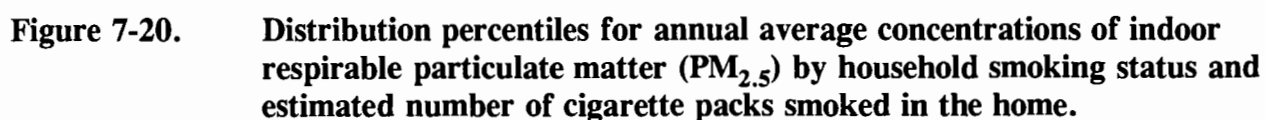
Source: Neas et al. (1995).

1 children for whom complete information on smoking consumption was available, 36% were  
2 exposed to less than one-half pack daily, 40% to between 1/2 and 1 pack daily, and 25% to  
3 > 1 pack daily. The distribution of household concentrations for children in these smoking  
4 categories is shown in Figure 7-20. (The authors stated that the estimated number of  
5 cigarette packs smoked daily in the home was "highly predictive" of the annual average  
6  $PM_{2.5}$  concentration, but did not provide the results of any tests for significance.

7 Spengler et al. (1985) reported on the Kingston-Harriman (TN) portion of the 6-city  
8 study. An initial study design meant to compare exposures among individuals categorized by  
9 residence (Kingston or Harriman), ETS exposure, and occupational status (office worker,  
1 blue collar, or nonworking) was abandoned due to poor response rates of 30%; the sample  
2 was filled out with volunteers and thus cannot be extrapolated to the population of the two  
3 towns. 101 participants took part, with 28 having cigarette smoke exposure at home. Each  
4 participant had an indoor and personal monitor with cutpoints of  $3.5 \mu m$ . Each town had a  
5 centrally located outdoor dichotomous sampler providing two size fractions, with cutpoints of  
6  $2.5 \mu m$  and  $15 \mu m$ . Both towns had similar outdoor  $PM_{2.5}$  concentrations of  $18 \mu g/m^3$ , so  
7 the values were pooled for subsequent analyses. Indoor concentrations averaged  $42 \pm$   
8  $2.6$  (SE)  $\mu g/m^3$ . Indoor values in homes with smoking averaged  $74 \pm 6.6 \mu g/m^3$ , compared  
9 to  $28 \pm 1.1 \mu g/m^3$  in homes without smoking ( $p < 0.0001$ ). No difference in exposure  
10 between the unemployed and employed population was noted.

11 Lebret et al. (1987) reported on the Watertown MA portion of the Harvard 6-city  
12 study. 265 homes were monitored for two one-week periods. Homes with smoking  
13 averaged  $54 \mu g/m^3$  ( $N = 147$  and  $152$  during weeks 1 and 2), while homes without smoking  
14 averaged  $21.6 \mu g/m^3$  ( $N = 70$  and  $74$ ). The effect of smoking one cigarette/day was  
15 estimated at  $0.8 \mu g/m^3$  of  $PM_{2.5}$ .

16 Spengler et al. (1987) reported on a new round of measurements in three communities  
17 within the 6-city study. In each community, about 300 children are selected to take part in a  
18 year-long diary and indoor air quality study. Measurements of  $PM_{2.5}$  were taken indoors at  
19 home for two consecutive weeks in winter and again in summer. The sampler was the  
20 automated Harvard sampler, which collected an integrated sample for the week except for the  
21 8 a.m. to 4 p.m. weekday period when the child was at school. During this 40-h period,  
22 samples were taken in one classroom in each of the elementary schools involved. The three



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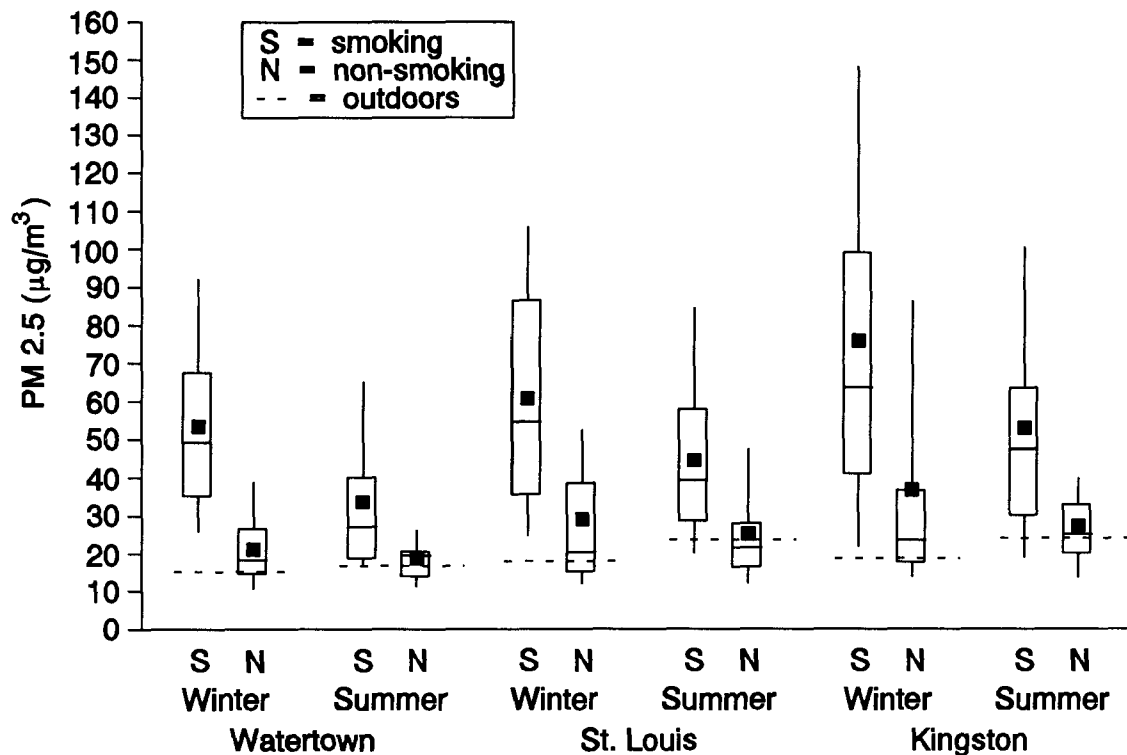


1 communities were Watertown, MA, St. Louis, MO., and Kingston-Harriman, TN. Results  
2 were presented for smoking and non-smoking homes in each city by season (Figure 7-21);  
3 the authors noted that mean concentrations in homes with smokers were about  $30 \mu\text{g}/\text{m}^3$   
4 greater than homes without smokers. The difference was greater in winter than in summer in  
5 all cities.

6 Santanam et al. (1990) reported on a more recent and larger-scale monitoring effort in  
7 Steubenville and Portage as part of the Harvard 6-city study; 140 homes in each city were  
8 monitored for one week in summer and in winter. The Harvard impactor sampler was used  
9 with an automatic time unit to collect  $\text{PM}_{2.5}$  samples between 4 p.m. and 8 a.m. on  
10 weekdays and all day on weekends, corresponding to likely times of occupancy for school-  
11 age children. Outdoor samples were collected from one site in each city. Elements were  
12 determined by XRF. A source apportionment using principal components analysis (PCA)  
13 and linear regressions on the elemental data was carried out. Cigarette smoking was the  
14 single largest source, accounting for 20 to  $27 \mu\text{g}/\text{m}^3$  indoor  $\text{PM}_{2.5}$  in Steubenville and 10 to  
15  $25 \mu\text{g}/\text{m}^3$  in Portage (Table 7-10); unfortunately, the authors do not state the number of  
16 homes in the smoking and nonsmoking categories. Wood smoke was estimated to account  
17 for about  $4 \mu\text{g}/\text{m}^3$  indoors and outdoors in Steubenville in winter, but only for about  $1 \mu\text{g}/\text{m}^3$   
18 indoors and outdoors in Portage. Sulfur-related sources accounted for 8 to  $9 \mu\text{g}/\text{m}^3$  indoors  
19 and  $16 \mu\text{g}/\text{m}^3$  outdoors in Steubenville in the summer, but were apparently not important in  
20 winter. Auto-related sources accounted for 2 to  $5 \mu\text{g}/\text{m}^3$  in the two cities. Surprisingly, soil  
21 sources accounted for only about 1 to  $3 \mu\text{g}/\text{m}^3$  indoor and outdoor  $\text{PM}_{2.5}$  concentrations.  
22 Nonsmoking homes in both cities had indoor mean  $\text{PM}_{2.5}$  concentrations very close to the  
23 outdoor mean concentrations (ratios of 1.00 and 1.04 in Steubenville, 1.02 and 1.4 in  
24 Portage). Homes with smokers exceeded outdoor levels by 25 and  $20 \mu\text{g}/\text{m}^3$  in Steubenville,  
25 and 24 and  $11 \mu\text{g}/\text{m}^3$  in Portage.

### 26 *The New York State ERDA Study*

27 Sheldon et al. (1989) studied  $\text{PM}_{2.5}$  and other pollutants in 433 homes in two New  
28 York State counties. One goal of the study was to determine the effect of kerosene heaters,  
29 gas stoves, wood stoves or fireplaces, and cigarette smoking on indoor concentrations of  
30



**Figure 7-21. PM<sub>2.5</sub> (µg/m<sup>3</sup>) in smoking (S) and non-smoking (N) homes in three of the Harvard Six-City Study sites.**

Source: Spengler et al. (1987).

combustion products. A stratified design to include all 16 combinations of the four combustion sources was implemented, requiring about 22,000 telephone calls.

The sampler was a portable dual-nozzle impactor developed at Harvard University. Two oiled impactor plates in series were employed to reduce the probability that some particles larger than 2.5 µm would reach the filter. Samples were collected in the main living area and in one other room (containing a combustion source if possible) using a solenoid switch to collect alternate 15-min samples over a 7-day period. Outdoor samples were collected at a subset of 57 homes. All samples were collected during the winter (January to April) of 1986.

PM<sub>2.5</sub> mean concentrations indoors were approximately double those outdoors in both counties (Table 7-11). Of the four combustion sources, only smoking created significantly higher indoor PM<sub>2.5</sub> concentrations in both counties (Table 7-12). Use of kerosene heaters was associated with significantly higher concentrations in Suffolk (N = 22) but not in

**TABLE 7-10a. RECONSTRUCTED SOURCE CONTRIBUTIONS TO PM<sub>2.5</sub>  
MASS FOR STEUBENVILLE**

Source	WINTER			SUMMER		
	Smokers' homes	Non-smokers' homes	Outdoor site	Smokers' homes	Non-Smokers' homes	Outdoor site
Soil	7.9 (3.45)	17.6 (3.45)	9.6 (1.79)	NA	NA	NA
Wood smoke	9.5 (4.15)	21.2 (4.15)	23.0 (4.31)	NA	NA	NA
O.C.-I	10.3 (4.47)	22.9 (4.47)	24.8 (4.65)	NA	NA	NA
Tobacco Smoke	45.6 (19.9)	NA	NA	53.7 (26.8)	NA	NA
Sulfur-related	NA	NA	NA	17.8 (8.90)	33.3 (8.23)	52.5 (15.5)
Auto-related	NA	NA	NA	7.3 (3.65)	14.8 (3.65)	5.3 (1.55)
O.C.-II	NA	NA	NA	8.8 (4.40)	16.5 (4.07)	26.0 (7.67)
Indoor dust	NA	NA	NA	7.4 (3.70)	15.0 (3.70)	NA
Unexplained	26.7 (11.6)	38.3 (7.47)	42.6 (7.95)	5.0 (2.4)	20.4 (5.05)	16.2 (4.78)
Total	100 (43.57)	100 (19.54)	100 (18.7)	100 (49.85)	100 (29.5)	100 (29.5)

**TABLE 7-10b. RECONSTRUCTED SOURCE CONTRIBUTIONS TO PM<sub>2.5</sub>  
MASS FOR PORTAGE**

Source	WINTER			SUMMER		
	Smokers' homes	Non-smokers' homes	Outdoor site	Smokers' homes	Non-Smokers' homes	Outdoor site
Sulfur-related	13.2 (4.56)	30.7 (4.56)	39.2 (4.04)	23.3 (5.80)	38.1 (5.30)	45.8 (6.23)
Auto-related	5.1 (1.78)	12.0 (1.78)	17.3 (1.78)	18.1 (4.50)	29.6 (4.12)	35.6 (4.84)
Soil	3.8 (1.31)	8.8 (1.31)	13.4 (1.38)	7.5 (1.86)	13.4 (1.86)	16.5 (2.25)
Tobacco Smoke	71.0 (24.6)	NA	NA	40.1 (9.99)	NA	NA
Wood smoke	2.7 (0.94)	6.3 (0.94)	13.0 (1.34)	NA	NA	NA
Unexplained	4.2 (1.38)	42.2 (6.23)	17.1 (1.80)	11.0 (2.75)	18.9 (2.62)	2.10 (0.28)
Total	100 (34.6)	100 (14.8)	100 (10.3)	100 (24.9)	100 (13.9)	100 (13.6)

All figures in % ( $\mu\text{g m}^{-3}$ )

O.C.-I: Iron and steel, and auto-related sources.

O.C.-II: Iron and steel, and soil sources.

Source: Santanna et al. (1990)

1 Onondaga (N = 13). Use of wood stoves/fireplaces and gas stoves did not elevate indoor  
2 concentrations in either county.

3 Leaderer et al. (1990) extended the analysis of these data by collapsing the gas stove  
4 category, reducing the number of categories from 16 to 8 (Table 7-13). By inspection of the

**TABLE 7-11. WEIGHTED SUMMARY STATISTICS BY COUNTY FOR  
RESPIRABLE SUSPENDED PARTICULATE (PM<sub>2.5</sub>) CONCENTRATIONS (µg/m<sup>3</sup>)**

	Main Living Area		Outdoors	
	Onondaga	Suffolk	Onondaga	Suffolk
Percent Detected	98.9	99.6	100	100
Sample Size	224	209	37	20
Population Estimate	94,654	286,580		
Arithmetic Mean (µg/m <sup>3</sup> )	36.7 <sup>a</sup>	46.4	16.8	21.8
Arithmetic Standard Error (µg/m <sup>3</sup> )	2.14	2.77	1.00	4.54
Geometric Mean (µg/m <sup>3</sup> )	25.7 <sup>a</sup>	35.9	15.8	18.6
Geometric Standard Error	1.07	1.06	1.06	1.11
Minimum (µg/m <sup>3</sup> )	0.72	2.18	6.32	12.0
Maximum (µg/m <sup>3</sup> )	172	284	28.4	106
Percentiles				
10th	9.93	13.8		
16th	11.2	16.8		
25th	13.5	18.9	12.8	13.6
50th (median)	23.9	33.6	15.1	16.7
75th	48.4	62.8	20.5	22.3
84th	68.0	76.6		
90th	85.2	89.4		
95th	112	112		
99th	136	155		

<sup>a</sup>Significantly different between counties at 0.05 level.

Source: Sheldon et al. 1989.

table, it is clear that smoking was the single most powerful source of indoor fine particles, with geometric means ranging from 28.5 to 61.4 µg/m<sup>3</sup>, whereas the four nonsmoking categories ranged from 14.1 to 22.0 µg/m<sup>3</sup>.

Leaderer and Hammond (1991) continued their analysis of the New York State data by selecting a subset of 96 homes for which both nicotine and PM<sub>2.5</sub> data were obtained. In the 47 homes in which nicotine was detected (detection limit = 0.1 µg/m<sup>3</sup>), the mean concentration of RSP was 44.1 (± 25.9 SD) µg/m<sup>3</sup> compared to 15.2 (± 7.4) µg/m<sup>3</sup> in the 49 homes where no nicotine was detected. Thus homes with smoking had an increased weekly geometric mean PM<sub>2.5</sub> concentration of about 29 µg/m<sup>3</sup>. Imperfect agreement with reported smoking was observed, with nicotine being measured in 13% of the residences that reported no smoking, while nicotine was not detected in 28% of the residences that reported

**TABLE 7-12. WEIGHTED ANALYSIS OF VARIANCE OF RESPIRABLE  
SUSPENDED PARTICULATE (PM<sub>2.5</sub>) CONCENTRATIONS (µg/m<sup>3</sup>) IN THE MAIN  
LIVING AREA OF HOMES VERSUS SOURCE CLASSIFICATION**

	F Value	Probability	Coefficient
<b>Onondaga</b>			
Model	20.5	0.00	
Independent Variables:			
Intercept			20.3
Gas Stove	1.87	0.17	5.25
Kerosene Heater	1.06	0.30	5.05
Tobacco	81.6	0.00	45.1
Wood Stove/Fireplace	2.42	0.12	7.81
$R^2 = 0.17$			
<b>Suffolk</b>			
Model	36.9	0.00	
Independent Variables:			
Intercept			26.1
Gas Stove	0.13	0.72	-1.52
Kerosene Heater	12.0	0.00	30.1
Tobacco	114	0.00	46.8
Wood Stove/Fireplace	0.71	0.40	9.88
$R^2 = 0.21$			

Source: Sheldon et al. 1989.

**TABLE 7-13. RESPIRABLE SUSPENDED PARTICULATE CONCENTRATION  
(µg/m<sup>3</sup>)**

Source	Suffolk			Onondaga		
	N	Mean	Standard	N	Mean	Standard
None	30	17.3	1.7	45	14.1	1.7
W	15	18.1	1.6	16	19.1	1.7
K	7	22.0	1.6	4	21.2	1.0
S	61	49.3	1.8	80	36.5	2.4
KW				4	19.7	1.5
SW	29	38.0	1.8	31	33.9	2.2
SK	23	61.4	2.0	4	35.3	1.5
SKW	6	30.3	1.4	4	28.5	1.6
Outdoor	19	16.9	1.3	36	15.8	1.5

Abbreviations: W = woodstove; K = kerosene heater; S = smoking.

Source: Leaderer et al. 1990.

1 smoking. A regression of  $PM_{2.5}$  on total number of cigarettes smoked during the week (T)  
2 gave the result:

$$PM_{2.5} = 17.7 + 0.322T \text{ (N = 96; } R^2 = 0.55\text{)}$$

5 For the homes with measured nicotine, the regression gave the result:

$$PM_{2.5} = 24.8 + 0.272T \text{ (N = 47; } R^2 = 0.40\text{)}$$

9 Thus each cigarette produces about a  $0.3 (\pm 0.03) \mu\text{g}/\text{m}^3$  increase in the weekly mean  $PM_{2.5}$   
10 concentration, equivalent to a  $2.1 (\pm 0.2) \mu\text{g}/\text{m}^3$  increase in the daily concentration.

11 Koutrakis et al. (1992) also analyzed the New York State data, using a mass-balance  
12 model to estimate  $PM_{2.5}$  and elemental source strengths for cigarettes, wood burning stoves,  
13 and kerosene heaters. Homes with cigar or pipe smoking and fireplace use were eliminated,  
14 resulting in 178 indoor air samples.  $PM_{2.5}$  source strength for smoking was estimated at  
15  $12.7 \pm 0.8$  (SE) mg/cigarette;  $PM_{2.5}$  source strengths could not be estimated for wood  
16 burning or kerosene heater usage, but only 7 homes in each category were available for  
17 analysis. For a final category of all other residual indoor sources, a source strength of  
18  $1.16 \text{ mg/h}$  was calculated. For nonsource homes (N = 49) the authors estimated that 60%  
19 ( $9 \mu\text{g}/\text{m}^3$ ) of the total  $PM_{2.5}$  mass was from outdoor sources, and 40% ( $6 \mu\text{g}/\text{m}^3$ ) from  
20 unidentified indoor sources. For smoking homes, they estimated that 54% ( $26 \mu\text{g}/\text{m}^3$ ) of the  
21  $PM_{2.5}$  mass was from smoking, 30% ( $15 \mu\text{g}/\text{m}^3$ ) from outdoor sources, and 16% ( $8 \mu\text{g}/\text{m}^3$ )  
22 from unidentified sources. These authors also developed an elemental emissions profile for  
23 cigarettes, woodburning, and kerosene heaters. For cigarettes, the elemental profile included  
24 potassium ( $160 \mu\text{g}/\text{cig}$ ), chlorine ( $69 \mu\text{g}/\text{cig}$ ), and sulfur ( $65 \mu\text{g}/\text{cig}$ ), as well as smaller  
25 amounts of bromine, cadmium, vanadium, and zinc. The woodburning profile included three  
26 elements: potassium ( $92 \mu\text{g}/\text{h}$ ), silicon ( $44 \mu\text{g}/\text{h}$ ) and calcium ( $38 \mu\text{g}/\text{h}$ ). The kerosene heater  
27 profile included a major contribution from sulfur ( $1500 \mu\text{g}/\text{h}$ ) and fairly large inputs of  
28 silicon ( $195 \mu\text{g}/\text{h}$ ) and potassium ( $164 \mu\text{g}/\text{h}$ ). A drawback of the mass-balance model was an  
29 inability to separately estimate the value of the penetration coefficient  $P$  and the decay rate  
30  $k$  for particles and elements; Koutrakis et al. (1992) assumed a constant rate of  $0.36 \text{ h}^{-1}$  for  
31  $k$ , and then solved for  $P$ .

### *The EPA Particle TEAM (PTEAM) Study*

The EPA sponsored a study of personal, indoor, and outdoor concentrations of  $PM_{10}$  particles, and indoor and outdoor concentrations of  $PM_{2.5}$  particles in Riverside, CA (Pellizzari et al., 1993a,b; Clayton et al., 1993; Thomas et al., 1993). The personal exposure results of this study are discussed in Section 7.3.3. The main goal of the study was to estimate the frequency distribution of exposures to  $PM_{10}$  particles for all nonsmoking Riverside residents aged 10 and above. 178 households were selected using probability sampling to represent about 61,000 households throughout most of the City of Riverside. Homes were sampled at the rate of four per day between Sept. 22 and Nov. 9, 1990. Each home had two 12-h samples for both size fractions. A central site operated throughout the 48 days of the study, producing 96 12-h samples collected by side-by-side reference samplers (dichotomous samplers and modified hi-volume samplers) along with the low-flow (4 Lpm) impactor designed for this study. The impactors had very sharp cutpoints at 2.5 and 11  $\mu m$ . A second filter treated with citric acid to collect nicotine was placed behind the main Teflon filter.

A subset of the homes was monitored for PAHs (Sheldon et al., 1992). 125 homes were monitored indoors and 65 of those were monitored outdoors for two consecutive 12-h periods using a 20 lpm pump with an XAD cartridge.

Precision of the three types of particle samplers at the central site was excellent, with median RSDs of about 4 to 5% (Wallace, 1991a). The low-flow sampler was noted to produce estimates about 12% greater than the dichotomous sampler, which in turn was about 7% greater than the hi-vol sampler (Wallace, 1991b). Part of the difference may be due to the different cutpoints, which are estimated to be 11  $\mu m$  for the new sampler, 9.5 for the dichot, and 9.0 for the hi-vol. Part of the difference may also be due to particle bounce (large particles bouncing off the impactor and being reentrained in the flow to the filter), such that the  $PM_{2.5}$  and  $PM_{10}$  fractions in the low-flow sampler may be contaminated with a small number of larger-size particles; however, particle bounce was found in laboratory tests to account for less than 7% of the total mass.

The population-weighted distributions of personal, indoor, and outdoor particle concentrations are provided in Table 7-14.  $PM_{10}$  mean concentrations ( $150 \mu g/m^3$ ) were more than 50% higher than either indoor or outdoor levels ( $95 \mu g/m^3$ ). Overnight mean

**TABLE 7-14. WEIGHTED DISTRIBUTIONS OF PERSONAL, INDOOR, AND  
OUTDOOR<sup>a</sup> PARTICLE CONCENTRATIONS ( $\mu\text{g}/\text{m}^3$ )**

	DAYTIME					NIGHTTIME				
	PM <sub>2.5</sub>		PM <sub>10</sub>			PM <sub>2.5</sub>		PM <sub>10</sub>		
	SAM	SIM	SAM	SIM	PEM	SAM	SIM	SAM	SIM	PEM
Sample Size	167	173	165	169	171	161	166	162	163	168
Minimum	7.4	2.8	16.2	16.6	35.1	3.4	2.9	13.6	14.1	19.1
Maximum	187.8	238.3	506.6	512.8	454.8	164.2	133.3	222.9	180.3	278.3
Mean	48.9	48.2	94.9	94.7	149.8	50.5	36.2	86.3	62.7	76.8
(Std. Error)	(3.5)	(4.1)	(5.5)	(5.7)	(9.2)	(3.7)	(2.2)	(4.4)	(3.2)	(3.5)
Geometric Mean	37.7	35.0	82.7	78.2	128.7	37.2	26.7	74.5	53.1	67.9
(Std. Error)	(2.5)	(3.3)	(4.1)	(5.0)	(8.5)	(3.1)	(1.9)	(4.0)	(3.1)	(3.1)
Std. Deviation	37.6	41.2	57.2	61.4	84.3	40.3	29.5	47.7	37.4	39.7
Geometric Std. Deviation <sup>b</sup>	2.07	2.25	1.68	1.88	1.75	2.23	2.21	1.74	1.78	1.64
Percentiles										
10th	14.9	11.5	42.8	30.9	59.9	14.5	10.0	39.3	25.2	36.6
25th	23.4	19.3	56.9	49.5	86.1	23.0	14.8	53.6	33.5	48.1
50th (median)	35.5	33.5	84.1	81.7	129.7	35.0	25.9	74.1	51.6	66.2
75th	60.1	61.5	110.8	127.2	189.1	64.9	48.9	103.7	84.8	98.8
90th	102.2	101.0	157.2	180.7	263.1	120.7	82.7	167.8	116.9	135.0
Std. Errors of Percentiles										
10th	1.6	3.4	2.3	3.4	4.0	2.1	0.9	7.4	1.5	1.5
25th	2.1	1.4	4.5	4.3	9.4	2.7	1.3	3.4	2.4	3.1
50th	4.0	4.5	4.7	8.3	7.5	2.4	2.4	4.8	3.5	4.3
75th	3.9	3.3	4.0	9.4	10.8	4.6	5.3	5.1	4.7	8.2
90th	4.6	6.7	7.2	11.0	12.0	5.8	5.8	4.3	5.3	10.1

<sup>a</sup>Statistics other than the sample size, minimum, and maximum are calculated using weighted data; they provide estimates for the target population of person-days (PEM) or of household-days (SIM, SAM).

<sup>b</sup>In contrast to the other statistics, the gsd is a unitless quantity.



personal PM<sub>10</sub> concentrations (77 µg/m<sup>3</sup>) were similar to the indoor (63 µg/m<sup>3</sup>) and outdoor (86 µg/m<sup>3</sup>) levels. The reason for the higher daytime personal exposures is not completely understood; it may be due to the fact that the person is often close to the source of particles, such as cooking, dusting, or vacuuming. It may also be due to re-entrainment of household dust. It appears not to be due to skin flakes or clothing fibers; many skin flakes were found on filters but their mass does not appear to account for more than 10% of the excess personal exposure (Mamane 1992).

Mean PM<sub>2.5</sub> daytime concentrations were similar indoors (48 µg/m<sup>3</sup>) and outdoors (49 µg/m<sup>3</sup>), but indoor concentrations fell off during the sleeping period (36 µg/m<sup>3</sup>) compared to 50 µg/m<sup>3</sup> outdoors. Thus the fine particle contribution to PM<sub>10</sub> concentrations averaged about 51% during the day and 58% at night both indoors and outdoors. The distributions of these ratios are provided in Table 7-15.

**TABLE 7-15. WEIGHTED DISTRIBUTIONS<sup>a</sup> OF PM<sub>2.5</sub>/PM<sub>10</sub> CONCENTRATION RATIO**

	DAYTIME		NIGHTTIME	
	Outdoor	Indoor	Outdoor	Indoor
Sample Size	160	167	154	160
Mean	0.470	0.492	0.522	0.550
(Std. Error)	(0.016)	(0.021)	(0.017)	(0.014)
Geometric Mean	0.444	0.455	0.497	0.517
(Std. Error)	(0.017)	(0.022)	(0.019)	(0.016)
Percentiles				
10th	0.274	0.250	0.308	0.301
25th	0.371	0.347	0.406	0.440
50th (median)	0.469	0.498	0.515	0.556
75th	0.571	0.607	0.646	0.694
90th	0.671	0.735	0.731	0.771
Std. Errors of Percentiles				
10th	0.018	0.030	0.023	0.023
25th	0.018	0.046	0.028	0.017
50th	0.015	0.020	0.022	0.015
75th	0.019	0.024	0.027	0.023
90th	0.012	0.028	0.016	0.012

<sup>a</sup>Statistics other than sample size are calculated using weighted data; they provide estimates for the target population of household-days.

Unweighted distributions are displayed in Figures 7-22 and 7-23 for 24-h average  $PM_{10}$  and  $PM_{2.5}$  personal, indoor, and outdoor concentrations. Most of the distributions were not significantly different from log-normal distributions, as determined by a chi-square test. About 25% of the population of Riverside was estimated to have 24-h personal  $PM_{10}$  exposures exceeding the  $150 \mu g/m^3$  24-h NAAQS for ambient air.

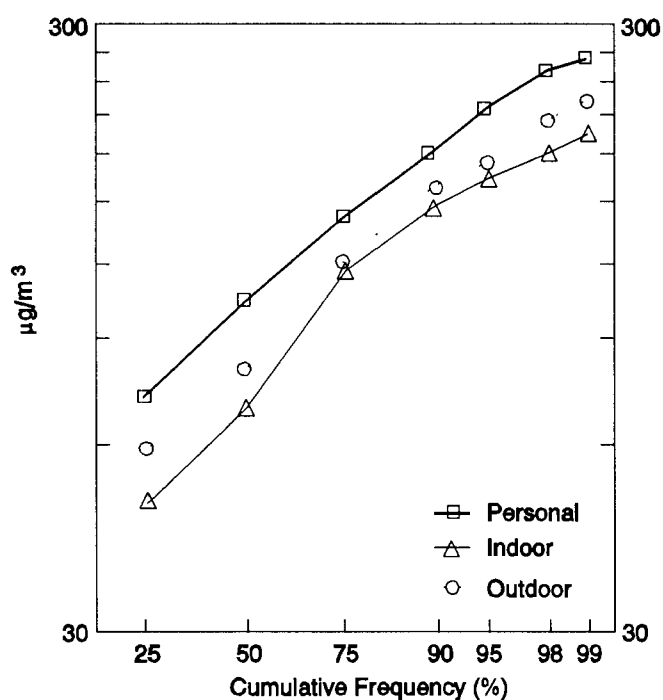
The 48-day sequence of outdoor  $PM_{10}$  and  $PM_{2.5}$  concentrations is shown in Figure 7-24 (Wallace et al., 1991a). At least two extended episodes of high fine-particle concentrations occurred. Also about 6 days of high Santa Ana winds, with correspondingly high coarse-particle concentrations from desert sand, were observed.

Central-site  $PM_{2.5}$  and  $PM_{10}$  concentrations agreed well with back yard concentrations. Pearson correlations of the log-transformed data were 0.96 and 0.92 for overnight and daytime  $PM_{2.5}$ , and 0.93 for the overnight  $PM_{10}$  values (Özkaynak et al., 1993). The correlation dropped to 0.64 for the daytime  $PM_{10}$  values; however on this day two homes in one part of Riverside showed very high outdoor concentrations of 380 and  $500 \mu g/m^3$  while two homes in another part of Riverside and the central-site monitor showed more typical concentrations. It is believed that a local event produced the higher concentrations at those two homes. If they are removed from the data set, the correlation improves to 0.90. This suggests that a single central-site monitor can represent well the  $PM_{2.5}$  and  $PM_{10}$  concentrations throughout a wider area such as a town or small city, at least in the Los Angeles basin.

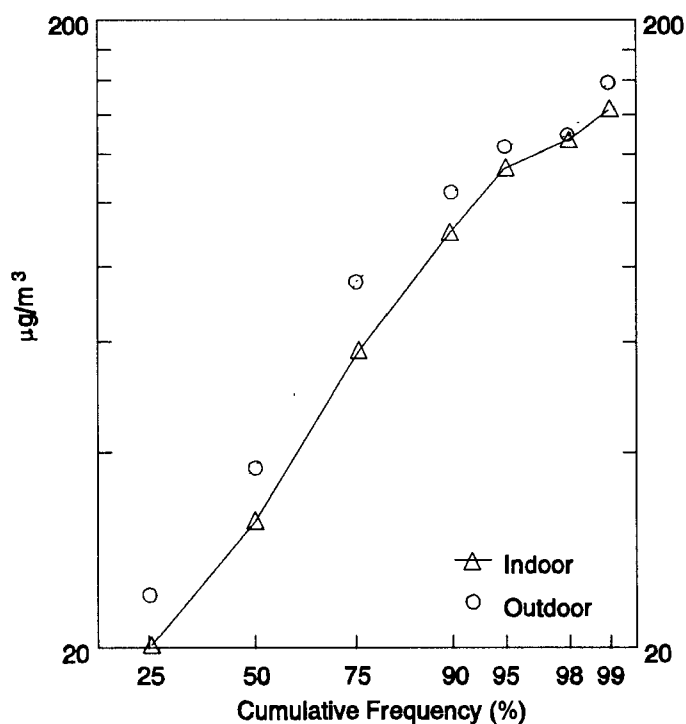
Daytime indoor  $PM_{10}$  and  $PM_{2.5}$  concentrations showed low-to-moderate Pearson correlations of 0.46 and 0.55, respectively, with outdoor concentrations ( $N = 158$  to  $173$ ). At night, the correlations improved somewhat to 0.65 and 0.61, respectively ( $N = 50$  to  $168$ ). Outdoor  $PM_{10}$  concentrations explained about 27% of the variance of indoor levels (Figure 7-25).

Simple regressions of outdoor on indoor  $PM_{10}$  and  $PM_{2.5}$  resulted in the following equations:

$$\begin{array}{ll} \text{Indoor } PM_{10} = 51 + 0.49 \times \text{Outdoor } PM_{10} \text{ (day)} & R^2 = 0.20 \\ \text{Indoor } PM_{10} = 20 + 0.51 \times \text{Outdoor } PM_{10} \text{ (night)} & R^2 = 0.41 \\ \text{Indoor } PM_{2.5} = 10 + 0.81 \times \text{Outdoor } PM_{2.5} \text{ (day)} & R^2 = 0.49 \\ \text{Indoor } PM_{2.5} = 9 + 0.56 \times \text{Outdoor } PM_{2.5} \text{ (night)} & R^2 = 0.55 \end{array}$$



**Figure 7-22. Cumulative frequency distribution of 24-h personal, indoor, and outdoor PM<sub>10</sub> concentrations in Riverside, CA.**



**Figure 7-23. Cumulative frequency distribution of 24-h indoor and outdoor PM<sub>2.5</sub> concentrations in Riverside, CA.**

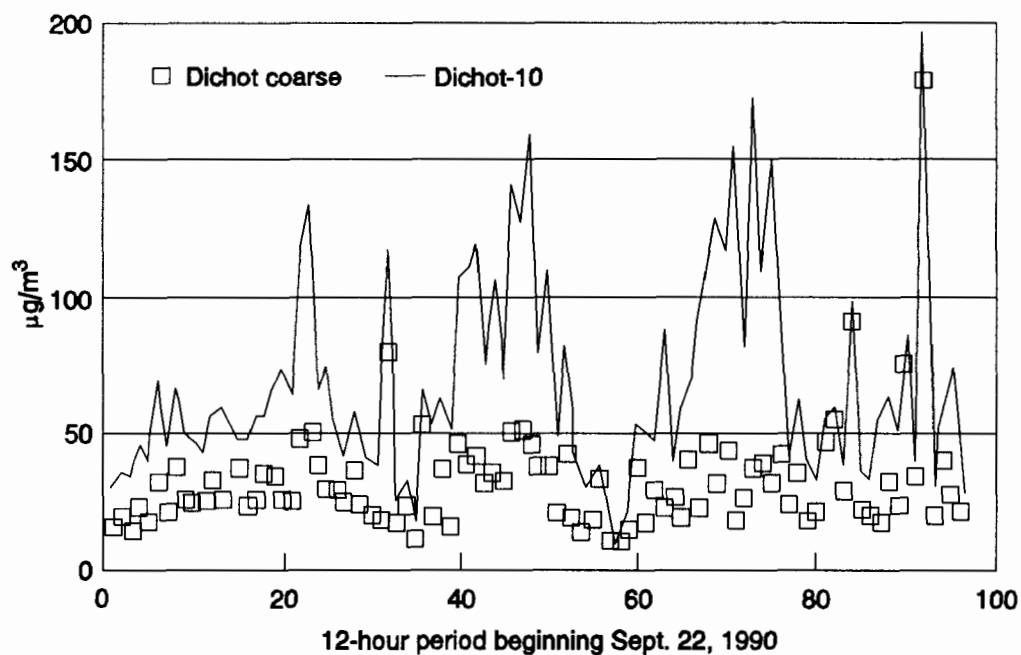


Figure 7-24. Forty eight day sequence of  $PM_{10}$  and  $PM_{2.5}$  in Riverside, CA, PTEAM study.

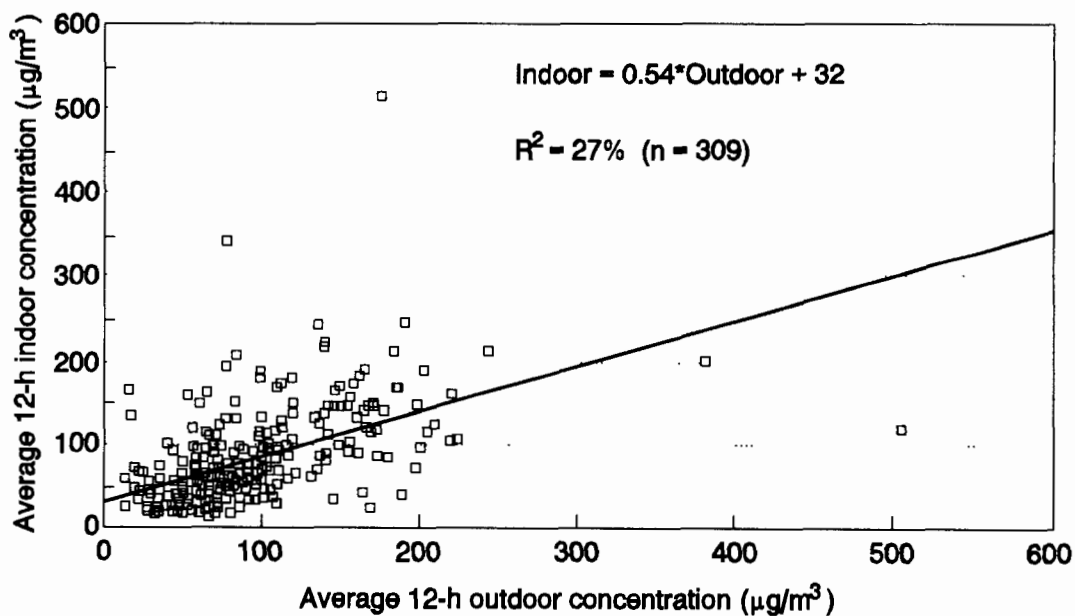


Figure 7-25. Average indoor and outdoor 12-h concentrations of  $PM_{10}$  during the PTEAM study in Riverside, CA.

Source: Özkaynak et al. (1993).

Stepwise regressions resulted in smoking, cooking, and either air exchange rates or house volumes being added to outdoor concentrations as significant variables (Table 7-16). Homes with smoking added about 27 to 32  $\mu\text{g}/\text{m}^3$  to the total  $\text{PM}_{2.5}$  concentrations and about 29 to 37  $\mu\text{g}/\text{m}^3$  to the  $\text{PM}_{10}$  values. Cooking added 13 to 26  $\mu\text{g}/\text{m}^3$  to the daytime  $\text{PM}_{10}$  concentration and about 13  $\mu\text{g}/\text{m}^3$  to the daytime  $\text{PM}_{2.5}$  concentration, but was not significant during the overnight period. At night, air exchange added about 4.5  $\mu\text{g}/\text{m}^3$  to the  $\text{PM}_{2.5}$  concentration per unit increase (in air changes per hour) and about 12  $\mu\text{g}/\text{m}^3$  to the  $\text{PM}_{10}$  concentration, but was not significant during the day. By contrast, the house volume was not significant at night, but was significant during the day, with larger homes resulting in smaller PM concentrations.

**TABLE 7-16. STEPWISE REGRESSION RESULTS FOR INDOOR AIR CONCENTRATIONS OF  $\text{PM}_{10}$ ,  $\text{PM}_{2.5}$ , AND NICOTINE: COEFFICIENTS (STANDARD ERRORS OF ESTIMATES)**

Variable	$\text{PM}_{10}$			$\text{PM}_{2.5}$			Nicotine		
	All	Day	Night	All	Day	Night	All	Day	Night
N	310	158	147	324	156	149	222	93	109
R <sup>2</sup>	41%	39%	58%	55%	53%	71%	34%	28%	35%
Intercept		57 (21)			21 (7.8)				0.28 (0.07)
Outdoor air	0.52 (0.05)	0.66 (0.09)	0.45 (0.05)	0.64 (0.04)	0.71 (0.07)	0.53 (0.04)			
Smoking <sup>a</sup>	37 (6)	29 (8)	38 (11)	28 (3.5)	27 (7)	32 (10)	1.1 (0.1)	1.1 (0.3)	1.0 (0.3)
No. cigarettes <sup>b</sup>	3.2 (0.7)	3.0 (1.0)	3.9 (0.9)	2.5 (0.4)	2.4 (0.6)	4.0 (0.6)	0.11 (0.01)	0.1 (0.03)	0.2 (0.06)
Cooking <sup>c</sup>	20 (5)	26 (9)	12 (5)	9.4 (2.9)	13 (5)				
Air exchange	5.2 (2.0)		12 (5)			4.5 (2)			
House volume <sup>d</sup>	-0.08 (0.02)	-2.7 (1)			-2.0 (0.6)				

All listed coefficients significantly different from zero at  $p < 0.05$ .

<sup>a</sup>Binary variable: 1 = at least 1 cigarette smoked in home during monitoring period.

<sup>b</sup>This variable was interchanged with the smoking variable in alternate regressions to avoid colinearity problems.

<sup>c</sup>Binary variable: 1 = cooking reported for at least 1 min in home during monitoring period.

<sup>d</sup>Volume in thousands of cubic feet.

A model developed by Koutrakis *et al.* (1992) was solved using nonlinear least squares to estimate penetration factors, decay rates, and source strengths for particles and elements from both size fractions in the PTEAM study. In this model, which assumes perfect instantaneous mixing and steady-state conditions throughout each 12-h monitoring period, the indoor concentration of particles or elements is given by

$$\frac{C_{in} = P\alpha C_{out} + Q_{is}/V}{\alpha + k} \quad (7-5)$$

where

- $C_{in}$  = indoor concentration (ng/m<sup>3</sup> for elements, µg/m<sup>3</sup> for particles)
- $P$  = penetration coefficient
- $\alpha$  = air exchange rate (h<sup>-1</sup>)
- $C_{out}$  = outdoor concentration (ng/m<sup>3</sup> or µg/m<sup>3</sup>)
- $Q_{is}$  = mass flux generated by indoor sources (ng/h or µg/h)
- $V$  = volume of room or house (m<sup>3</sup>)
- $k$  = decay rate due to diffusion or sedimentation (h<sup>-1</sup>)

From initial multivariate analyses, the most important indoor sources appeared to be smoking and cooking. Therefore the indoor source term  $Q_{is}$  was replaced by the following expression:

$$Q_{is} = (N_{cig}S_{cig} + T_{cook}S_{cook})/t + Q_{other} \quad (7-6)$$

where

- $t$  = duration of the monitoring period (h)
- $N_{cig}$  = number of cigarettes smoked during monitoring period
- $S_{cig}$  = mass of elements or particles generated per cigarette smoked (ng/cig or µg/cig)
- $T_{cook}$  = time spent cooking (min) during monitoring period
- $S_{cook}$  = mass of elements or particles generated per hour of cooking (ng/min or µg/min)
- $Q_{other}$  = mass flux of elements or particles from all other indoor sources (ng/h or µg/h)

With these changes, the equation for the indoor concentration due to these indoor sources becomes

$$C_{in} = \frac{P\alpha C_{out}}{\alpha + k} + \frac{N_{cig}S_{cig} + T_{cook}S_{cook}}{(\alpha + k)Vt} + \frac{Q_{other}}{(\alpha + k)V} \quad (7-7)$$

The indoor and outdoor concentrations, number of cigarettes smoked, monitoring duration, time spent cooking, house volumes, and air exchange rates were all measured or recorded. The penetration factor, decay rates, and source strengths for smoking, cooking, and all other indoor sources ( $Q_{other}$ ) were estimated using a nonlinear model (NLIN in SAS software). The Gauss-Newton approximation technique was chosen to regress the residuals onto the partial derivatives of the model with respect to the unknown parameters until the estimates converge. On the first run, the penetration coefficients were allowed to "float" (no requirement was made that they be  $< 1$ ). Since nearly all coefficients came out close to one, a second run was made bounding them from above by one. The NLIN program provides statistical uncertainties (upper and lower 95% confidence intervals) for all parameter estimates. However, it should be noted that these uncertainties assume perfect measurements and are therefore underestimates of the true uncertainties.

Results are presented in Table 7-17 for the combined day and night samples. Penetration factors are very close to unity for nearly all particles and elements. The calculated decay rate for fine particles is  $0.39 \pm 0.16 \text{ h}^{-1}$ , and for  $PM_{10}$  is  $0.65 \pm 0.28 \text{ h}^{-1}$ . Since  $PM_{10}$  contains the  $PM_{2.5}$  fraction, a separate calculation was made for the coarse particles ( $PM_{10}$  to  $PM_{2.5}$ ) with a resulting decay rate of  $1.0 \text{ h}^{-1}$ . Each cigarette emits  $22 \pm 8$  mg of  $PM_{10}$  on average, about two-thirds of which ( $14 \pm 4$  mg) is in the fine fraction. Cooking emits  $4.1 \pm 1.6$  mg/min of inhalable particles, of which about 40% ( $1.7 \pm 0.6$  mg/min) is in the fine fraction. All elements emitted by cooking were limited almost completely to the coarse fraction. Sources other than cooking and smoking emit about  $5.6 \pm 3.1$  mg/h of  $PM_{10}$ , of which only about  $1.1 \text{ mg/h} \pm 1.0$  (20%) is in the fine fraction.

Similar calculations were carried out for day and night samples separately, and for the logarithms of the data as well as the untransformed data, to obtain more information on the sensitivity of the estimates. For  $PM_{10}$ , the lowest estimate of the source strength of the

**TABLE 7-17. PENETRATION FACTORS, DECAY RATES, AND SOURCE STRENGTHS: NONLINEAR ESTIMATES**

VAR	Penetration			Decay Rate (1/h)			S_cook (µg/min)			S_smoke (µg/cig)			Other Sources (µg/h)		
	mean	195	u95	mean	195 <sup>b</sup>	u95	mean	195 <sup>b</sup>	u95	mean	195 <sup>b</sup>	u95	mean	195 <sup>b</sup>	u95
PM <sub>2.5</sub> <sup>a</sup>	1.00	0.89	1.11	0.39	0.22	0.55	1.7	1.0	2.3	13.8	10.2	17.3	1.1	0.0	2.1
Al	1.00	0.95	1.05	0.03	-0.03	0.09	0.9	-1.4	3.1	9.0	-2.5	20.5	3.0	-3.7	9.8
Mn	0.87	0.78	0.95	0.23	0.07	0.38	0.1	-0.1	0.2	0.2	-0.4	0.8	0.5	0.2	0.9
Br	0.90	0.81	0.99	0.28	0.15	0.41	0.1	0.0	0.2	1.9	1.3	2.5	0.6	0.3	0.9
Pb			fail to converge												
Ti			fail to converge												
Cu	1.00	0.56	1.44	1.63	0.38	2.88	0.6	0.0	1.2	3.7	0.2	7.2	3.8	1.4	6.3
Sr	0.97	0.93	1.01	0.07	0.01	0.12	0.0	0.0	0.0	0.1	-0.1	0.2	0.1	0.0	0.2
P	1.00	0.98	1.02	0.04	0.02	0.06	0.1	-0.1	0.3	2.0	1.1	2.9	0.8	0.2	1.3
Si	0.98	0.75	1.20	0.54	0.04	1.05	6.1	-8.6	20.9	14.4	-58.3	87.2	57.3	12.5	102.0
Ca	1.00	0.65	1.35	0.61	-0.02	1.25	11.9	-0.6	24.4	165.6	72.0	259.1	34.1	3.4	64.8
Fe	1.00	0.76	1.24	0.70	0.11	1.29	4.5	-3.3	12.3	23.8	-16.3	63.9	23.8	1.8	45.7
K	1.00	0.81	1.19	0.16	-0.04	0.37	0.0	-4.4	4.4	121.3	85.7	156.9	8.9	-0.5	18.3
S	1.00	0.97	1.03	0.16	0.12	0.19	1.0	-3.9	5.9	27.1	2.4	51.7	4.0	-3.7	11.7
Zn	0.71	0.57	0.86	0.78	0.31	1.25	0.4	-0.5	1.2	2.9	-1.5	7.4	7.5	4.2	10.9
Cl	0.50	0.28	0.72	0.64	0.05	1.24	5.9	0.1	11.6	102.6	54.0	151.2	20.6	7.2	34.0
PM <sub>10</sub> <sup>a</sup>	1.00	0.85	1.15	0.65	0.36	0.93	4.1	2.6	5.7	21.9	13.6	30.2	5.6	2.6	8.7
Al	1.00	0.80	1.20	0.80	0.38	1.21	69.5	16.6	122.4	97.6	-159.0	354.2	154.5	52.0	257.0
Mn	1.00	0.80	1.20	0.69	0.30	1.07	0.9	0.1	1.7	1.1	-2.7	4.9	1.2	-0.2	2.6
Br	1.00	0.90	1.10	0.21	0.11	0.32	0.1	0.0	0.3	1.8	1.2	2.5	0.4	0.1	0.6
Pb	1.00	0.89	1.11	0.14	0.01	0.26	0.0	-0.3	0.3	2.1	0.4	3.9	0.0	-0.6	0.6
Ti	1.00	0.80	1.20	0.60	0.22	0.98	4.0	0.3	7.8	10.0	-8.4	28.4	10.3	2.6	18.1
Cu	0.83	0.62	1.05	0.77	0.18	1.36	0.5	0.0	1.1	3.5	0.4	6.5	3.2	1.3	5.1
Sr	1.00	0.83	1.16	0.62	0.28	0.97	0.3	0.0	0.5	2.6	1.2	3.9	0.9	0.3	1.5
P			fail to converge												
Si	1.00	0.81	1.19	0.62	0.26	0.97	149.3	26.9	271.8	296.4	-293.9	886.6	237.8	16.1	459.6
Ca	1.00	0.68	1.32	0.63	0.06	1.20	118.7	37.3	200.1	800.0	329.0	1271.0	107.6	-27.0	242.3
Fe	1.00	0.80	1.20	0.66	0.26	1.06	46.7	8.5	84.8	73.0	-109.8	255.9	51.5	-15.5	118.5
K	1.00	0.83	1.17	0.46	0.17	0.75	17.6	0.1	35.2	215.7	116.9	314.5	43.6	8.6	78.5
S	1.00	0.96	1.04	0.21	0.17	0.26	6.8	-0.7	14.3	68.0	29.3	106.7	22.7	10.4	34.9
Zn	1.00	0.81	1.19	0.37	0.10	0.64	1.2	-0.2	2.5	4.0	-3.0	11.0	7.4	3.4	11.4
Cl	0.94	0.44	1.43	2.36	0.48	4.24	45.7	17.6	73.9	320.2	107.0	533.4	148.4	49.4	247.4

<sup>a</sup>Mass units in mg for PM<sub>2.5</sub> and PM<sub>10</sub> only.<sup>b</sup>A negative lower confidence interval implies a nonzero mean is not statistically significant.



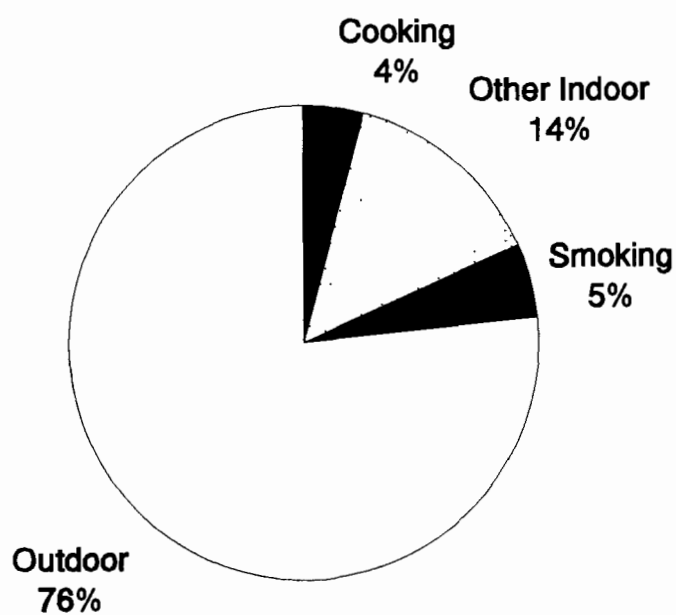
cigarettes was  $9 \pm 4$  mg/cig and the highest estimate was  $29 \pm 7$  mg/cig. The estimates for cooking ranged from a low of  $1.5 \pm 0.6$  mg/min to a high of  $4.9 \pm 1.3$  mg/min. The estimate for other sources ranged from  $2.5 \pm 0.9$  mg/h to  $12 \pm 4$  mg/h.

Decay rates for elements associated with the fine fraction were generally lower than for elements associated with the coarse fraction, as would be expected. For example, sulfur, which has the lowest mass median diameter of all the elements, had calculated decay rates of  $0.16 \pm 0.04$  and  $0.21 \pm 0.04$  h<sup>-1</sup> for the PM<sub>2.5</sub> and PM<sub>10</sub> fractions, respectively. The crustal elements (Ca, Al, Mn, Fe), on the other hand, had decay rates ranging from 0.6 to 0.8 h<sup>-1</sup>.

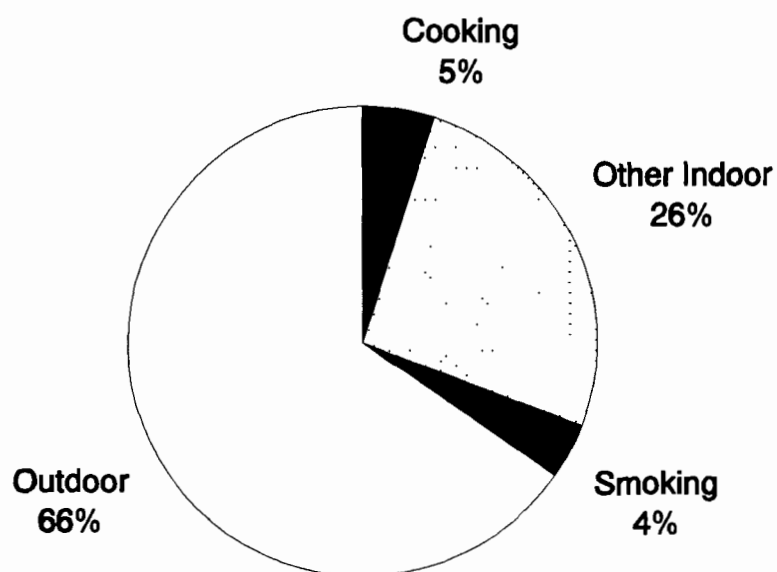
Based on the mass-balance model, outdoor air was the major source of indoor particles, providing about 3/4 of fine particles and 2/3 of inhalable particles in the average home. It was also the major source for most elements, providing 70 to 100% of the observed indoor concentrations for 12 of the 15 elements. Only copper and chlorine were predominantly due to indoor sources in both the fine particle and inhalable particle fractions. It should be noted that these conclusions are applicable only to Riverside, CA. In five of the six cities studied by Harvard and in both New York counties, outdoor air could not have provided as much as half of the indoor air particle mass, because the observed indoor-outdoor ratios of the mean concentrations were  $\geq 2$ .

Unidentified indoor sources accounted for most of the remaining particle and elemental mass collected on the indoor monitors. The nature of these sources is not yet understood. They do not include smoking, other combustion sources, cooking, dusting, vacuuming, spraying, or cleaning, since all these sources together account for less than the unidentified sources. For example, the unidentified sources accounted for 26% of the average indoor PM<sub>10</sub> particles, whereas smoking accounted for 4% and cooking for 5% (Figure 7-26).

Of the identified indoor sources, the two most important were smoking and cooking (Figures 7-27 and 7-28). Smoking was estimated to increase 12-h average indoor concentrations of PM<sub>10</sub> and PM<sub>2.5</sub> by 2 to 4  $\mu\text{g}/\text{m}^3$  per cigarette, respectively. Homes with smokers averaged about 30  $\mu\text{g}/\text{m}^3$  higher levels of PM<sub>10</sub> than homes without smokers. Most of this increase was in the fine fraction. Cooking increased indoor concentrations of PM<sub>10</sub> by about 0.6  $\mu\text{g}/\text{m}^3$  per minute of cooking, with most of the increase in the coarse particles.

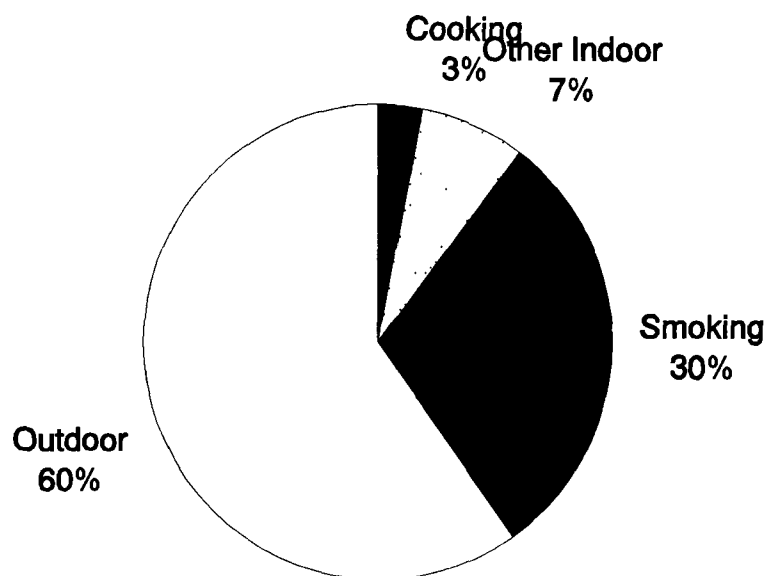


**N = 352 Samples from 178 homes**

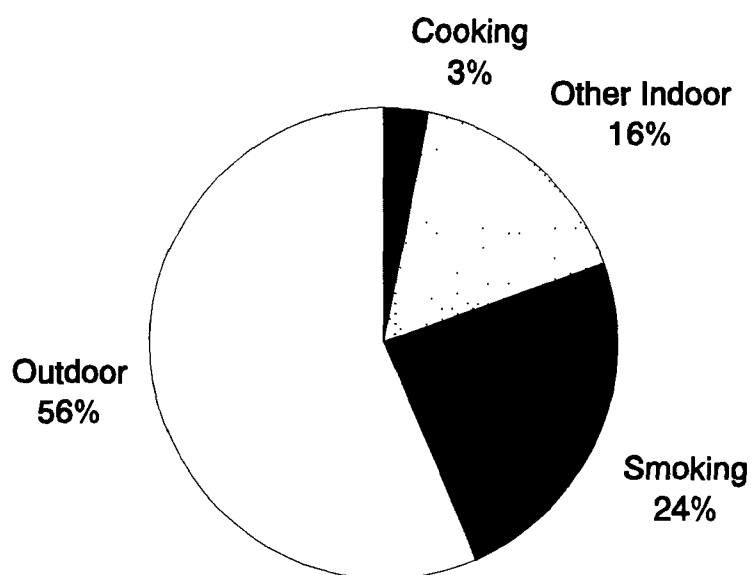


**N = 350 Samples from 178 homes**

**Figure 7-26. Sources of fine particles ( $PM_{2.5}$ ) and respirable particles ( $PM_{10}$ ) in all homes (Riverside, CA).**

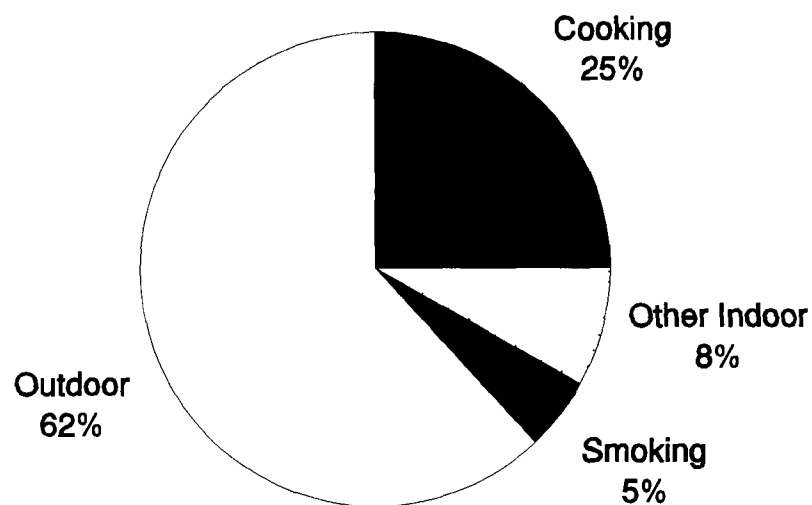


N = 61 Samples from 31 homes

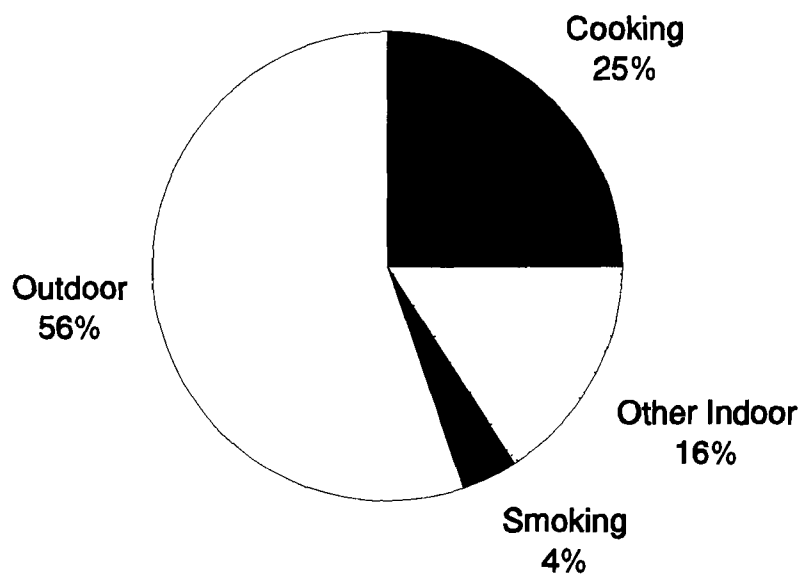


N = 61 Samples from 31 homes

**Figure 7-27. Sources of fine particles ( $PM_{2.5}$ ) and respirable particles ( $PM_{10}$ ) in homes with smokers (Riverside, CA).**



N = 62 Samples from 33 homes



N = 62 Samples from 33 homes

**Figure 7-28. Sources of fine particles ( $PM_{2.5}$ ) and respirable particles ( $PM_{10}$ ), top and bottom panels respectively, for homes with cooking during data collection (Riverside, CA).**

Source: Özykaynak et al. (1993).

1 Emission profiles for elements were obtained for smoking and for cooking. Major  
2 elements emitted by cigarettes were potassium, chlorine, and calcium. Elements associated  
3 with cooking included aluminum, iron, calcium, and chlorine.

4 Other household activities such as vacuuming and dusting appeared to make smaller  
5 contributions to indoor particle levels. An interesting finding was that commuting and  
6 working outside the home resulted in lower particle exposures than for persons staying at  
7 home.

8 As with the particle mass, daytime personal exposures to 14 of 15 elements were  
9 consistently higher than either indoor or outdoor concentrations. At night, levels of the  
10 elements were similar in all three types of samples.

### 11 12 *Comparison of the three large-scale studies*

13 The three studies had somewhat different aims and therefore different study designs.  
14 The Harvard study selected homes based on various criteria, in particular the requirement  
15 that a school-age child be in the home, but did not employ a probability-based study.  
16 Therefore the results strictly apply only to the homes in the sample and not to a wider  
17 population; however, the very large number of homes suggests that the results should be  
18 broadly applicable to homes with school-age children in the six cities. The New York study  
19 used a probability-based sample, but stratified on the basis of combustion sources. Therefore  
20 there are likely to be a higher number of homes with kerosene heaters, wood stoves, and  
21 fireplaces in the sample than in the general population. The PTEAM study used a fully  
22 probability-based procedure, and therefore its results are the most broadly applicable to the  
23 entire population of Riverside households. However, the participants were limited to  
24 nonsmokers, and therefore homes with only smokers were excluded; therefore indoor  
25 concentrations are likely to be slightly underestimated.

26 The three studies employed different monitors with different cutpoints; therefore exact  
27 comparisons are not possible. However, large differences between the  $PM_{3.5}$  and  $PM_{2.5}$   
28 cutpoints are not likely, and therefore these results can be more readily compared. In what  
29 follows, we will use the term "fine particles" to refer to the  $PM_{3.5}$  and  $PM_{2.5}$  size fractions  
30 collected in the three studies.

**Indoor-outdoor relationships.** Outdoor concentrations of fine particles in five of the six cities and the two New York counties were relatively low, typically in the range of 15 to 25  $\mu\text{g}/\text{m}^3$  (Table 7-18). Only Steubenville, with an annual mean of 40  $\mu\text{g}/\text{m}^3$  (but a range among the outdoor sites of 20 to 60  $\mu\text{g}/\text{m}^3$ ) approached the mean outdoor level of 50  $\mu\text{g}/\text{m}^3$  observed in Riverside. It is interesting to note that indoor concentrations exceeded outdoor concentrations in the seven sites with low outdoor levels, (indoor/outdoor ratios were contained in a small range between 1.9 and 2.4), but were slightly less than outdoor concentrations in the two sites with high outdoor levels (ratios of 0.9).

**TABLE 7-18. INDOOR-OUTDOOR MEAN CONCENTRATIONS ( $\mu\text{g}/\text{m}^3$ ) OF FINE PARTICLES IN THREE LARGE-SCALE STUDIES**

Study Name	Homes	Out	In	In/Out
Harvard 6-City Study				
Portage, WI	11	10	20	2.0
Topeka, KN	10	10	22	2.2
Kingston-Harriman, TN	8	18	44	2.4
Watertown, MA	8	15	29	1.9
St. Louis, MO	10	18	42	2.3
Steubenville, OH	8	45	42	0.9
New York State ERDA Study				
Onondaga County	224	17	37	2.2
Suffolk County	209	22	46	2.1
EPA Particle TEAM Study				
Riverside, CA	178	50	43	0.9

Harvard:  $\text{PM}_{3.5}$  measured using cyclone sampler. Samples collected every sixth day for one year (May 1986 to April 1987).

NYS:  $\text{PM}_{2.5}$  measured using impactor developed at Harvard. Samples collected for one week at each household between January and April 1986.

PTEAM:  $\text{PM}_{2.5}$  measured using Marple-Harvard-EPA sampler. Samples collected for two 12-h periods at each home between September and November 1990.

Source: Harvard data—Spengler et al., 1981.

NYS data—Sheldon et al., 1989.

PTEAM data—Pellizzari et al., 1993.

**Effect of smoking.** All three studies found cigarette smoking to be a major source of indoor fine particles. All three studies compared fine particle concentrations in homes with

1 smokers to those in homes without smokers. The annual mean (every sixth day)  
2 concentration in the 35 six-city homes with no smokers was  $24.4 \mu\text{g}/\text{m}^3$ , compared to a  
3 mean of  $36.5 \mu\text{g}/\text{m}^3$  in 15 homes with one smoker and a mean of  $70 \mu\text{g}/\text{m}^3$  in five homes  
4 with two or more smokers. Neas et al. (1990) derived a difference of  $31.2 \mu\text{g}/\text{m}^3$  in  
5 smoking homes compared to nonsmoking homes based on all 1237 homes in Phase II of the  
6 6-City Study. In the New York State study, 62 Onondaga homes with smokers had a mean  
7 indoor  $\text{PM}_{2.5}$  concentration of  $69 \mu\text{g}/\text{m}^3$  compared to  $24 \mu\text{g}/\text{m}^3$  in 182 nonsmoking homes;  
8 the indoor value in 80 Suffolk homes with smokers was  $76 \mu\text{g}/\text{m}^3$  compared to  $30 \mu\text{g}/\text{m}^3$  in  
9 129 homes without smokers. Thus homes with smokers had  $\text{PM}_{2.5}$  weekly mean increases of  
10 about 45 to  $46 \mu\text{g}/\text{m}^3$ . A similar calculation was done for the PTEAM Study, resulting in a  
11 mean of  $36 \mu\text{g}/\text{m}^3$  in 119 homes with no smokers,  $63 \mu\text{g}/\text{m}^3$  in 18 homes with one smoker  
12 and at least one cigarette smoked during the 24-h monitoring period, and  $69 \mu\text{g}/\text{m}^3$  in 15  
13 homes with two or more smokers and at least one cigarette smoked during the monitoring  
14 period. The latter result is somewhat muddled by the fact that outdoor concentrations were  
15 somewhat higher at the homes with smokers (about  $60 \mu\text{g}/\text{m}^3$  in 33 homes with smokers and  
16 only  $49 \mu\text{g}/\text{m}^3$  in 119 homes without smokers). Thus homes with smokers were about 20  
17  $\mu\text{g}/\text{m}^3$  higher (after allowing for higher outdoor concentrations) than homes without smokers.  
18 A similar correction for outdoor concentrations cannot be made in the New York State study,  
19 due to the lack of sufficient matched outdoor measurements. These bivariate calculations are  
20 not highly trustworthy, since they assume that all other sources affecting indoor air are  
21 independent of smoking status, which may not be the case. For example, smokers are more  
22 likely to be found in the lower socioeconomic brackets. Therefore they may have smaller  
23 homes, which would lead to higher indoor concentrations in general. They may also be  
24 located in less desirable (more polluted) parts of town, which would lead to higher outdoor  
25 concentrations, as was observed in the PTEAM Study. This would lead to overestimates of  
26 the effect of smoking on indoor concentrations. On the other hand, persons in homes with  
27 smokers may open windows or otherwise ventilate more extensively to reduce perceived  
28 smoke or particle loadings. This would lead to underestimates of the effect of smoking.  
29 Therefore multivariate regressions accounting for the effect of volume, air exchange, and  
30 outdoor concentrations are more trustworthy than the above bivariate calculations.

1 Multivariate calculations in all three studies result in rather similar estimates of the  
2 effect of smoking on fine particle concentrations. Spengler et al. (1981) estimated an  
3 increase of about 20  $\mu\text{g}/\text{m}^3$  per smoker based on 55 homes from all six cities. Since homes  
4 with at least one smoker probably average at least 1.3 smokers per home, this corresponds to  
5 about 26  $\mu\text{g}/\text{m}^3$  per smoking home. Spengler et al. (1985) found a smoking effect of about  
6 32  $\mu\text{g}/\text{m}^3$  for smoking homes in multivariate models based on the Kingston-Harriman data.  
7 Sheldon et al. (1989) found an increase of 45 (Onondaga) and 47 (Suffolk)  $\mu\text{g}/\text{m}^3$  per  
8 smoking home in a multivariate model of the New York State data. Ozkaynak et al. (1993)  
9 found an increase of about 30 to 35  $\mu\text{g}/\text{m}^3$  in smoking homes in a multivariate regression  
10 model of the PTEAM data. Thus the estimates of the effect of a smoking home on indoor  
11 fine particle concentrations range from about 26 to about 47  $\mu\text{g}/\text{m}^3$ .

12 Dockery and Spengler (1981) found an effect of 0.88  $\mu\text{g}/\text{m}^3$  per cigarette for homes  
13 without air conditioning, and 1.23  $\mu\text{g}/\text{m}^3$  per cigarette for homes with air conditioning, based  
14 on 68 homes from all six cities. Lebreton found an effect of 0.8  $\mu\text{g}/\text{m}^3$  per cigarette for homes  
15 in the Watertown area. Leaderer et al. (1991) found an effect ranging between 0.27 and  
16 0.33  $\mu\text{g}/\text{m}^3$  per cigarette smoked over a week's time, corresponding to 1.9 to 2.3  $\mu\text{g}/\text{m}^3$  per  
17 cigarette contribution to a 24-h average. In a series of stepwise regressions on the PTEAM  
18 data, Özkaynak et al. (1993) found an effect ranging between 2.5 and 4.7  $\mu\text{g}/\text{m}^3$  per cigarette  
19 per 12-h monitoring period; this corresponds to an effect ranging between 1.2 and 2.4  $\mu\text{g}/\text{m}^3$   
20 per cigarette smoked during a 24-h period. Taking the midpoint of these ranges leads to  
21 estimates for the three studies of about 1.1, 2.1, and 1.8  $\mu\text{g}/\text{m}^3$  increases in fine particle  
22 concentrations per cigarette smoked in the home over a 24-h period.

23 Both the New York State study and the PTEAM study were able to estimate source  
24 strengths for different variables using a mass-balance model. The estimates for  $\text{PM}_{2.5}$   
25 emissions from cigarettes were very comparable, with Koutrakis et al. (1992) estimating  
26 12.7 mg/cig compared to the PTEAM estimate of 13.8 mg/cig (Ozkaynak et al., 1993).  
27 Both studies also found similar elemental profiles for smoking, with potassium and chlorine  
28 being emitted in substantial amounts.

29  
30 *Effect of other variables.* In the PTEAM Study, the second most powerful indoor  
31 source of  $\text{PM}_{10}$ , and possibly  $\text{PM}_{2.5}$  particles, was cooking. Quite large emission strengths



1 of several mg/minute of cooking were determined from the mass-balance model, while  
2 multiple regressions indicated that cooking could contribute between 10 and 20  $\mu\text{g}/\text{m}^3$   $\text{PM}_{10}$ ,  
3 and somewhat smaller amounts of  $\text{PM}_{2.5}$ , to the 12-h concentration. Apparently neither of  
4 the other studies analyzed for the effect of cooking, although Dockery and Spengler (1981)  
5 suggested cooking as one possible reason for the observed 15  $\mu\text{g}/\text{m}^3$  residual in their indoor  
6 particle model.

7 In the New York State study, homes with kerosene heaters had increased  $\text{PM}_{2.5}$   
8 concentrations of 15.8  $\mu\text{g}/\text{m}^3$  in Suffolk ( $p < 0.03$ ) and 3.65  $\mu\text{g}/\text{m}^3$  in Onondaga ( $p < 0.3$ ,  
9 not significant). Both the New York State and PTEAM studies also measured air exchange  
10 in every home, and both studies found that air exchange significantly affected indoor particle  
11 concentrations. In the PTEAM study, increased air exchange led to increased indoor air  
12 concentrations for both  $\text{PM}_{2.5}$  and  $\text{PM}_{10}$  at night only, perhaps because outdoor  
13 concentrations were larger than indoor levels at night. In the New York State study,  
14 increased air exchange led to decreased RSP concentrations in Onondaga ( $p < 0.02$ ) but no  
15 effect was noted in Suffolk ( $p < 0.90$ ). In both of these counties, indoor levels generally  
16 exceeded outdoor levels, so increased air exchange would generally reduce indoor  
17 concentrations.

18 Both the New York State and PTEAM studies found a very small but significant effect  
19 of house volume. In Onondaga,  $\text{PM}_{2.5}$  concentrations decreased by  $-1.1 \mu\text{g}/\text{m}^3$  per  
20 1,000 cubic foot increase in volume; in Suffolk concentrations decreased by  $-0.75 \mu\text{g}/\text{m}^3$   
21 per 1,000 cubic feet. In the PTEAM study,  $\text{PM}_{2.5}$  daytime concentrations decreased by  
22  $-2.0 \mu\text{g}/\text{m}^3$  per thousand cubic feet. Probably because of a significant negative correlation  
23 between house volume and air exchange rate, the two variables did not both reach  
24 significance in the same regression.

## 25 *Other Studies*

26 Several other large-scale studies of homes have taken place in other countries, and a  
27 number of smaller studies have occurred in the U.S. These will be discussed in order of the  
28 number of homes included in the study.

29 Lebre et al. (1990) carried out week-long RSP measurements (cutpoint not described)  
30 in 260 homes in the cities of Ede and Rotterdam, the Netherlands, during the winters of 1981  
31

1 to 1982 and 1982 to 1983, respectively. 60% of the Ede homes and 66% of the Rotterdam  
2 homes included smokers. Diary information collected during the measurement period  
3 indicated that, on average, 1 to 2 cigarettes were smoked during the week, presumably by  
4 guests, even in the nonsmoking homes. Homes with one smoker averaged 7 cigarettes  
5 smoked per day at home in Ede (N = 53) and 11 per day in Rotterdam (N = 35). Homes  
6 with two smokers averaged 21 cigarettes per day in Ede (N = 23) and 25 cigarettes per day  
7 in Rotterdam (N = 15).

8 Geometric means for the combined smoking and nonsmoking homes were similar in the  
9 two cities (61 and 56  $\mu\text{g}/\text{m}^3$ , respectively), with maxima of 560 and 362  $\mu\text{g}/\text{m}^3$ . Outdoor  
10 concentrations averaged about 45  $\mu\text{g}/\text{m}^3$  (N not given). Indoor concentrations in the homes  
11 with smokers averaged about 70  $\mu\text{g}/\text{m}^3$  (calculated from data in the paper), compared to  
12 levels in the nonsmoking homes of about 30  $\mu\text{g}/\text{m}^3$ . Multiple regression analysis indicated  
13 that the number of smoking occupants explained about 40% of the variation in the log-  
14 transformed RSP concentrations—family size, frequency of vacuuming, volume of the living  
15 room, type of space heating, and city (Ede versus Rotterdam) had no significant effect on  
16 RSP concentrations. In a second regression, the number of smoking occupants was replaced  
17 by the number of cigarettes and cigars smoked during the week. The regression equation  
18 was

$$\begin{aligned} \log(\text{RSP}) &= 1.4 + 0.37 \log(\# \text{ cigarettes}) + 0.53 \log(\# \text{ cigars}) \\ &\quad + 0.03 \log(\text{family size}) \\ R^2 &= 0.49; \text{d.f.} = 250 \quad F = 83.7 \quad p < 0.0001 \end{aligned}$$

24 From this equation, the authors estimated that one cigarette smoked per day would increase  
25 weekly average indoor RSP concentrations by 2 to 5  $\mu\text{g}/\text{m}^3$ , whereas one cigar smoked per  
26 day would increase indoor levels by 10  $\mu\text{g}/\text{m}^3$ .

27 Instantaneous RSP concentrations were made using a TSI Piezobalance on the day the  
28 technicians were setting up the equipment. The influence of smoking on these measurements  
29 may be seen in Table 7-19:

**TABLE 7-19. INFLUENCE OF RECENT CIGARETTE SMOKING ON INDOOR CONCENTRATIONS OF PM (SIZE UNSPECIFIED)**

Time Since Smoking	N	RSP (geom. mean) ( $\mu\text{g}/\text{m}^3$ )
No smoking	98	41
More than 1 h ago	18	52
Between 1/2 and 1 h ago	7	76
Less than 1/2 an hour ago	27	141
During the measurements	54	191

Source: Lebre et al. (1990).

Diemel et al. (1981) measured particles in 101 residences as part of an epidemiological study related to a lead smelter in Arnhem, the Netherlands. The indoor sampler was adapted from a small aquarium-type pump, collecting samples at a flowrate of 1 to 1.5 lpm. The authors state that particles smaller than 3 to 4  $\mu\text{m}$  in diameter should have been sampled efficiently, but present no laboratory data on measured cutpoint size. The outdoor samplers (number not given) were high-volume samplers. The 28-day average levels indoors ranged from 20 to 570  $\mu\text{g}/\text{m}^3$ , with an arithmetic mean of 140  $\mu\text{g}/\text{m}^3$  (SD not presented) and a geometric mean of 120  $\mu\text{g}/\text{m}^3$ ; corresponding outdoor concentrations (2-mo averages of 24-h daily samples) ranged from 53.7 to 73.3  $\mu\text{g}/\text{m}^3$  (N not given), with nearly identical arithmetic and geometric means of 64  $\mu\text{g}/\text{m}^3$ .

Kulmala et al. (1987) measured indoor and outdoor air in approximately 100 dwellings (including some office buildings) in Helsinki, Finland between 1983 and 1986. Samples were collected on Nuclepore filters using a stacked foil technique. Mean concentrations were presented in Table 7-20 for fine ( $< 1 \mu\text{m}$ ) and coarse ( $> 1 \mu\text{m}$ ) particles (standard deviations not provided):

**TABLE 7-20 INDOOR AND OUTDOOR PM IN BUILDINGS IN HELSINKI, FINLAND, AS A FIUNCTION OF SEASON AND LOCATION.**

	Location	Season	Outdoors	Indoors
Fine particles				
	Urban	Summer	40	25
	Urban	Winter	30	30
	Suburban	Summer	15	20
	Suburban	Winter	30	20
Coarse particles				
	Urban	Summer	75	20
	Urban	Winter	30	15
	Suburban	Summer	20	25
	Suburban	Winter	25	20

Source: Kulmala et al. (1987).

The authors noted that the geometric mean for the combined fine particle samples indoors was  $16 \mu\text{g}/\text{m}^3$ , with a 95% range of 4 to  $67 \mu\text{g}/\text{m}^3$ . Corresponding values for the indoor coarse particles were  $13 \mu\text{g}/\text{m}^3$  with a range of 3 to  $63 \mu\text{g}/\text{m}^3$ . Outdoors, the fine particles had a geometric mean of  $20 \mu\text{g}/\text{m}^3$  with a 95% range of 5 to  $82 \mu\text{g}/\text{m}^3$ , and the coarse particles had a geometric mean of  $16 \mu\text{g}/\text{m}^3$  with a range of 3 to  $91 \mu\text{g}/\text{m}^3$ .

Quackenboss et al. (1989) reported  $\text{PM}_{10}$  and  $\text{PM}_{2.5}$  results from 98 homes in the Tucson, Arizona area. Homes were selected as part of a nested design for an epidemiological study. The Harvard-designed dual-nozzle indoor air sampler (Marple et al., 1987) was employed for indoor air measurements. Outdoor air was measured within each geographic cluster by the same instrument; supplementary data were obtained from the Pima County Air Quality control District, but these data did not include  $\text{PM}_{2.5}$  measurements, and some data were apparently  $\text{PM}_{15}$ . Homes were classified by tobacco smoking and by use of evaporative ("swamp") coolers; these coolers apparently act as a significant removal mechanism for particles (Table 7-21). Homes without smoking averaged about  $16 \mu\text{g}/\text{m}^3$   $\text{PM}_{2.5}$ , compared to  $24 \mu\text{g}/\text{m}^3$  for homes reporting less than a pack a day, and  $51 \mu\text{g}/\text{m}^3$  for homes reporting more than a pack a day.  $\text{PM}_{2.5}$  particles formed the bulk of the  $\text{PM}_{10}$  fraction even in nonsmoking homes, ranging from nearly 80% in those homes to nearly 90% in homes with heavy smoking. This is somewhat surprising in view of the statement made in the paper that the bulk of the PM in Tucson is silica quartz averaging around  $5 \mu\text{m}$

**TABLE 7-21. INDOOR AVERAGE PM<sub>2.5</sub> AND PM<sub>10</sub> (µg/m<sup>3</sup>) BY REPORTED SMOKING IN THE HOME AND EVAPORATIVE COOLER USE DURING SAMPLING WEEK**

Smoking Cigarettes/day	Evaporative Cooler	PM <sub>2.5</sub>			PM <sub>10</sub>		
		Mean	S.D.	Homes	Mean	S.D.	Homes
None	Yes	8.8	5.0	(20)	21.0	9.7	(20)
	No	20.3	19.0	(25)	38.4	22.9	(23)
	Total	15.2	15.5	(45)	30.3	19.9	(43)
1-20	Yes	19.3	8.8	(10)	33.9	12.0	(10)
	No	32.3	28.5	(16)	53.4	33.9	(17)
	Total	27.3	23.6	(26)	46.2	29.1	(27)
> 20	Yes	36.2	32.9	(8)	47.4	39.6	(9)
	No	82.7	55.4	(9)	102.5	60.6	(9)
	Total	60.8	50.8	(17)	75.0	57.2	(18)

PM<sub>2.5</sub>: Significant (p < 0.01) main effects for smoking and evaporative cooler use; two-way interaction nearly significant (p = 0.06).

PM<sub>10</sub>: Significant (p < 0.01) main effects for evaporative cooler and smoking.

Source: Quackenboss et al. (1989)

in mean aerodynamic diameter; that should result in the coarse fraction being larger than the fine fraction. Outdoor PM<sub>10</sub> particles were not strongly correlated with indoor levels (R<sup>2</sup> = 0.18; N about 90). Although about 30% of homes in the larger sample reported using fireplaces, no estimate of an effect on indoor air quality was made in the paper.

Quackenboss et al. (1991) extended the analysis of the Tucson homes over three seasons. Median indoor PM<sub>2.5</sub> levels in homes with smokers were about 20 µg/m<sup>3</sup> in the summer and spring/fall seasons compared to about 10 µg/m<sup>3</sup> in homes without smokers in those seasons (Table 7-22). In winter, however, the difference was considerably increased, with the median level in 24 homes with smokers at about 36 µg/m<sup>3</sup> compared to 13 µg/m<sup>3</sup> in 26 homes without smokers.

Revsbech et al. (1987) studied 44 apartments in Aarhus, Denmark. All were retrofitted or tight apartments in three-story brick buildings. Particles were measured by an open filter surface directed downwards. The authors considered that the low suction rate and the downward facing surface would result in collecting predominantly the respirable fraction, but

**TABLE 7-22. INDOOR PM<sub>10</sub> AND PM<sub>2.5</sub> (μg/m<sup>3</sup>) BY SEASON AND ENVIRONMENTAL TOBACCO SMOKE (ETS)**

	Season <sup>a</sup>	Smokers at home				No smokers at home			
		Median	Q1	Q3	N	Median	Q1	Q3	N
PM <sub>10</sub>	Summer	35.3	29.3	49.8	49	17.5	14.1	24.4	49
	Spring/Fall	43.3	28.7	64.3	38	30.0	20.5	40.1	37
	Winter	80.3	40.8	104.9	24	31.4	24.3	42.9	26
PM <sub>2.5</sub>	Summer	20.5	13.7	27.0	49	8.9	5.9	11.9	50
	Spring/Fall	20.1	12.8	43.6	39	10.6	8.7	14.8	37
	Winter	35.7	26.7	77.8	24	13.4	10.2	19.9	26

<sup>a</sup>Seasons: Summer = May through September;  
Spring/Fall = March, April, October, November;  
Winter = December through February  
Q1, Q3: 1st and 3rd quartiles of distribution  
N: number of households

presented no evidence of work done to determine the sampling efficiency curve or cutpoints. Sampling occurred at the rate of 3 lpm for 16 h beginning in the evening and including the overnight sleeping period. Outdoor levels were not recorded, although existing outdoor measurements were quoted as having yearly averages of 30 to 38 μg/m<sup>3</sup>, with 84th percentiles at 41 to 51 μg/m<sup>3</sup>. Ventilation rates were measured by introducing CO<sub>2</sub> at 5,000 ppm and recording the decay with an infrared gas analyzer for at least 1 h. The median number of cigarettes smoked was 8; in eleven homes (25% of the total) no cigarettes were smoked. The median ventilation rate was 0.23 h<sup>-1</sup>, with an interquartile range of 0.19 to 0.31 h<sup>-1</sup>. In the 11 dwellings without smoking, the median concentration was 91 μg/m<sup>3</sup> (IQR 57 to 107 μg/m<sup>3</sup>); in the homes with <10 cigarette equivalents, the median (IQR) was 169 (49 to 338) μg/m<sup>3</sup>; and in homes with more than 10 cigarette equivalents, the median (IQR) was 475 (309 to 587) μg/m<sup>3</sup>. The particle concentration correlated positively with tobacco consumption ( $r_s = 0.716$ ,  $p < 0.001$ ) and length of daily residence ( $r_s = 0.405$ ,  $p < 0.01$ ) but not with the frequency of cleaning ( $r_s = 0.203$ , n.s.), time of airing of living rooms (n.s.), or the ventilation rate ( $r_s = 0.277$ , n.s.).

Sexton et al. (1984) reported on a study in Waterbury VT. This study included 24 homes, 19 with wood-burning appliances, and none with smokers. 24-h samples (0800 to 0800) were collected in each home every other day for two weeks, providing 163 valid

1 indoor samples. Indoor RSP levels ranged from 6 to 69  $\mu\text{g}/\text{m}^3$  with a mean value of 25  
2  $\mu\text{g}/\text{m}^3$ . Outdoor levels ranged from 6 to 30  $\mu\text{g}/\text{m}^3$  with a mean value of 19  $\mu\text{g}/\text{m}^3$ . Indoor  
3 concentrations were not correlated with outdoor concentrations ( $r = 0.11$ ,  $p > 0.16$ .)

4 Kim and Stock (1986) reported results from 11 homes in the Houston area. (The year  
5 and the season were not supplied in the paper.) For most homes, two 12-h  $\text{PM}_{2.5}$  samples  
6 (day and night) were collected for approximately one week. Sampling methods were not  
7 fully discussed, but apparently involved samples collected using a mobile van near each  
8 home. The mean weekly concentrations in the five smoking homes averaged  $33.0 \pm$   
9  $4.7$  (SD)  $\mu\text{g}/\text{m}^3$ , versus mean outdoor concentrations averaging  $24.7 \pm 7.4$   $\mu\text{g}/\text{m}^3$  (calculated  
10 from data presented in paper). Indoor concentrations in the six nonsmoking homes averaged  
11  $10.8 \pm 4.9$   $\mu\text{g}/\text{m}^3$  compared to outdoor levels of  $12.0 \pm 5.9$   $\mu\text{g}/\text{m}^3$ .

12 Morandi, Stock and Contant (1986) reported on 13 Houston homes monitored during  
13 1981 as part of a larger personal monitoring study of 30 nonsmoking participants. The TSI  
14 Piezobalance (cutpoint at about  $\text{PM}_{3.5}$ ) was employed for the personal monitoring, with  
15 technicians "shadowing" the participants and taking consecutive 5-min readings. At the  
16 homes, dichotomous samplers (cutpoints at  $\text{PM}_{2.5}$  and  $\text{PM}_{10}$ ) were used for two 12-h daytime  
17 samples (7 a.m. to 7 p.m.) both inside and outside the homes for seven consecutive days.  
18 Little difference was noted in the indoor concentrations at homes ( $25 \pm 30$  (SD)  $\mu\text{g}/\text{m}^3$ ) and  
19 at work or school ( $29 \pm 25$   $\mu\text{g}/\text{m}^3$ ). The authors noted that the highest overall respirable  
20 suspended particle (RSP) concentrations occurred in the presence of active smoking  
21 ( $89$   $\mu\text{g}/\text{m}^3$ ), significantly different from mean RSP values measured in the absence of  
22 smokers ( $19$   $\mu\text{g}/\text{m}^3$ ;  $p < 0.0001$ ). Among homes with smokers, those homes with central  
23 air conditioning were significantly ( $p < 0.0001$ ) higher ( $114$  versus  $52$   $\mu\text{g}/\text{m}^3$ ) than those with  
24 no air conditioning; in this case, the outdoor differences only increase this contrast. Cooking  
25 was associated with significantly higher RSP concentrations ( $27$   $\mu\text{g}/\text{m}^3$  compared to  $20$   
26  $\mu\text{g}/\text{m}^3$ ,  $p < 0.01$ ). The single highest RSP concentration ( $202$   $\mu\text{g}/\text{m}^3$ ) was found in a home  
27 with no smokers and no air conditioning but with active cooking. The authors concluded that  
28 cooking was a more important source of indoor RSP than smoking, at least in the small  
29 number of homes they studied.

30 Coultas et al. (1990) measured  $\text{PM}_{2.5}$  and nicotine in 10 homes containing at least one  
31 smoker. The authors used the Harvard aerosol impactor with sodium bisulfate-treated filters

for nicotine collection, with analysis by GC-FID using a modified Hammond method. Samples were collected for 24 h every other day for 10 days and then for 24 h every other week for 10 weeks, resulting in 10 samples per household. The mean concentrations of PM<sub>2.5</sub> ranged from 32.4 ± 13.1 (SD) to 76.9 ± 32.9 µg/m<sup>3</sup>; of nicotine, from 0.6 ± 0.7 to 6.9 ± 8.2 µg/m<sup>3</sup>. Outdoor particle concentrations were not reported; thus it is difficult to calculate the portion of the observed PM<sub>2.5</sub> that might be due to ETS. The authors employed a regression technique together with questionnaire variables indicating the periods of smoking to derive an estimate of 17 µg/m<sup>3</sup> as the contribution of smoking to indoor PM<sub>2.5</sub>; however, the 95% confidence bounds for this estimate ranged from -3 to 38 µg/m<sup>3</sup>, indicating that it is not significantly different from zero. The Spearman correlation between total PM<sub>2.5</sub> and nicotine was 0.54 (N = 99).

Kamens et al. (1991) measured indoor particles in three homes without smokers in North Carolina in November and December 1987 (no measurements of outdoor particles were taken). Two dichotomous samplers (PM<sub>2.5</sub> and PM<sub>10</sub>), several prototype personal samplers (also PM<sub>2.5</sub> and PM<sub>10</sub>, and three particle sizing instruments including a TSI electrical aerosol mobility analyzer (EAA) with 10 size intervals between 0.01 and 1.0 µm, and two optical scattering devices covering the range of 0.09 to 3.0 and 2.6 to 19.4 µm were employed. Air exchange measurements were made using SF<sub>6</sub> decay over the course of the seven 8-h (daytime) sampling periods. There were also three 13-h (evening and overnight) sampling periods. For the entire study, 37% of the estimated total mass collected was in the fine fraction, and another 37% in the fraction greater than 10 µm. The remainder (26%) was in the coarse (PM<sub>10</sub> - PM<sub>2.5</sub>) fraction. However, considerable variation was noted in these size distributions. For example, on one day with extensive vacuuming, cooking, and vigorous exercising of household pets, 52% of the total mass appeared in the fraction larger than 10 µm, with only 18% in the fine fraction. The peak in particle mass on that day coincided with vacuuming and sweeping of the carpets and floors. On another day, stir-fried vegetables and rice produced a large number of small particles, with those less than 0.1 µm accounting for 30% of the total EAA particle volume, much larger than the normal amount. The cooking contribution of that one meal to total 8-h daytime particle volume exposure was calculated to be in the range of 5 to 18%. The authors concluded that the most significant source of small particles (<2.5 µm) in all three of these nonsmoking homes was cooking,



1 while the most significant source of large particles ( $> 10 \mu\text{m}$ ) was vacuum sweeping. Coarse  
2 particles ( $\text{PM}_{10}$  -  $\text{PM}_{2.5}$ ) appeared to be of largely biological (human dander and insect parts)  
3 and mineral (clay, salt, chalk, etc.) origin.

4 In a test of a new sampling device (a portable nephelometer), Anuszewski, Larson and  
5 Koenig (1992) reported results from indoor and outdoor sampling at nine Seattle homes  
6 sampled for an average of 18 days each during the winter of 1991 to 1992. The  
7 nephelometer is a light-scattering device with rapid (1-min) response to various household  
8 activities such as sweeping, cigarette smoking, frying, barbecuing, and operating a fireplace.  
9 Homes with fewer activities showed high correlations of indoor and outdoor light-scattering  
10 coefficients, both between hourly averages and 12-h averages. However, homes with  
11 electrostatic precipitators, with weather-stripped windows or doors, and with gas cooking or  
12 heating devices showed weak 12-h indoor-outdoor correlations. One home with a fireplace  
13 produced the strongest indoor-outdoor light scattering relationship ( $R^2 = 0.99$ ); this is  
14 presumably due to the very high air exchange rate produced by the fireplace.

15 Chan et al. (1995) studied particles and nicotine in seven homes with one smoker each  
16 in Taiwan. Sampling was carried out in summer and winter of 1991. Each home had one  
17 indoor  $\text{PM}_5$  sampler in the living room and another in the yard. In the winter study, two  
18 homes had  $\text{PM}_{10}$  samplers added inside and outside and at two central sites. Indoor mean  
19  $\text{PM}_5$  concentrations averaged  $44 \pm 32$  (SD)  $\mu\text{g}/\text{m}^3$  in summer compared to outdoor  
20 concentrations of  $27 \pm 15 \mu\text{g}/\text{m}^3$ . Corresponding winter values were  $107 \pm 44 \mu\text{g}/\text{m}^3$  and  
21  $92 \pm 40 \mu\text{g}/\text{m}^3$ . Mean cigarette butt counts were only 11.1 in the summer and 6.1 in the  
22 winter, and nicotine levels were only 0.4 to 0.5  $\mu\text{g}/\text{m}^3$  in the two seasons; thus the homes  
23 appeared to include fairly light smokers. It was calculated that these smokers produced an  
24 average of about 16  $\mu\text{g}/\text{m}^3$  of  $\text{PM}_5$  daily.

25 Daisey et al. measured RSP, PAH, and extractable organic matter (EOM) in seven  
26 Wisconsin homes with wood stoves; one 48h (1,000  $\text{m}^3$ ) sample was collected during  
27 woodburning and a second sample was collected when no woodburning occurred. Five of  
28 seven homes had somewhat higher RSP levels during woodburning, but the mean difference  
29 was not significant. On the other hand, all homes had from 2 to 40 times higher levels of  
30 PAH during woodburning, with the means being significantly different. Mean values of  
31 EOM were also significantly higher during woodburning.

1 Highsmith et al. (1991) reported on the results of two 20-home studies in Boise, ID and  
2 Roanoke, VA. The Boise study was designed to assess the effects of wood burning on  
3 ambient and indoor concentrations in the area. Ten homes with wood burning stoves were  
4 matched with 10 homes without wood burning stoves. One matched pair of homes was  
5 monitored from Saturday through Tuesday for eight consecutive 12-h periods. Ambient  
6  $PM_{2.5}$  concentrations increased by about 50% at night, suggesting an influence of  
7 woodburning. Indoor  $PM_{2.5}$  concentrations also were increased (by about 45%) in the homes  
8 with the wood burning stoves compared to those without ( $26.3$  versus  $18.2 \mu g/m^3$ ), although  
9 coarse particles showed no increase ( $10.2$  versus  $9.7 \mu g/m^3$ ). The Roanoke study, designed  
10 to assess the effects of residential oil heating, showed no effects on indoor levels of fine or  
11 coarse particles.

12 Löfroth et al. (1991) measured particle emissions from cigarettes, incense sticks,  
13 "mosquito coils," and frying of various foods. Emissions were 27 and 37 mg/g for two  
14 brands of Swedish cigarettes, 51 and 52 mg/g for incense sticks and cones, and 61 mg/g for  
15 the mosquito coil. Emissions from pork, hamburgers, herring, pudding, and Swedish  
16 pancakes ranged from 0.07 to 3.5 mg/g. Extracts of some of the foods showed mutagenic  
17 activity. Other studies of mutagenicity of foods from cooking were referenced: Berg et al.  
18 (1988) and Teschke et al. (1989). The authors concluded that indoor air pollution from  
19 cooking requires further study.

20 Mumford et al. (1991) measured  $PM_{10}$ , PAH, and mutagenicity in eight mobile homes  
21 with kerosene heaters. Each home was monitored for 2.6 to 9.5 h/day (mean of 6.5 h) for  
22 three days a week for two weeks with the kerosene heaters off and for two weeks with them  
23 on (average on-time of 4.5 h). Mean  $PM_{10}$  levels were not significantly increased when the  
24 heaters were on ( $73.7 \pm 7.3$  (SE)  $\mu g/m^3$  versus  $56.1 \pm 5.7 \mu g/m^3$ ), but in two homes levels  
25 increased to 112 and 113  $\mu g/m^3$  when the heaters were on. Outdoor concentrations averaged  
26  $18.0 \pm 2.1 \mu g/m^3$ . PAH and CO concentrations and mutagenicity were significantly  
27 increased when the heaters were on.

28 Colome et al. (1990) measured particles using  $PM_{10}$  and  $PM_5$  (cyclone) samplers inside  
29 and outside homes of 10 nonsmokers, including eight asthmatics, living in Orange County,  
30 CA. Indoor  $PM_{10}$  samples were well below outdoor levels for all homes (mean of  $42.5 \pm$

3.7 (SE)  $\mu\text{g}/\text{m}^3$  indoors versus  $60.8 \pm 4.7 \mu\text{g}/\text{m}^3$  outdoors). No pets, wood stoves, fireplaces, or kerosene heaters were present in any of these homes.

Liroy et al. (1990) measured  $\text{PM}_{10}$  at eight homes (no smokers) for 14 days in the winter of 1988 in the town of Phillipsburg, NJ, which has a major point source consisting of a grey iron pipe manufacturing company. The Harvard impactor was used indoors to collect 14 24-h samples beginning at 4:30 p.m. each day; Wedding hi-vol  $\text{PM}_{10}$  samples were deployed at three outdoor sites. A fourth outdoor site was located on a porch directly across the street from the pipe sampler. The first three sites showed little difference from one another, whereas on day 4 and day 6 of the study, the outdoor sampler on the porch had readings that were considerably (about  $40 \mu\text{g}/\text{m}^3$ ) higher than the other outdoor samplers, suggesting an influence of the nearby point source. The geometric mean outdoor  $\text{PM}_{10}$  concentration was  $48 \mu\text{g}/\text{m}^3$  (GSD not provided) compared to  $42 \mu\text{g}/\text{m}^3$  indoors. A simple regression equation for all homes ( $N = 101$  samples) explained 45% of the variance in indoor  $\text{PM}_{10}$ :

$$\text{Indoor } \text{PM}_{10} = 0.496 \text{ Outdoor } \text{PM}_{10} + 21.5$$

Thatcher and Layton (1994) measured particle size distributions inside and outside a residence in the summer. Measured deposition velocities for particles between 1 and  $5 \mu\text{m}$  closely matched the calculated gravitational settling velocities; however, for particles  $> 5 \mu\text{m}$ , the deposition velocity was less than the calculated settling velocity, perhaps due to the non-spherical nature of these particles. The authors calculated a penetration factor of 1, agreeing with the findings of the PTEAM Study. They also determined that resuspension of particles had a significant impact on indoor particle concentrations. Merely walking into a room increased the particle concentration by 100% for particles  $> 1 \mu\text{m}$ . The authors calculated a resuspension rate of  $2 \text{ to } 8 \times 10^{-3} \text{ h}^{-1}$  for four persons in a house performing normal activities (i.e., close to 0.01%) of the total collected house dust could be resuspended in an hour. For a surface mass of house dust per unit area of  $220 \mu\text{g}/\text{cm}^2$ , this rate resulted in an airborne concentration due to resuspension of about  $10 \mu\text{g}/\text{m}^3$ , compared to an outdoor contribution of similar magnitude.

Because house dust can be resuspended, it will contribute to total airborne exposure to particles and constituents such as metals and pesticides. Roberts et al. (1990) studied 42 homes in Washington State. Geometric mean lead concentration in 6 homes where shoes were removed on entry was  $240 \mu\text{g}/\text{m}^2$  on carpets, compared to  $2,900 \mu\text{g}/\text{m}^2$  on carpets in homes where shoes were kept on. This finding suggests that most of the carpet dust in a home enters via track-in on shoes rather than infiltration by air.

#### **7.6.2.2 Studies in buildings**

The single largest study of particles in buildings was carried out by the Lawrence Berkeley Laboratory (LBL) for the Bonneville Power Administration (BPA) (Turk et al., 1987, 1989). 38 buildings were chosen from two climatic regions in the Pacific Northwest: Portland-Salem, Oregon (representing mild coastal conditions), and Spokane-Cheney, Washington (representing extreme inland conditions). The buildings were studied for a variety of pollutants to determine how ventilation rates affect indoor air quality. Buildings were measured in winter (21 buildings in both regions), spring (10 buildings in both regions) and summer (nine buildings in the inland region only). All but four buildings were government or public properties, and therefore cannot be considered to represent the full mix of building types.

Each building was monitored for 10 working days over a two-week period. From 4 to 8 particle sampling sites were chosen in each building according to size. The sampler was an LBL-developed flow controlled device with a  $3\mu\text{m}$  cutpoint. The pumps sampled only during hours the building was occupied. If filters had to be changed due to excessive loading, the combined weight of all filters from one site was determined—thus all values are approximately 10 working-day (80-h) averages.

Buildings had varied types of smoking policies, from relatively unrestricted to very tightly controlled, as in one elementary school. In most buildings, an attempt was made to site at least one monitor in an area where smoking was allowed. Data was obtained from smoking areas in about 30 of the 38 buildings.

Results comparing smoking and non-smoking areas are provided in Table 7-23 and Figure 7-29. Mean RSP concentrations in the smoking areas were more than three times higher than in the non-smoking areas (70 versus  $19 \mu\text{g}/\text{m}^3$ ). Since these arithmetic means

**TABLE 7-23. SMOKING, NON-SMOKING, AND OUTDOOR RSP  
CONCENTRATIONS AND RATIOS**

Building No.	Outdoor	Indoor			Ratios		
	( $\mu\text{gm}^{-3}$ )	( $\mu\text{gm}^{-3}$ )			Indoor Non-Smoking ÷ Outdoor	Indoor Smoking ÷ Outdoor	Indoor Mean ÷ Outdoor
	Arithmetic Mean (Range)						
		Non-Smoking	Smoking <sup>c</sup>	Mean <sup>d</sup>			
1	ND	25(19-36)	ND	25(19-36)	NA	NA	NA
2	ND	19(18-21)	ND	19(18-21)	NA	NA	NA
3	ND	ND	20(16-25)	20(16-25)	NA	NA	NA
4	8	7(6-8)	ND	7(6-8)	0.9	NA	0.9
5	BD	13(13)	14(14)	13(13-14)	NA	NA	NA
6	35	12(11-13)	35(23-59)	28(11-59)	0.3	1.0	0.8
7	35	38(32-44)	39(39)	38(32-44)	1.1	1.1	1.1
8	8	7(7-8)	ND	7(7-8)	0.9	NA	0.9
9	8	11(11)	16(13-20)	15(11-20)	1.3	2.0	1.9
10	9	65(53-74)	95(67-127)	86(53-127)	7.0	11.0	9.6
11	8	23(9-49)	209(209)	63(9-209)	2.9	26.1	7.9
12	ND	10(10)	63(63)	36(10-63)	NA	NA	NA
13	10	5(5-6)	ND	5(5-6)	0.5	NA	0.5
14	6	ND	30(26-34)	30(26-34)	NA	5.0	5.0
15	BD	11(7-14)	12(12)	11(7-14)	NA	NA	NA
16	10	9(8-11)	73(73)	31(8-73)	0.9	7.3	3.1
17	7	11(10-13)	105(105)	40(10-105)	1.6	15.0	6.1
18	7	ND	19(19)	19(19)	NA	2.7	2.7
19	7	ND	20(11-29)	20(11-29)	NA	2.9	2.9
20	18	11(10-11)	ND	11(10-11)	0.6	NA	0.6
21	17	11(9-12)	ND	11(9-12)	0.7	NA	0.7
22	20	18(18)	57(22-165)	50(18-165)	0.9	2.9	2.5
23	11	9(BD-20)	ND	9(BD-20)	0.8	NA	0.8
24	11	44(10-77)	24(24)	37(10-77)	4.0	2.2	3.4
25	68	35(32-38)	109(109)	60(32-109)	0.5	1.6	0.9
26	32	45(20-70)	82(55-123)	67(20-123)	1.4	2.6	2.1
27	52	36(33-38)	61(33-89)	48(33-89)	0.7	1.2	0.9
28	65	36(29-43)	BD	24(BD-43)	0.6	NA	0.4
29	29	10(8-12)	144(144)	32(8-144)	0.3	5.0	1.1
30 <sup>b</sup>	33	24(20-30)	113(113)	37(20-113)	0.7	3.4	1.1
31	13	12(8-18)	268(268)	64(8-268)	0.9	20.6	4.9
32	ND	13(10-17)	36(21-52)	21(10-52)	NA	NA	NA
33	ND	ND	29(12-74)	29(12-74)	NA	NA	NA
34	16	13(10-16)	54(13-117)	28(10-117)	0.8	3.4	1.8
35	18	20(6-35)	50(50)	23(6-50)	1.1	2.8	1.3
36 <sup>a</sup>	20	14(9-18)	72(17-127)	28(9-127)	0.7	3.6	1.4
37	19	21(12-32)	27(11-62)	25(11-62)	1.1	1.4	1.3
38	14	7(BD-9)	308(308)	46(BD-308)	0.5	22.0	3.3
39	11	8(8-9)	13(11-14)	11(8-14)	0.7	1.3	1.0
40	11	10(8-12)	26(11-40)	15(8-40)	0.9	2.4	1.4
AM	19	19	70	30	1.2	6.0	2.3
ASD	16	14	73	19	1.3	7.2	2.2
GM	14	15	44	24	0.9	3.6	1.7
GSD	2.2	1.9	2.7	2.0	2.0	2.6	2.3

<sup>a</sup>Repeat test of building #11.

<sup>b</sup>Repeat test of building #17.

<sup>c</sup>Smoking within 10 m radius of site.

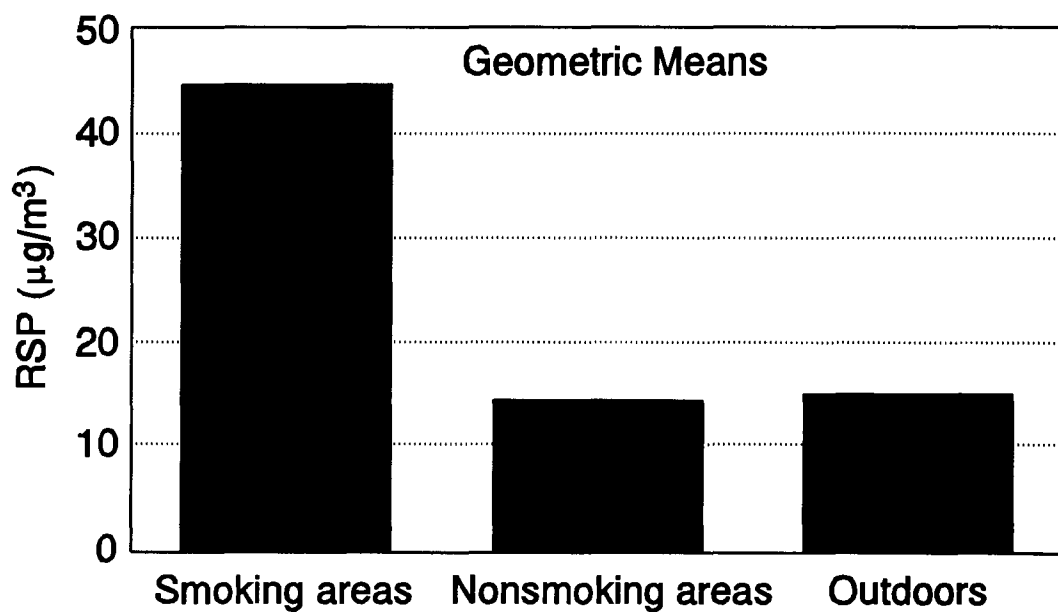
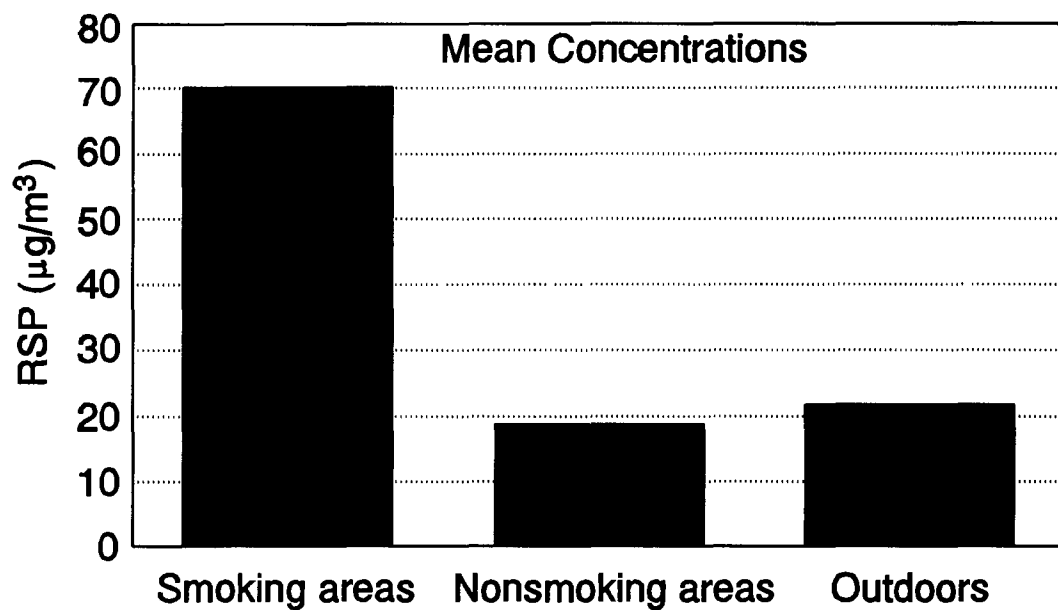
<sup>d</sup>Arithmetic average of all sites in building.

NA = Not applicable.

ND = No data collected.

BD = Below detection limit.

- 1 showed evidence of being driven by one or two high values, the geometric mean (averaged
- 2 across all sites in a building) may be a better comparison. Here the ratio is very close to



**Figure 7-29. Comparison of respirable particles in smoking and non-smoking areas of 38 buildings in the Pacific Northwest.**

Source: Turk et al. (1987).

3 to 1 (44 versus 15  $\mu\text{g}/\text{m}^3$ ). If each of the 70 smoking and 106 nonsmoking sites is allowed to contribute equally to the average, the ratio of geometric means declines (34 versus 14  $\mu\text{g}/\text{m}^3$ ). However, the geometric standard deviation (GSD) for the smoking sites is 2.5 compared to only 1.9 for the nonsmoking sites—thus, the 97.7th percentile is likely to be more than 6 ( $2.5^2$ ) times the geometric mean in the smoking areas (i.e., about 200  $\mu\text{g}/\text{m}^3$ ) compared to only about 4 ( $1.9^2$ ) times the geometric mean in the nonsmoking areas (i.e., about 56  $\mu\text{g}/\text{m}^3$ ). Outdoor results at 30 sites had the identical arithmetic mean as the indoor non-smoking sites: 18.9  $\mu\text{g}/\text{m}^3$ .

Repace and Lowrey (1980) sampled 19 establishments allowing smoking (seven restaurants, three bars, church bingo games, etc.) and 14 where no smoking occurred (including five residences and four restaurants) between March and early May of 1978. Sampling occurred for short periods of time (2 to 50 min) using a TSI Piezobalance to measure  $\text{PM}_{3.5}$ . Indoor concentrations ranged from 24 to 55  $\mu\text{g}/\text{m}^3$  in the areas without smoking, and from 86 to 697  $\mu\text{g}/\text{m}^3$  in places with active smoking. Five of the locations with active smoking were sampled at a time or place when no smoking was occurring; the matched concentrations (smoking/no smoking) were 279/30; 110/55; 109/30; 86/51; and 107/30  $\mu\text{g}/\text{m}^3$ . Because ventilation conditions may have changed between visits, these values cannot be considered fully quantitative.

Miesner et al. (1989) sampled particles and nicotine in 57 locations within 21 indoor sites in Metropolitan Boston between July 1987 and Feb. 1988.  $\text{PM}_{2.5}$  was sampled using Harvard aerosol impactors. Nicotine was sampled using sodium bisulfate-impregnated filters placed downstream from the Teflon filters for the particles. Sampling times ranged from about 3 h in a bus station to 16 h in a library, depending partly on how "clean" the environment was perceived to be.  $\text{PM}_{2.5}$  concentrations ranged from 6  $\mu\text{g}/\text{m}^3$  (in the library) to 521  $\mu\text{g}/\text{m}^3$  in a smoking room in an office building. For 42 measurements in non-smoking areas, the mean  $\text{PM}_{2.5}$  concentration was  $25 \pm 30$  (SD)  $\mu\text{g}/\text{m}^3$ . Six of these measurements included a classroom with visible levels of chalk dust on the impactor, four measurements in subways, and the bus station. The remaining 36 nonsmoking areas had a mean  $\text{PM}_{2.5}$  concentration of  $15 \pm 7$   $\mu\text{g}/\text{m}^3$ . The 15 smoking areas ranged from 20 to 520  $\mu\text{g}/\text{m}^3$  with a mean of  $110 \pm 120$   $\mu\text{g}/\text{m}^3$ .

1 Turner, Cyr, and Gross (1992) measured RSP using the TSI Piezobalance (cutpoint  
2 about 3.5  $\mu\text{m}$ ) in 585 office environments during 1989. The offices were selected because  
3 they had contracted with a commercial group (Healthy Buildings International) to perform  
4 indoor air quality evaluations—thus they cannot be considered a probability sample. Each  
5 office was measured for 1 h (ten 6-min measurements). If smoking was observed during the  
6 hour, the office was so classified. Mean RSP concentrations were  $46 \pm 57$  (SD)  $\mu\text{g}/\text{m}^3$  for  
7 331 smoking offices,  $20 \pm 17.6$   $\mu\text{g}/\text{m}^3$  for 254 nonsmoking offices. Further discriminant  
8 analysis reclassified the smoking offices into light smoking (mean smoking density of  
9 0.075 cig/ $\text{m}^2\text{h}$ ) and heavy smoking (0.30 cig/ $\text{m}^2\text{h}$ ). This analysis suggested that particle  
10 concentrations in the light smoking offices were very similar to those in the nonsmoking  
11 offices ( $19 \pm 9.2$  versus  $17 \pm 9.5$   $\mu\text{g}/\text{m}^3$ ) while concentrations were much higher in the  
12 heavy smoking offices ( $85 \pm 72$   $\mu\text{g}/\text{m}^3$ ). It must be pointed out that funding for this work  
13 was supplied ultimately by tobacco companies, and that serious allegations have been made  
14 by Congressional staff (U.S. House of Representatives, 1994) regarding data irregularities,  
15 including possible data alteration and fabrication, systematic misreporting of room size,  
16 misclassification of smoking and nonsmoking rooms, and other charges.

17 Vaughan and Hammond (1990) measured particles and nicotine before and after a large  
18 corporation adopted a smoking policy limiting smoking to the cafeteria on the 32nd floor.  
19 Nicotine levels in offices on various floors ranged from 1.6 to 24  $\mu\text{g}/\text{m}^3$  before the policy  
20 was instituted, but dropped to 0.1 to 0.5  $\mu\text{g}/\text{m}^3$  afterwards, an improvement by 84 to 98%.  
21 Particle levels dropped from a range of 20 to 270  $\mu\text{g}/\text{m}^3$  before the policy to ND-35  $\mu\text{g}/\text{m}^3$   
22 afterwards (only three measurements due to loss of several samples). The authors noted  
23 some evidence that ETS vapors were spilling over from the snack bar to offices on the same  
24 floor and two adjacent floors on the same air handler (offices on these floors had nicotine  
25 levels about 4 times higher than those on more distant floors).

26 Sheldon (1988a,b) reported on the EPA 10-building study of hospitals, homes for the  
27 elderly, schools, and office buildings. Although the main focus of the study was VOCs,  
28 particle measurements were taken in all buildings. Measurements were taken in six buildings  
29 using a National Bureau of Standards portable particle sampler (NBS 1982; McKenzie et al.,  
30 1982) to collect two size fractions:  $\text{PM}_3$  and a coarse fraction between  $\text{PM}_3$  and  $\text{PM}_{15}$ . The  
31 sampler employed two filters in series: an 8.0  $\mu\text{m}$  Nuclepore filter for  $\text{PM}_{15}$  and a 3  $\mu\text{m}$



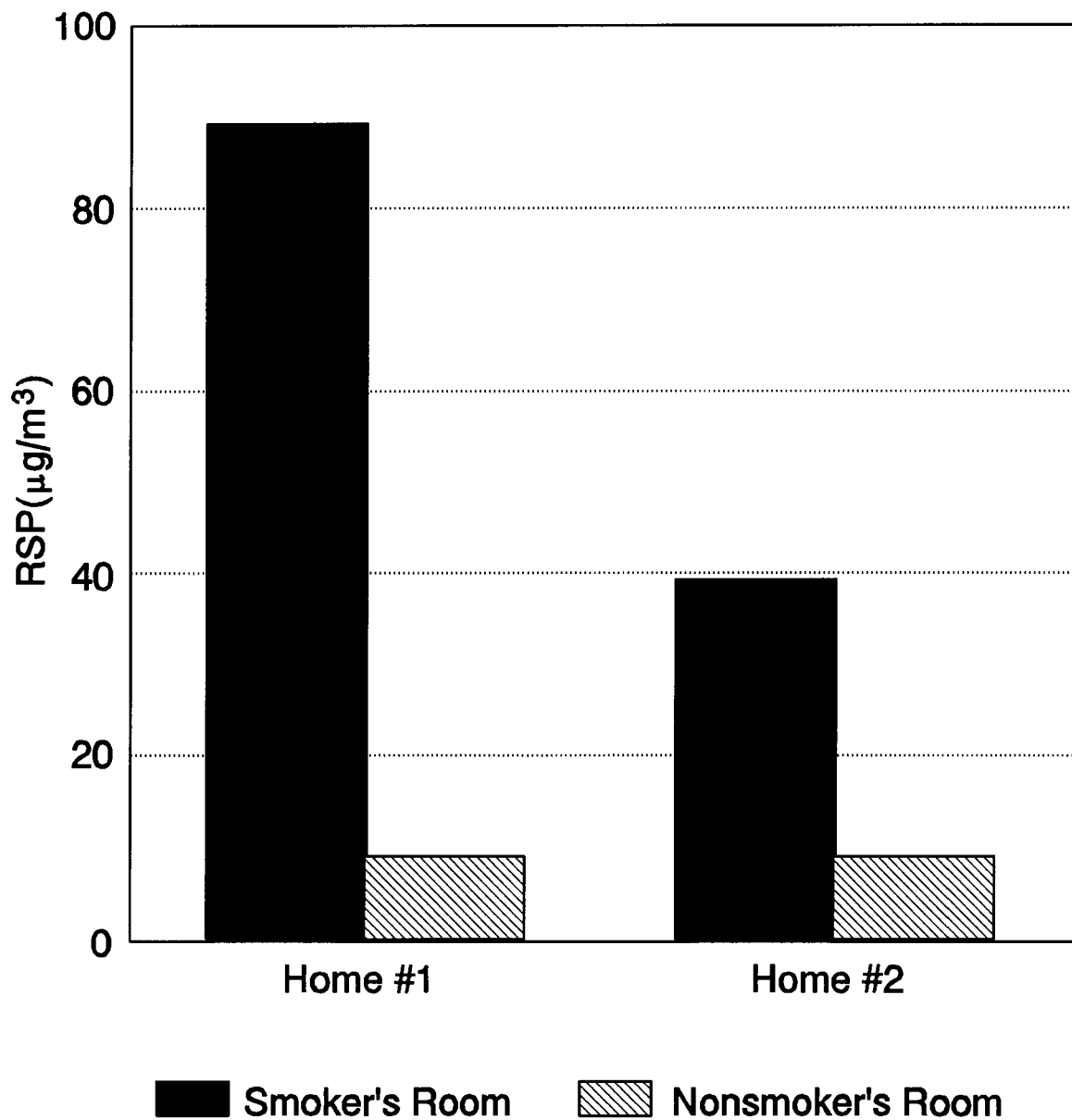
1 Ghia Zefluor Teflon filter for fine particles. The flow rate was 6 L/min for a 24-h sample.  
2 Three consecutive 24-h samples were collected at each building. Additional particle  
3 monitoring was provided at certain locations (e.g., smoking lounge, cafeteria) using a  
4 Piezobalance (PM<sub>3.5</sub>) and a dichotomous sampler (PM<sub>2.5</sub> and PM<sub>10</sub>).

5 In areas without smoking, indoor concentrations of both size fractions were generally  
6 lower than outdoor levels; for example, the coarse fraction ranged from 0.2 to 0.66 of the  
7 outdoor level (13 to 17 µg/m<sup>3</sup>) in the three buildings with no smoking. The fine fraction was  
8 present at higher indoor-outdoor ratios, ranging from 0.56 to 0.99 in the same three  
9 buildings (outdoor fine fraction ranged from 16 to 33 µg/m<sup>3</sup>). The fine fraction was elevated  
10 in the regions of smoking (range of 14 to 56 µg/m<sup>3</sup>). Piezobalance results for several  
11 buildings showed uniformly low (7 to 29 µg/m<sup>3</sup>) for 800 min of monitoring in nonsmoking  
12 areas.

13 Concentrations in the areas allowing smoking were more often in the 40 to 60 µg/m<sup>3</sup>,  
14 with short-term peaks as high as 345 µg/m<sup>3</sup> (Figure 7-30). It was possible to use the  
15 observed declines in PM<sub>3.5</sub> following cessation of smoking to calculate an effective air  
16 exchange rate and thus a source strength for PM<sub>3.5</sub> emissions from cigarettes. Four  
17 estimates gave an average value of about 6 mg/cigarette, somewhat below the chamber study  
18 estimates of 10 to 15 mg/cig. An estimate due to Repace and Lowrey (1980) of  
19 concentrations of respirable particulates due to smoking was also tested, with good  
20 agreement. The Repace and Lowrey equation is

$$C = 25.6 P_a / a$$

24 where  $P_a$  is smoking occupancy in persons per 1,000 square feet and  $a$  is the air exchange  
25 rate. The equation was developed assuming 1/3 of the occupants are smokers who smoke  
26 two cigarettes per hour. Assuming a background concentration of 15 µg/m<sup>3</sup>, the estimates  
27 for the smoking lounge for 0, 3, and 9 smokers were 10, 78, and 284 µg/m<sup>3</sup>, respectively.  
28 Repace's equation predicts 0, 99, and 296 µg/m<sup>3</sup>, respectively. In two of the homes for the  
29 elderly, apartments with smokers and nonsmokers were measured for three consecutive days  
30 using the NBS samplers. In one building, the smoker's apartment had a 3-day PM<sub>3</sub> average



**Figure 7-30. Respirable particles in smoking and non-smoking areas of homes for the elderly (arithmetic mean for 72 h).**

1 of 39  $\mu\text{g}/\text{m}^3$ , compared to 9.2  $\mu\text{g}/\text{m}^3$  in the nonsmoker's apartment; in the other home for  
 2 the elderly, where two smokers shared one apartment, the average 3-day  $\text{PM}_{2.5}$  concentration  
 3 was 89  $\mu\text{g}/\text{m}^3$  compared to 8.6  $\mu\text{g}/\text{m}^3$  in the nonsmoking apartment.

### 7.6.2.3 Studies in locations other than homes and buildings

Nagda et al. (1990) measured RSP in aircraft cabins using both gravimetric and optical methods. Although the methods did not agree well, they were averaged to produce an estimate of  $75 \mu\text{g}/\text{m}^3$  in the smoking sections,  $54 \mu\text{g}/\text{m}^3$  in the several "boundary rows" bordering the smoking sections, and 31 to  $35 \mu\text{g}/\text{m}^3$  in the middle and remote seats. Average concentrations on nonsmoking flights were 35 to  $40 \mu\text{g}/\text{m}^3$ . Nicotine concentrations were  $13.4 \mu\text{g}/\text{m}^3$  in the smoking section, but very low in all other sections (0.04 to 0.26 in nonsmoking sections of smoking flights, 0.00 to 0.08 in all areas on nonsmoking flights).

Oldaker et al. (1990) measured  $\text{PM}_{3.5}$  and nicotine in 33 restaurants in the Winston-Salem area during the summer of 1986 and the winter of 1988 to 1989. (In the winter season, the cutpoint was changed to  $\text{PM}_{2.5}$ .) A wide range of particle concentrations was noted, from 18 to  $1,374 \mu\text{g}/\text{m}^3$  in the summer, and  $<25$  to  $281 \mu\text{g}/\text{m}^3$  in winter. Nicotine concentrations also ranged over wide intervals, from 0.9 to  $25.6 \mu\text{g}/\text{m}^3$  in the summer, and  $<0.1$  to  $35.2 \mu\text{g}/\text{m}^3$  in the winter.

Lowrey et al. (1993) measured  $\text{PM}_{3.5}$  using a TSI Piezobalance in a number of outdoor and indoor locations in Budapest. Outdoor concentrations measured over 6 to 16-min periods ranged from 28 to  $150 \mu\text{g}/\text{m}^3$ , with three of the four values above  $100 \mu\text{g}/\text{m}^3$  associated with roadways (tram or bus stops). Indoor concentrations in seven areas without visible smoking ranged from 42 to  $100 \mu\text{g}/\text{m}^3$ ; in 19 areas with active smoking the range was from 56 to  $650 \mu\text{g}/\text{m}^3$ .

## 7.6.3 Indoor air quality models and supporting experiments

Indoor concentrations of particles are a function of penetration of outdoor particles and generation of particles indoors. The concentrations are modified by air exchange rates and decay rates of the particles onto indoor surfaces.

### 7.6.3.1 Mass Balance Models

Mass balance models have been used for more than a century in various branches of science. All such models depend on the law of the conservation of mass. They simply state that the change in mass of a chemically inert substance in a given volume is equal to the amount of mass entering that volume minus the amount leaving the volume. Usually they

are written in the form of first-order linear differential equations. That is, consider a volume  $V$  filled with a gas of mass  $m$ . The change in mass  $\Delta m$  over a small time  $\Delta t$  will simply be the difference between the mass entering the volume ( $m_{gain}$ ) and the mass leaving the volume ( $m_{loss}$ ):

$$\Delta m = m_{gain} - m_{loss} \quad (7-8)$$

Taking the limit as  $\Delta t$  approaches zero, we have the differential equation for the rate of change of the mass:

$$dm/dt = d/dt(m_{gain} - m_{loss}) \quad (7-9)$$

If we require that the mass be uniformly distributed throughout the volume at all times, we have a condition that the physical chemists call "well-mixed". We assume that any mass gained or lost in the volume  $V$  is instantaneously distributed evenly throughout the volume. We may then replace the mass terms by the concentration  $C = m/V$ :

$$VdC/dt = d/dt (m_{gain} - m_{loss}) \quad (7-10)$$

The above equation is the basis for all such mass-balance models. It takes on many forms depending on the type of processes involved in transporting mass into or out of the volume being considered. A large class of models assume that the volume is a single compartment. More complex models assume multiple compartments. As an example of a single compartment model, we may consider a room of volume  $V$  that exchanges air with the outside at a constant flow rate  $Q$ . We also assume that a mass of gas has been released in the room at time  $t = 0$ , and that the outdoor concentration of this gas is 0. (This is the situation, for example, when a tracer gas such as  $\text{SF}_6$  is released to determine the air

exchange  $a$ .) In this case, the gain in mass  $m_{gain}$  is zero and the loss in mass is equal to the flow rate  $Q$  out of the house times the concentration  $C$ , so that equation (7-10) becomes:

$$VdC/dt = -aVC \quad (7-11)$$

Integrating this equation by separation of variables, we have

$$C = C_0 e^{-at}. \quad (7-12)$$

where  $C_0$  is the concentration at time  $t = 0$ , and  $a = Q/V$  is the air exchange rate.

Thus we find that the original concentration of tracer in the room decays with a time constant  $a$ : the air exchange rate.

For a nonreactive gas with a nonzero outdoor concentration (e.g., carbon monoxide), the mass balance equation takes the form

$$dC_{in}/dt = a(C_{out} - C_{in}) \quad (7-13)$$

where  $C_{in}$  is the indoor concentration, and  $C_{out}$  is the outdoor concentration.

Depending on the variation with time of  $C_{out}$ , this equation has a number of solutions. If  $C_{out}$  is constant, for example, and the initial indoor concentration is zero, then the indoor concentration rises at a rate determined by the air exchange rate to approach an asymptotic value equal to the outdoor concentration:

$$C_{in} = C_{out}(1 - e^{-at}) \quad (7-14)$$

An early effort at developing an indoor air quality model was made by Shair and Heitner (1974). This was a mass balance model in which the building was represented as a single well-mixed chamber. A single first-order linear differential equation represented the change in mass of a pollutant due to infiltration, exfiltration, recirculation, source generation, and removal due to filters in the circulation system or deposition on surfaces. Shair and

Heitner (1974) solved the equation for certain simple inputs, such as a linearly increasing or decreasing outdoor concentration:

$$C_{out} = mt + b \quad (7-15)$$

Since the outdoor concentration normally is a slowly-varying function, Shair and Heitner's linear approximation is actually an excellent approximation for time intervals of moderate length.

If an indoor source  $S(t)$  exists, it enters the mass balance model in the following way:

$$dC_{in}/dt = a(C_{out} - C_{in}) + S(t)/V \quad (7-16)$$

where  $S(t)$  has the units of mass per unit time.

If the source has a constant generation rate (e.g., CO<sub>2</sub> emissions from a person at rest), then  $S(t)$  is a constant value  $S_0$  and the equation becomes

$$dC_{in}/dt = a(C_{out} - C_{in}) + S_0/V \quad (7-17)$$

If the substance of interest reacts or is adsorbed on surfaces while indoors, the equation becomes

$$dC_{in}/dt = aC_{out} - (a+k)C_{in} + S(t)/V \quad (7-18)$$

where  $k$  represents the loss of the substance due to chemical reaction, adsorption on surfaces, sedimentation, etc. The decay rate  $k$  has the same units as the air exchange rate  $a$  (1/time); their sum  $(a+k)$  may be thought of as an effective air exchange rate. The decay rate  $k$  is often used to apply to particles, which disappear faster indoors than a nonreactive gas such as CO. Since particles experience more difficulty than of a gas in penetrating the building envelope, a penetration factor  $f$  ( $f \leq 1$ ) is often applied that multiplies the outdoor concentration in Equation 7-18 above.

Alzona et al. (1979) applied the mass-balance equation with terms including a penetration coefficient  $f$  through the building envelope, adsorption on surfaces given by a rate  $k$  proportional to the indoor concentration  $C_{in}$ , and a resuspension rate  $R$ :

$$dC_{in}/dt = a f C_{out} - aC_{in} - kC_{in} + R. \quad (7-19)$$

Setting  $dC_{in}/dt = 0$ , the equilibrium solution is

$$C_{in} = (a f C_{out} + R)/(a+k) \quad (7-20)$$

The equation was tested against a series of experiments in which elements known to be of outdoor origin were collected under various experimental conditions and analyzed using X-rays. The authors concluded that  $f$  was of the order of 0.3 for many elements, and that resuspension did not appear to be particularly important. Measurement errors were fairly large (15 to 25%) and limited their ability to estimate values of these parameters.

As described above, Koutrakis et al. (1991) used least-squares analysis to solve a simplified form of the mass-balance model to determine source emission rates for particles and elements due to cigarettes, woodsmoke, and kerosene heater use. Koutrakis assumed a value for  $k$  in order to solve the equation for  $f$  and the source emission rates. Özkaynak et al. (1993) improved on Koutrakis' approach by using least-squares analysis of the PTEAM results to solve the equation simultaneously for  $k$ ,  $f$ , and source emission rates for  $PM_{2.5}$  and  $PM_{10}$  particles and associated elements for smoking and for cooking.

Axley and Lorenzetti (1991) developed an indoor model using an element-assembly computer language (STELLA) that is capable of handling any number of compartments and air flows between compartments. The model is based on an earlier model (CONTAM88) developed under EPA sponsorship.

Sparks et al. (1991) developed a more user-friendly version of the Axley model, with menus prompting the user to insert the necessary parameters.

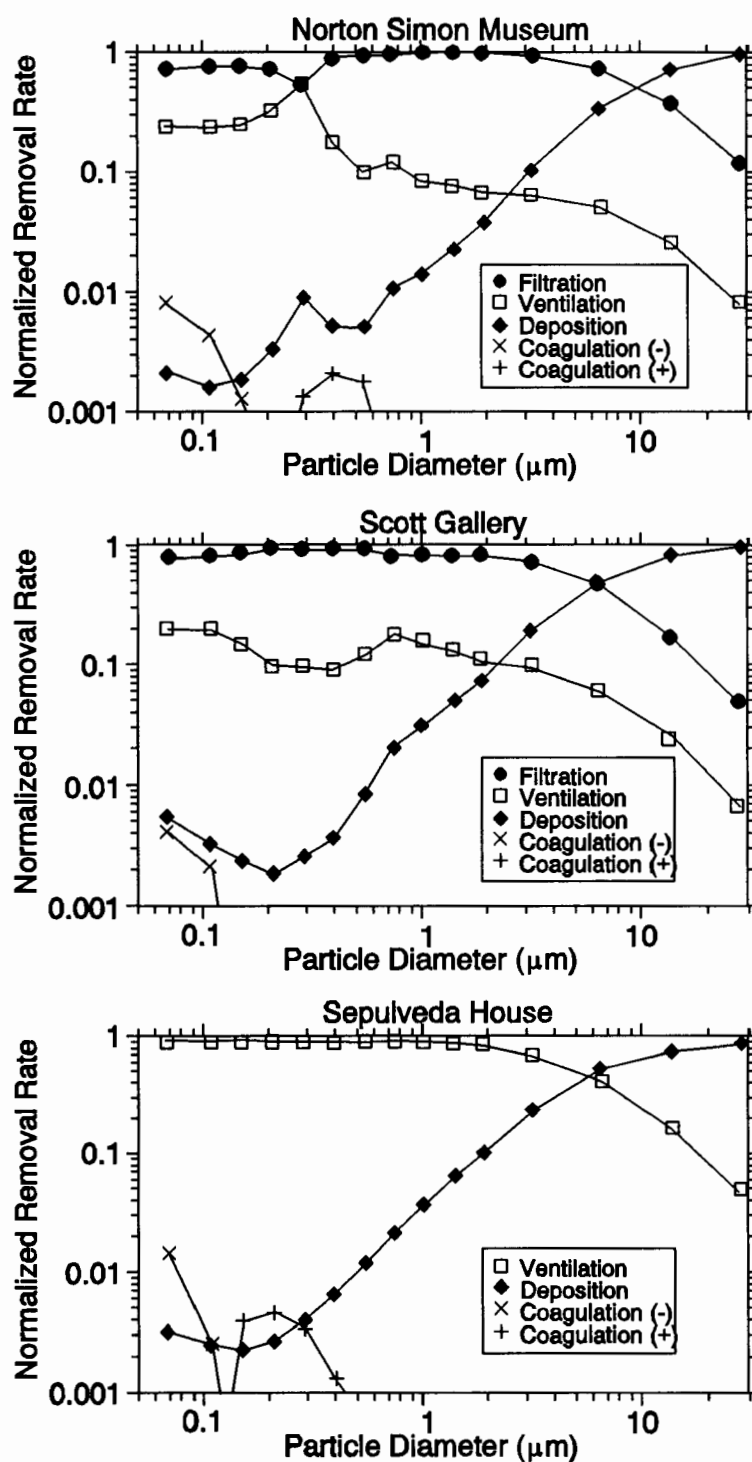
Traynor et al. (1989) developed a "macromodel" based on Monte Carlo simulations using global input data such as house volumes, air exchange rates, and emissions from combustion sources to assess residential concentrations of combustion-source pollutants such

1 as CO, NO<sub>2</sub>, and respirable suspended particles. For a home with only one combustion  
2 source during winter in upstate New York, at an outdoor temperature of 0 °C , and an  
3 outdoor RSP geometric mean concentration of 19 µg/m<sup>3</sup>, the model predicted geometric  
4 mean concentrations of about 80 µg/m<sup>3</sup> in a home with smoking, 75 µg/m<sup>3</sup> for a radiant  
5 kerosene heater, about 60 µg/m<sup>3</sup> for a convective unvented gas space heater and a non-  
6 airtight wood stove, and about 40 µg/m<sup>3</sup> for a radiant unvented gas space heater. An airtight  
7 wood stove was predicted to produce a geometric mean about 30 µg/m<sup>3</sup>. Gas ovens, dryers,  
8 hot water heaters, boilers, and forced-air furnaces were predicted to result in low indoor  
9 concentrations of 10 to 15 µg/m<sup>3</sup>, unless the gas oven was used for heating, in which case  
10 the predicted geometric mean was about 20 µg/m<sup>3</sup>.

11 At present, one of the most complete forms of the mass-balance indoor air quality  
12 model has been presented by Nazaroff and Cass (1989). These authors developed the model  
13 to allow for changes in particle size and chemical composition, including terms for  
14 homogenous turbulence, natural convection, thermophoresis, advection, and Brownian  
15 motion. Coagulation of particles is also included. The computer form of the model required  
16 40 to 60 min of CPU time to determine an 11-h evolution of an aerosol mixture of 16  
17 different sizes. The model was partially validated by checking it against the results of a  
18 chamber study using cigarette-generated aerosol to determine the effectiveness of air cleaners  
19 (Offermann et al., 1985).

20 A simplified form of the model was employed in a study of indoor air soiling potential  
21 in three California museums, two with new HVAC systems and one with only natural  
22 ventilation (Nazaroff et al., 1990a). Measured values of elemental carbon in fine (PM<sub>2</sub>)  
23 particles were 0.63, 0.16, and 5.6 µg/m<sup>3</sup> in the three museums compared to model estimates  
24 of 0.62 to 0.83, 0.22 to 0.23, and 4.9 µg/m<sup>3</sup>. The authors were able to predict the fate  
25 (i.e., the main removal process and the rate of removal) of particles of various sizes in the  
26 three museums (Figure 7-31). In the two newer museums, most particles below 10 µm were  
27 removed by filters; in the older museum, most PM<sub>10</sub> particles were removed by ventilation.  
28 In all three museums, the dominant fate of the larger particles was gravitational settling onto  
29 upward-facing surfaces. The authors concluded that perceptible soiling would occur in less  
30 than a year for the older museum, but would require 10 to 40 years for the newer museums.





**Figure 7-31. Predicted fate of particles penetrating into buildings of three California museums as a function of particle size. The ordinate of each point represents the fraction of the mass that is removed by the indicated process.**

Source: Nazaroff et al. (1990a).

1 The hanging of pictures at a slight downward-facing angle was predicted to greatly decrease  
2 the rate of soiling.

3 A crucial unknown parameter in the mass-balance model for particles is the rate of  
4 decay to surfaces. This rate of decay ( $k$ ) may be expressed as the product of a deposition  
5 velocity  $k_d$  with the surface to volume ratio in the room or building:

$$k = k_d S/V \quad (7-21)$$

7  
8 The deposition velocity will vary with particle size.

9 Both the Nazaroff study above and the series of studies by Weschler and colleagues  
10 below have provided useful data on deposition velocities for important anions such as  
11 sulfates.

12 A series of studies, also concerned with the effects of indoor particles on materials,  
13 were carried out by Weschler and colleagues at AT&T Bell Laboratories (Weschler et al.,  
14 1989; Sinclair et al., 1988, 1990, 1992). Studies of buildings with low occupancy, large  
15 amounts of electronic equipment, and high-quality filtering and HVAC systems succeeded in  
16 determining deposition velocities for coarse particles and various fine particle ions. For  
17 coarse particles, these velocities were about equal to velocities predicted for gravitational  
18 settling, similar to the results of Nazaroff et al. (1990a) described above. For fine particles,  
19 however, the deposition velocity was greater than that predicted for gravitational settling  
20 alone. For sulfates, the dominant anion in fine particles, deposition velocities at four  
21 buildings in Wichita, Lubbock, Newark, and Neenah were 0.004, 0.005, 0.005, and  
22 0.004 cm/s, respectively (Sinclair et al., 1992).

23 Nazaroff et al. (1993) reviewed these and other studies of deposition velocity. The  
24 authors pointed out that the studies by Weschler and colleagues and also one study in  
25 Helsinki (Raunemaa et al., 1989) had produced values of 0.003 to 0.005 cm/s for fine-mode  
26 sulfate, but that studies by Nazaroff and colleagues (Ligocki et al., 1990; Nazaroff et al.,  
27 1990) resulted in much smaller values of 0.00002 to 0.001 cm/s. It is not clear whether the  
28 differences are due to the many differences in surface materials and filtration systems in the  
29 different types of buildings (museums versus telephone equipment buildings) or to the  
30 different methods of determining deposition velocities. However, the discrepancy is clear  
31 evidence that further work is needed.

1 Because all large-scale studies of indoor air quality agree that the most important indoor  
2 source of fine particles is tobacco smoke, a brief review of models and chamber studies  
3 dealing with ETS is provided here.

#### 4 5 **7.6.3.2 Models of ETS**

6 Using the mass balance approach, a number of efforts have been undertaken to model  
7 mathematically the pollutant concentrations from tobacco smoke in indoor locations. For  
8 example, Brief (1960) proposed a simple graph to determine transient concentrations for  
9 pollutants in indoor settings that is based on an exponential decay as a function of time.  
10 Turk (1963) proposed a general equation for calculating the concentrations in a chamber that  
11 includes both exterior and interior sources, as well as the removal effect of pollutants by air  
12 treatment systems. Bridge and Corn (1972) reported that a solution to the equations  
13 proposed by Turk (1963) adequately predicts tobacco smoke in occupied spaces. Jones and  
14 Fagan (1974) used Turk's equation to calculate carbon monoxide (CO) concentrations versus  
15 time from cigarette smoke in an office building and a single-family dwelling. Ishizu (1980)  
16 examined experimentally the inclusion of a mixing factor in these models, and Repace and  
17 Lowrey (1980) developed a modification of the Turk equation incorporating a mixing factor.  
18 They model the concentration as a function of time (assuming an initial concentration of  
19 zero) as :

$$C = C_{\infty} [(1 - \exp(-(a+k)mt))] \quad (7-22)$$

21 where

22  $C_{\infty} = G/Vm$  (a+k) is the equilibrium concentration of ETS particles;

23  $m = a$  "mixing factor" to account for imperfect mixing'

24  $G =$  the generation rate, a function of the number of cigarettes being smoked and the total  
25 particle mass emitted from sidestream and exhaled mainstream smoke.

26 Using an estimated value for  $G$  of 24 mg/cigarette, Repace (1978b) arrived at an  
27 estimate for the steady-rate concentration of  $PM_{3.5}$  (in  $\mu g/m^3$ ) due to smoking:  
28  
29

$$PM_{3.5} = 217 D_{hs}/a \quad (7-23)$$

where  $D_{hs}$  is the density of "habitual smokers" (i.e., those who smoke two cigarettes per hour) per 100 m<sup>3</sup>, and the value of 217 incorporates a mixing factor and a particle decay rate based on empirical observations in a number of locations.

As reported in Repace and Lowrey (1982), equation 7-23 was partially validated by a chamber experiment reported later by Leaderer et al. (1984), in which the measured equilibrium concentration was 620 µg/m<sup>3</sup> compared to 478 µg/m<sup>3</sup> predicted by the equation, a difference of about 23%. Since equation 7-23 assumes a nation-wide sales-weighted average tar content, a small experiment using one or two brands of cigarettes would be expected to give somewhat different values (see discussion on page 7-49).

The concentrations of pollutants from ETS in a large mixing volume, such as a room, have been observed to increase once a cigarette starts to burn and to decay exponentially once the cigarette is put out (Brief, 1960; Ishizu, 1980; Repace and Lowrey, 1980, 1982; Leaderer et al., 1984; Repace, 1987). These exponential functions are solutions to the mass balance equation for the case of a source that emits at a fixed rate when it is on—and at zero rate when it is off—with a fixed air exchange rate. This source can be viewed as a "rectangular" input "time series" (concentration as a function of time) to the mass balance model.

Smokers ordinarily engage in a sequential smoking "activity pattern" over time: one cigarette is smoked after another, with a recovery period between each cigarette. A person in a room with a smoker (an office, an automobile, a smoking lounge, a restaurant) is exposed to a time series of concentrations resulting from a succession of cigarettes reflecting the smoking activity patterns of the smoker.

In recent research, the basic mass-balance model was adapted to the case of a sequence of cigarettes smoked one after another, and its effectiveness in predicting the pollutant concentrations as a function of time (the "time series" of concentrations) was tested using real-time monitoring instruments (Ott et al., 1992). This work has developed a model for computing the time series of pollutants generated by sequential cigarette smoking activity patterns, the Sequential Cigarette Exposure Model (SCEM). If  $t_i$  is the time at which

cigarette  $i$  begins, and  $s_i$  is the duration of cigarette  $i$ , then during the time the cigarette is being smoked, the particle concentration rises according to:

$$C = \frac{S(1 - \exp(-(a+k)(t-t_i)))}{V(a+h)} + C_{2i-2} \exp(-(a+k)(t-t_i)) \quad (7-24)$$

whereas between cigarettes the concentration declines:

$$C = C_{2i-1} \exp(-(a+k)(t-s_i-t_i)) \quad (7-25)$$

In these equations,  $C_{2i-2} = C(t_i)$  and  $C_{2i-1} = C(t_i + s_i)$ .

A computer program for the SCEM has been written in Microsoft QuickBASIC Version 4.5 programming language to apply to equations 7-24 and 7-25. This research also has derived theoretical equations for the minimum, maximum, and mean pollutant concentration in a well-mixed microenvironment for any cigarette smoking activity pattern. General expressions also have been derived for the case of the habitual smoker (uniform cigarette duration and same time between cigarettes) and for the case of multiple habitual smokers.

The equations used to derive the SCEM are general and are consistent with earlier ETS indoor air quality models that were derived for special cases (for example, Repace and Lowrey, 1980). Repace (1987), for example, described a person with uniform smoking activity (a constant rate of smoking per unit time) as an "habitual smoker." He considers the special case in which the habitual smoker smokes two cigarettes per hour, which is based on a national average smoking rate. The SCEM considers the general case in which each habitual smoker can have any smoking rate, and concentration is measured on a "real-time" (that is, continuous) basis.

Solutions to the mass balance equation provide a theoretical basis for calculating all parameters of the model—air exchange rate, source strength, and sink removal terms—in a single experiment. Because of the SCEM's fine time resolution, experiments to validate the model require monitoring instruments that operate with fine time resolution (minutes or seconds). The air exchange rate is determined from the exponential decay of concentrations

seconds). The air exchange rate is determined from the exponential decay of concentrations in the microenvironment (Ott et al., 1992). The source strength is determined from the equilibrium concentration with continuous smoking. The sink removal term for pollutants that adhere to surfaces, such as particles, is determined by subtracting the particle decay rate from the decay rate for a pollutant that has no surface sinks, such as CO.

Klepeis et al. (1995) applied an extension of the SCEM model (now called the Multiple Cigarette Exposure Model, or MCEM) to smoking lounges at the San Francisco, CA and San Jose, CA airports. Three Piezobalances were placed at each end and the center of the lounges. One investigator counted the number of lit cigarettes every minute while the other took readings from the Piezobalances. A Langan CO monitor took carbon monoxide readings continuously and logged them automatically. Five visits to each airport were made. During the fifth visit to each airport, an experiment was done to calculate the air exchange rate when there were few or no smokers present: several cigars were smoked and the decay of the CO level was measured, giving air exchange rates of 10.7 and 13.0 ach at the two airports. The calculated PM<sub>3.5</sub> source strengths for cigarettes during these two visits were identical at 1,340 µg/min. Air exchange rates were not determined at the other visits, but assuming the same rates resulted in an average PM<sub>3.5</sub> emission rate of 1,450 µg/min. The decay rate of the ETS-related PM<sub>3.5</sub> was estimated to be 0.048 and 0.034 min<sup>-1</sup>, or 2.88 and 2.04 h<sup>-1</sup>.

Ott et al. (1995a) tested the model in a tavern before and after smoking was prohibited. During 26 visits over a period of two years while smoking was allowed, indoor concentrations averaged 56.9 µg/m<sup>3</sup> above outdoor concentrations, compared to 5.9 µg/m<sup>3</sup> above outdoor levels on 24 visits in the first six weeks after smoking was prohibited. A second set of follow-up visits (matched by time of day, day of week, and season to the earlier visits) yielded an average concentration 13.1 µg/m<sup>3</sup> above outdoor levels. Using cigarette emission rates from the literature, the measured tavern volume of 521 m<sup>3</sup>, and a measured air exchange rate under "typical" conditions, a mass-balance model predicted 42.5 µg/m<sup>3</sup> for an average "continuous smoking" count of 1.17 cigarettes, comparing favorably with the observed average of 43.8 µg/m<sup>3</sup>.

Ott et al. (1995b) used Laplace transforms to apply the model to an experiment in which three Kentucky reference 2R1 cigarettes were smoked one after another in a 25.7 m<sup>3</sup>

1 bedroom. Resulting  $PM_{3.5}$  concentrations were measured in the bedroom and living room  
2 with a Piezobalance. Peak values reached  $5,500 \mu\text{g}/\text{m}^3$ , and about  $2,000 \mu\text{g}/\text{m}^3$  in the living  
3 room. The living room window was opened 2 h later, but concentrations were still in excess  
4 of  $100 \mu\text{g}/\text{m}^3$  after 4 h.

#### 6 **7.6.4 Summary and Conclusions**

7 At low outdoor levels of fine ( $PM_{3.5}$  or  $PM_{2.5}$ ) particles (as in most of the cities in the  
8 Six-City and New York State studies), mean indoor concentrations have been found to be  
9 twice as high as outdoor levels. At high outdoor levels, mean indoor concentrations have  
10 been about 10% lower than the mean outdoor concentrations in the two areas studied  
11 (Steubenville and Riverside). Indoor concentrations are considerably higher during the day,  
12 when people are active, than at night. Based on a mass-balance model, outdoor air was the  
13 major source of indoor particles in the PTEAM study, providing about 3/4 of fine particles  
14 ( $PM_{2.5}$ ) and 2/3 of inhalable particles ( $PM_{10}$ ) in the average home.

15 The three largest studies of indoor air particles in U.S. homes have all found that the  
16 single largest indoor source of fine particles is cigarette smoke, for homes with smokers.  
17 (EPA's NHAPS data show that 31% of U.S. homes have a smoker, down from 50 to 60% in  
18 years past). Estimates of the impact of a smoking home range from about  $30$  to  $45 \mu\text{g}/\text{m}^3$ ,  
19 and a of a single cigarette from  $1$  to  $2 \mu\text{g}/\text{m}^3$  for a 24-h period. Homes without smoking  
20 have indoor particle concentrations (both  $PM_{10}$  and  $PM_{2.5}$ ) that are sometimes below and  
21 sometimes above the outdoor levels. At low outdoor levels (as in most of the cities in the 6-  
22 City and New York State studies) indoor concentrations are generally higher—at high  
23 outdoor levels, they are slightly lower. Indoor concentrations are considerably higher during  
24 the day, when people are active, than at night.

25 The second largest identified indoor source of particles, as determined by the PTEAM  
26 Study and several smaller studies, is cooking. Slightly less than half of the PTEAM homes  
27 reported cooking on the day they were monitored. Estimates of the effect of cooking ranged  
28 from about  $10$  to  $20 \mu\text{g}/\text{m}^3$ . A few small studies confirm the effect of cooking on indoor  
29 particle levels, both  $PM_{10}$  and  $PM_{2.5}$ . The two other large-scale studies did not directly test  
30 for the effect of cooking, although the residual indoor concentrations in multivariate  
31 calculations led the authors to suggest that cooking could have contributed to the residual.

1 Kerosene heater use was determined to contribute about  $15 \mu\text{g}/\text{m}^3$  to indoor  
2 concentrations in one county but not the other in the New York State study. Also, a later  
3 effort using mass-balance calculations was unsuccessful in determining a contribution to  
4 particle mass from kerosene heater use in either county, although a somewhat smaller set of  
5 homes may have been responsible for this result. Gas stoves, wood stoves, and fireplaces  
6 were found to have no noticeable impact on total concentrations of particles, although many  
7 studies show an increase in PAH concentrations and some show an increase in mutagenicity  
8 of indoor air due to these combustion sources.

9 Vacuuming, dusting, and sweeping were found to contribute slightly but with doubtful  
10 significance to indoor levels in the PTEAM Study. House volume had a significant but small  
11 effect on particle concentrations, with values of  $-1$  to  $-2 \mu\text{g}/\text{m}^3$  per 1,000 cubic feet. Air  
12 exchange rates were also significant at times, but with different impacts depending on the  
13 relative indoor and outdoor concentrations—at high outdoor concentrations, increased air  
14 exchange resulted in increases in the indoor air particle levels.

15 Unknown indoor sources were found to account for a substantial fraction (25%) of  
16 indoor concentrations (both  $\text{PM}_{2.5}$  and  $\text{PM}_{10}$ ) in the PTEAM study. This suggests a need for  
17 further research to determine the source or sources of these particles.

18 Decay rates for fine ( $\text{PM}_{2.5}$ ) particles were determined to be about  $0.4 \text{ h}^{-1}$  compared to  
19  $1 \text{ h}^{-1}$  for coarse particles, with an intermediate estimate of  $0.65 \text{ h}^{-1}$  for  $\text{PM}_{10}$ . For a home  
20 with no indoor sources whatever and a typical air exchange rate of about  $0.75 \text{ h}^{-1}$ , this  
21 would imply that fine particles indoors would be about  $0.75/(0.4+0.75) = 65\%$  of the  
22 outdoor value at equilibrium, indoor  $\text{PM}_{10}$  would be about 54% of outdoor levels, and indoor  
23 coarse particles would be about 43% of outdoor levels. Since very few homes were  
24 observed to have concentrations this low, it can be inferred that very few homes are free of  
25 important indoor sources of particles.

26 Studies in buildings also indicated that smoking was the major indoor source of  
27 particles, with a geometric mean of 44 versus  $15 \mu\text{g}/\text{m}^3$  (arithmetic mean of 70 versus  
28  $18 \mu\text{g}/\text{m}^3$ ) observed for smoking versus nonsmoking areas in 38 Pacific Northwest buildings.  
29 This difference of 29 to  $52 \mu\text{g}/\text{m}^3$  is similar to the difference of 30 to  $45 \mu\text{g}/\text{m}^3$  estimated  
30 from the three major studies of U.S. homes.



1 Indoor air quality models have been employed with increasing success to estimate  
2 source emission rates and particle decay rates. Cigarettes in homes with normal activities  
3 appear to emit about 14 mg/cigarette, a result that agrees well with various chamber studies  
4 using smokers or smoking machines. Cooking was estimated to emit 4 mg/min, a result that  
5 needs confirmation by other studies. Elemental emission profiles have been determined for  
6 both smoking and cooking, with potassium and chloride being major markers for smoking,  
7 and iron and calcium for cooking. Particle decay rates have been estimated for homes to  
8 range between 0.4 and 1.0 h<sup>-1</sup>. Studies in telephone equipment buildings and museums have  
9 established particle deposition velocities for sulfates and other ions, although differences in  
10 the estimates suggest that further research is needed.

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