External Review Draft No. 2
January 1981

Draft
Do Not Quote or Cite

Air Quality Criteria for Particulate Matter and Sulfur Oxides

Volume II

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.

Environmental Criteria and Assessment Office
Office of Health and Environmental Assessment
Office of Research and Development
U.S. Environmental Protection Agency
Research Triangle Park, N.C. 27711

NOTE TO READER

The Environmental Protection Agency is revising the existing criteria documents for particulate matter and sulfur oxides (PM/SO_x) under Sections 108 and 109 of the Clean Air Act, 42 U.S.C. §§ 7408, 7409. The first external review draft of a revised combined PM/SO_x criteria document was made available for public comment in April 1980.

The Environmental Criteria and Assessment Office (ECAO) filled more than 4,000 public requests for copies of the first external review draft. Because all those who received copies of the first draft from ECAO will be sent copies of the second external review draft, there is no need to resubmit a request.

To facilitate public review, the second external review draft will be released in five volumes on a staggered schedule as the volumes are completed. Volume I (containing Chapter 1), Volume II (containing Chapters 2, 3, 4, and 5), Volume III (containing Chapters 6, 7, and 8), Volume IV (containing Chapters 9 and 10), and Volume V (containing Chapters 11, 12, 13, and 14) will be released during January-February, 1981. As noted earlier, they will be released as volumes are completed, not in numerical order by volume.

The first external review draft was announced in the Federal Register of April 11, 1980 (45 FR 24913). ECAO received and reviewed 89 comments from the public, many of which were quite extensive. The Clean Air Scientific Advisory Committee (CASAC) of the Science Advisory Board also provided advice and comments on the first external review draft at a public meeting of August 20-22, 1980 (45 FR 51644, August 4, 1980).

As with the first external review draft, the second external review draft will be submitted to CASAC for its advice and comments. ECAO is also soliciting written comments from the public on the second external review draft and requests that an original and three copies of all comments be submitted to: Project Officer for PM/SO_x, Environmental Criteria and Assessment Office, MD-52, U.S. Environmental Protection Agency, Research Triangle Park, N. C. 27711. To facilitate ECAO's consideration of comments on this lengthy and complex document, commentators with extensive comments should index the major points which they intend ECAO to address, by providing a list of the major points and a cross-reference to the pages in the document. Comments should be submitted during the forthcoming comment period, which will be announced in the Federal Register once all volumes of the second external review draft are available.

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PREFACE

This document is a revision of External Review Draft No. 1, Air Quality Criteria for Particulate Matter and Sulfur Oxides, released in April 1980. Comments received during a public comment period from April 15, 1980 through July 31, 1980, and recommendations made by the Clean Air Scientific Advisory Committee in August have been addressed here.

Volume II contains Chapters 2, 3, 4, and 5 which cover analytical techniques, sources, emissions, environmental concentrations and exposure of sulfur oxides and particulate matter. A Table of Contents for Volumes I, II, III, IV, and V follows.

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2. PHYSICS AND CHEMISTRY OF SULFUR OXIDES AND PARTICULATE MATTER

2.1 INTRODUCTION

The purpose of this chapter is to present the state of our knowledge of the chemistry and physics of sulfur oxides and particulate matter that is pertinent to tropospheric phenomena, effects and sampling methodology. The 1970 Sulfur Oxides and Particulate Matter Air Quality Criteria Documents at the time of their publication provided an adequate description of our knowledge of the ambient chemistry and physics of sulfur oxides and particulate matter. However, significant progress has been made since that time in our understanding of tropospheric properties and processes. While this chapter focuses mainly on the advances of the past decade, earlier work is mentioned for the sake of completeness.

This chapter is organized into three principal parts with the following scope:

A. Atmospheric Domain and Processes
   - --global sulfur cycle
   - --atmospheric sulfur cycle
   - --pathways and processes

B. Physics and Chemistry of Sulfur Oxides
   - --gaseous physical properties
   - --solution physical properties
   - --gas-phase chemical reactions (elementary rate constants for SO_2 oxidation; influence of volatile organics and nitrogen oxides)
   - --solution-phase chemical reactions (reaction kinetics for oxidation by O_3, H_2O_2, and catalysts; limitations of reported studies)
   - --surface chemical reactions (metal oxides and carbon)

C. Physics and Chemistry of Particulate Matter
   - --definitions of aerosol science terms
   - --physical properties of gases and particles (size, shape, density, morphology, charging, optical, adhesion, vapor pressure)
   - --dynamics of single particles (sedimentation, impaction, diffusion, electrodynamics)
   - --formation and growth of particles (nucleation, coagulation, condensation, gas-particle chemical reaction)
   - --characterization of atmospheric aerosol (size, area, volume, mass distributions; atmospheric particle distributions; composition of fine and coarse particle mass fractions)
   - --modeling of general aerosol systems (theoretical formulations, results of model predictions)

The evidence cited (and in some cases the lack of available evidence) is presented in this chapter in order to reach the following conclusions in regard to SO_2 and particulate matter:

*

A. The physics and chemistry of SO_2

1. The thermodynamic properties, molecular structure and bonding, and electromagnetic absorption spectra in air and dissolved in water are well established, except for hygroscopic/deliquescent properties of internally mixed salts.

2. Of the homogeneous gas-phase SO_2 oxidation reactions, only three have been identified as being potentially significant in the troposphere:

a. OH radical attack on SO_2

b. HO_2 radical attack on SO_2

c. CH_3O_2 radical attack on SO_2

3. The auto-oxidation (uncatalyzed) reaction of SO_2 dissolved in liquid water is too slow to be an important reaction in the troposphere.

4. The Mn(II)- and Fe(III)- catalyzed oxidation of SO_2 dissolved in liquid water may be an important reaction in the troposphere. However, there is serious doubt regarding the rate expression for the Mn(II)-catalyzed oxidation.

5. The effectiveness of Cu(II), V(V), V(IV), Ni(II), Zn(II), and Pb(II) as catalysts for the oxidation of SO_2 dissolved in liquid water are unknown.

6. The lack of knowledge of the effectiveness of dissolved organics and of bicarbonate ion (HCO_3^-) as inhibitors prevents the use with confidence of aqueous-phase SO_2 catalyzed oxidation rate expressions for tropospheric model prediction.

7. Elemental carbon (soot) particles coated with an aqueous film are potentially important catalysts for SO_2 oxidation in the troposphere.

8. The reaction rate expressions of dissolved O_3 and dissolved NO_2 with dissolved SO_2 species are known, but these reactions appear to be ineffective for sulfate formation in the troposphere.

9. The rate expression for dissolved H_2O_2 and dissolved SO_2 species is known and appears to be a potentially highly effective reaction for sulfate formation in the troposphere.

10. SO_2 reactions with solid-particle surfaces are not effective for sustained sulfate formation in the troposphere.

B. The physics and chemistry of particulate matter

1. The physical properties of gases that affect aerosol behavior are well-known.

2. The physical characteristics of tropospheric particles are highly variable, but the physics through which they influence aerosol behavior is well-known.

3. For tropospheric aerosols over land, the particle mass distribution function ($\Delta M/\Delta$ log Diam. v. log Diam.) is often multi-modal. The fine particles (diameter less than 2.5 μm) may have two (or more) modes, usually at about 0.02 μm and at about 0.2 μm. The coarse particles (greater than 2.5 μm) generally have one mode in the range 5 to to 50 μm.

4. The mass composition of the coarse particles is dominated by minerals whose direct source types are well-known.

*

5. The mass composition of the fine particles is dominated by sulfate ions, organics, elemental carbon (soot), nitrate ions, and ammonium ions whose direct and indirect source types are well-known.

6. The chemical pathways for forming the sulfate ions, organics, and nitrate ions found in the fine particles are not established.

7. Strong acids are often found in the fine mass fraction, while bases are found in the coarse mass fraction.

8. The molecular composition of the organic compounds (generally found in the fine mass fraction) is not well-characterized.

9. Water is the major constituent of the particle mass, but the deliquescence and hygroscopic properties of mixed salts cannot be predicted reliably.

10. The dynamics of motion with a particle of diameter less than 10 μm can best be described in terms of the physical characteristics of the particle, the force fields present, and the motion of the suspending gas. However, our ability does not adequately extend to larger particles, especially in the presence of non-steady force fields and motions of the suspending gas. This limitation restricts our ability to properly sample ambient particles with diameters greater than 10 μm.

11. Fundamental problems remain in our knowledge of the aerosol process of nucleation, condensation, and coagulation, but these processes are sufficiently understood to explain and predict the behavior of aerosols in the troposphere.

12. Theoretical predictions confirm atmospheric observations that condensation, gas-particle reactions, and coagulation are important processes only for the growth of fine particles as opposed to coarse particles.

13. Qualitatively, a fairly reliable picture has been developed of the various rate processes that alter the composition and concentration of tropospheric particles over land. The rate of change of particle composition or concentration

= rate of change due to air motions (advection, convection, and dispersion)
+ rate of change due to particle coagulation
+ rate of change due to condensation and accretion
+ rate of change due to input of sources
+ rate of change due to dry removal at the earth's surface (sedimentation, impaction, diffusion)
+ rate of change due to wet removal

2.2 ATMOSPHERIC DOMAIN AND PROCESSES

The rationale for scientific interest in various physical properties and chemistry of sulfur oxides and particulate matter must be explained. Sulfur has an important natural cycle (see Figure 2-1) in the environment in which it goes through various oxidation and reduction reactions and translocations among the atmosphere, biosphere, hydrosphere, pedosphere, and

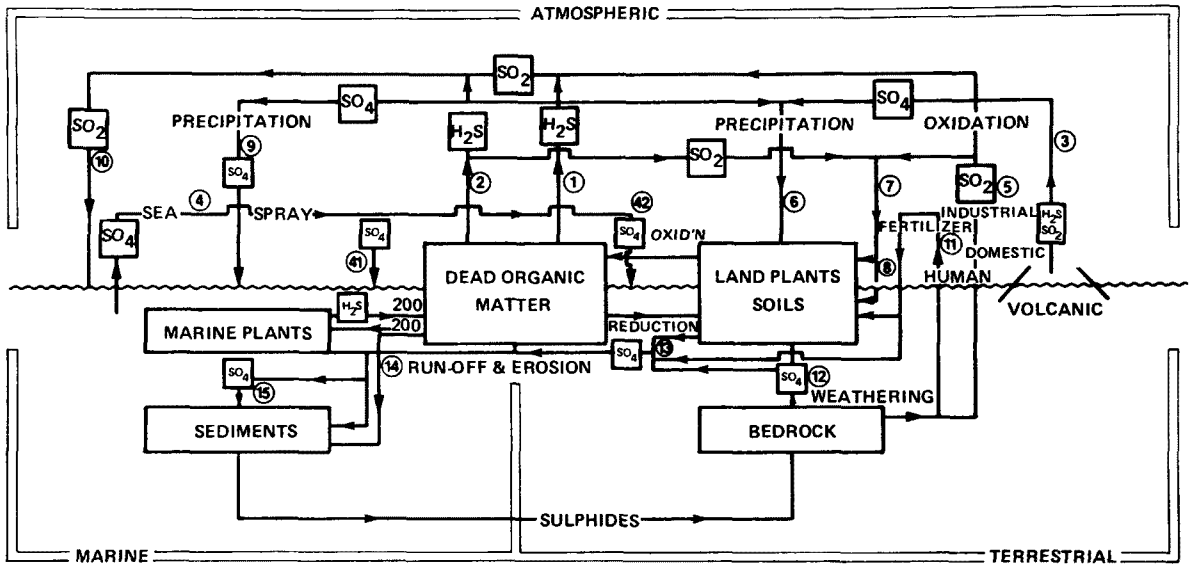

Figure 2-1. The global sulfur cycle, showing the major reservoirs, pathways, and forms of occurrence of sulfur. Figures enclosed in circles (e.g. 1) refer to the individual fluxes and correspond to figures in column 1, Table 2-1.

Source: Moss (1978).

*
lithosphere. Human activity (especially fossil-fuel combustion) has added a major perturbation to the natural cycle (and perhaps modified natural rates and reservoirs). The global sulfur cycle (Moss, 1978) is shown in Figure 2-1, with the major reservoirs, pathways, and forms of sulfur indicated. The fluxes of sulfur translocation between reservoirs have been estimated for the paths that are numbered in Figure 2-1. The estimates of annual fluxes are presented in Table 2-1. The agreement among the reported values is not good; for example, the estimates of annual anthropogenic sulfur fluxes to the atmosphere range from 11 to 45 percent of the total sulfur involved in the atmospheric balance. The global cycles of carbon and nitrogen and their mutual interactions with the sulfur cycle are important, but too complex to present here.

While the global sulfur cycle (Figure 2-1) and the annual fluxes of sulfur between compartments (Table 2-1) provide a broad view of the processes that may lead to adverse impacts upon mankind and ecological systems, the global scale is clearly beyond the scope of this document. Also, the sulfur and particulate matter emissions are not uniformly distributed over the land mass of the United States, nor is the time scale of one year adequately sensitive to relate emissions to effects.

Cause-effect relationships are described in terms of certain length and time scales. Consequently, our understanding of the physics and chemistry of sulfur oxides and particulate matter must correspond to those length and time scales. The characteristic time and length scales for typical effects are shown in Table 2-2; also the parameters that control the functions relating the effects to pollutants are given. The relationships of emissions to effects as shown in Table 2-2 require that we understand the physics and chemistry of sulfur oxides and particulate matter on time scales of one hour to decades and length scales of 10 to 100 km. With these constraints, our attention is focused on that portion of the global sulfur cycle that consists of the perturbed atmosphere over land surfaces. Most of the natural and anthropogenic emissions of sulfur oxides and particulate matter are contained within the troposphere, which is the layer of air contained in the zone from ground level to a height of 12 ± 5 km. This zone contains most of the pollutants emitted into the atmosphere.

Thus, in order to understand the relationships between sources and effects, we must have detailed knowledge of the pathways, properties, and processes that are shown in Figure 2-2.

Chapter 2 presents a discussion on the state of knowledge of physical properties, chemistry, and gas-to-aerosol transformations. The dry and wet removal pathways are discussed in Chapter 6, which also addresses modeling of atmospheric dispersion, transport, transformation, and removal.

2.3 PHYSICS AND CHEMISTRY OF SULFUR OXIDES

Knowledge of the physics and chemistry of sulfur oxides is necessary for the designing of satisfactory samplers and monitors, understanding the relationships between sources and effects, and understanding important processes in the troposphere such as chemical transformations and deposition.

*

TABLE 2-1. ANNUAL FLUXES (TG/YEAR) OF ENVIRONMENTAL SULFUR[a]

Source of Sulfur	Flux Number in Figure 2-1	Eriksson (1960, 1963)	Robinson and Robbins (1968, 1970)	Kellogg et al., (1972)	Friend (1973)	Granat et al. (1976)
Biological decay (land)	1	110	68	90	58	5
Biological decay (ocean)	2	170	30		48	27
Volcanic activity	3	--	--	1.5	2	3
Sea spray (total)	4	45	44	47	44	44
To ocean	4_1	(40)	--	(43)	(40)	(40)
To land	4_2	(5)	--	(4)	(40)	(40)
Anthropogenic	5	40	70	50	65	65
Precipitation (land)	6	65	70	86	86	43
Dry deposition	7	100	20	10	20	28
Absorption (vegetation)	8	75	26	15	15	
Precipitation and dry deposition (ocean)	9	100	71	72	71	73
Absorption (ocean)	10	100	25	--	25	
Total sulfur involved in atmospheric balance		365	212	183	217	144
Atmospheric balance						
Land → sea		-10	+26	+5	+8	+18
Sea → land		5	4	4	4	17
Fertilizer	11	10	11	--	26	--
Rock weathering	12	15	14	--	42	--
Pedosphere → river runoff	13	55	48	--	89	--
Total river runoff	14	80	73	--	136	122

[a]Sources: as cited in each column and, in part, Friend (1973, Table 4).

*

TABLE 2-2. CHARACTERISTIC TIMES AND LENGTHS FOR OBSERVATION OF EFFECTS

Types of Effects	Function	Time	Length
Damage to ecosystems and materials due to SO_2 and particulate mass deposition (see Chapters 7, 8, and 10)	Acid flux (= acid and SO_2 mass concentration x deposition velocity)	hours to years	$10\text{-}10^3$ km
Loss of visual quality (see Chapter 9)	Mass concentration, particle size distribution, and composition	Hours to days	$10\text{-}10^3$ km
Climate modification (see Chapter 9)	Atmospheric burden of particle mass, particle size, and composition	decades	global
Damage to human lungs due to SO_2 and particulate inhalation/ deposition (see Chapters 11 & 12)	Mass concentration, particle size distribution, composition	hour to years	<1 cm

In Section 2.3, the physical properties and reaction chemistry of sulfur oxides in the gas and solution phases are reviewed. The status of our knowledge in these important areas in presented at the end of each of the subsections.

2.3.1 Physical Properties of Sulfur Oxides in the Gas Phase

The four known monomeric sulfur oxides are sulfur monoxide (SO), sulfur dioxide (SO_2), sulfur trioxide (SO_3), and disulfur monoxide (S_2O). Of these, only SO_2 is present at significant concentrations in the gas phase of the troposphere. SO_3 is emitted directly into the atmosphere by combustion and manufacturing sources and is formed in the atmosphere by oxidation of SO_2; however, because of its high affinity for water (H_2O), it reacts within milliseconds to form sulfuric acid (H_2SO_4). Polymeric sulfur oxides are known to exist, but they are not stable in the presence of H_2O vapor and are not found in the atmosphere.

Since the standard enthalpy of formation of SO_2 is -70.9 kcal/mole (25°C), SO_2 is thermodynamically stable (Glasstone, 1947). SO_2 is capable of being oxidized to SO_3, which yields H_2SO_4 in the atmosphere (the important tropospheric reactions are discussed in Sections 2.3.3 to 2.3.5). SO_2 is also capable of being reduced by reaction with H_2S to form elemental S (known as the Clauss Reaction); this reaction is important commercially, but is not thought to be important in the troposphere. The physical properties of SO_2, including its molecular

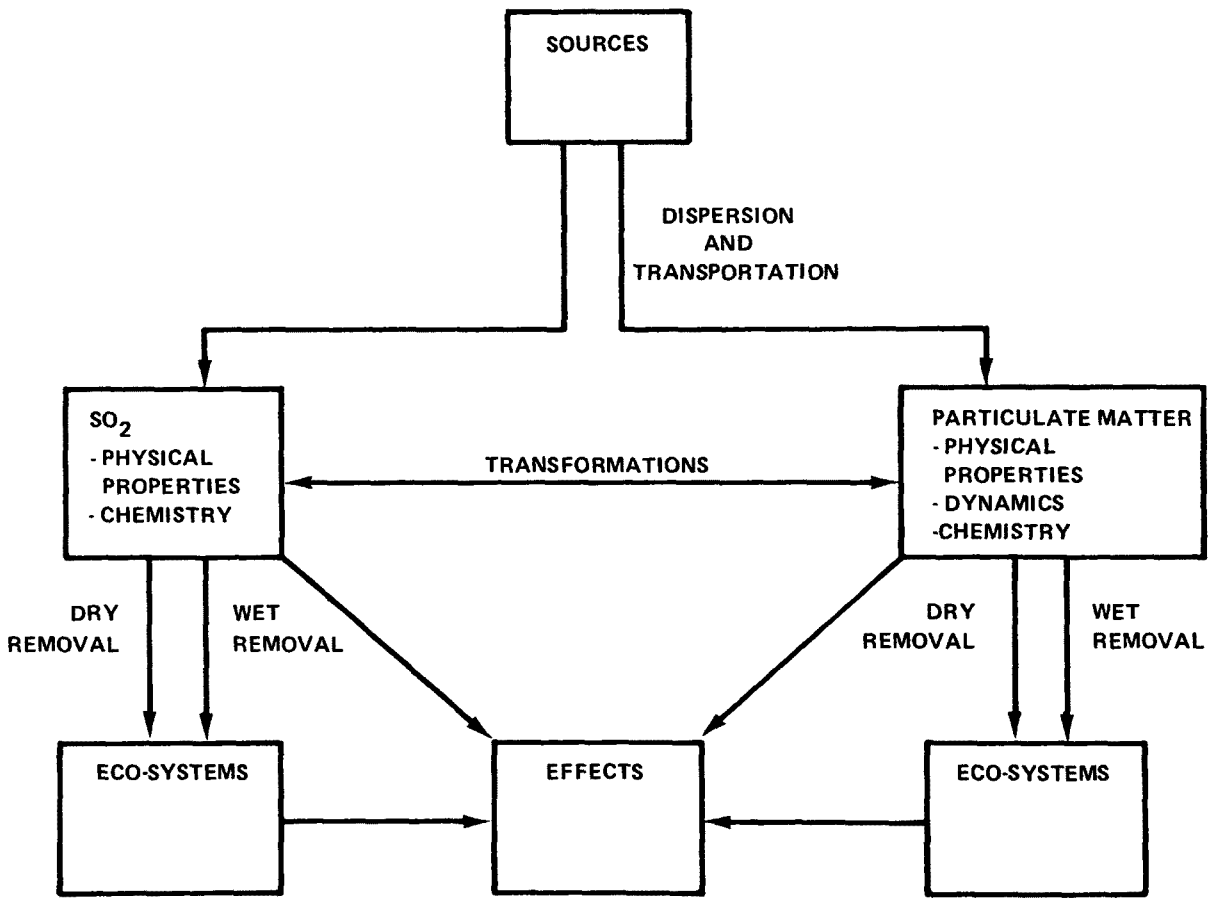

Figure 2-2. Inter-relations of pathways, processes, and properties of sulfur oxides and particulate matter and effects.

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structure and bonding, vapor pressure of liquid and solid phases, electro-magnetic absorption (ultra-violet, visible, and infrared) spectra, and thermodynamic constants are well established. Extensive descriptions and references to original work can be found in Schenk and Steudel (1968) and in Schroeter (1966).

The physical properties of gaseous SO_2 are well-known.

2.3.2 Solution Physical Properties

Knowledge of the physical properties of dissolved SO_2 solution species and sulfates is required for sampler design, interpretation of laboratory measurements of SO_2 oxidation, and modeling SO_2 oxidation in particles, fog, and rain.

2.3.2.1 SO_2--SO_2 dissolves in H_2O to form these species: $SO_2 \cdot H_2O$, HSO_3^-, and SO_3^{2-}. Although the formation of sulfurous acid, H_2SO_3, is often postulated instead of $SO_2 \cdot H_2O$, it has not been observed (Lyon and Nickless, 1968). The electronic absorption spectra (Hayon et al., 1972), redox potentials (Valensi et al., 1966), and structure and bonding (Lyons and Nickless, 1968) of HSO_3^- and SO_3^{2-} are known. The formation of these species in water occurs through the equilibrium reactions given in Table 2-3. Eigen et al. (1961) measured the forward (k_{+1}) and reverse (k_{-1}) rate constants at 20°C for reaction

$$SO_2 \cdot H_2O \rightleftarrows H^+ + HSO_3^-$$

and found that

$$k_{+1} = 3.4 \times 10^6 s^{-1}$$
$$k_{-1} = 2 \times 10^8 M^{-1} s^{-1}.$$

These measurements are important because they demonstrate that the $SO_2 \cdot H_2O$ - HSO_3^- reaction will achieve equilibrium within 1 μs of a perturbation. The rate constants k_{+2} and k_{-2} for the reaction

$$HSO_3^- \rightleftarrows H^+ + SO_3^{2-}$$

are unknown. It is reasonable that the value of the protonation rate constant (k_{-2}) is less than the theoretical diffusion limit (~5 x 10 $^{10}M^{-1}s^{-1}$), but greater than k_{-1}. The expected range of k_{+2} is therefore (0.008-2) x $10^3 s^{-1}$, which means that SO_3^{2-} will achieve equilibrium concentration within 0.5-125 ms of a perturbation. Thus, the equilibrium distribution of the $SO_2 \cdot H_2O$, HSO_3^-, and SO_3^{2-} is expected to achieve chemical equilibrium with a relaxation time of 0.5 to 125 ms. This time is too short to impact sulfate formation rates in particles, mists, and rain; that is, equilibrium conditions can be assumed to be continuously satisfied in these liquid systems. However, the relaxation times need to be considered in interpreting the kinetics of rapid oxidation, such as measured in flash photolysis and flash radiolysis experiments.

TABLE 2-3. DILUTE SULFUR DIOXIDE-WATER SYSTEM

Reaction	Constant (25°C)
$SO_{2(g)} \rightleftarrows SO_2 \cdot H_2O$	$H = 0.0332$
$SO_2 \cdot H_2O \rightleftarrows H^+ + HSO_3^-$	$K_{A1} = 1.39 \times 10^{-2}$ $pK_{A1} = 1.86$
$HSO_3^- \rightleftarrows H^+ + SO_3^{2-}$	$K_{A2} = 4 \times 10^{-8}$ $pK_{A2} = 7.40$

Notes:

1. H = Henry's law constant (dimensionless)
   $=(SO_{2(g)}$ molar concentration$)/(SO_2 \cdot H_2O$ molar concentration$)$
   Source of value: Hales and Sutter (1973)

2. K_{A1} = dissociation constant, mole/liter
   Source of value: Huss and Eckert (1977)

3. K_{A2} = dissociation constant, mole/liter
   Source of value: Salomaa et al. (1969)

An important feature of the $SO_2 \cdot H_2O$ - HSO_3^- - SO_3^{2-} system is the influence of H^+ in governing the distribution of these species, which is shown in Eigure 2-3. Ihe oxidation rate of this system is often pH dependent, indicating different oxidation rates for the three species. Ihe oxidation reactions are discussed in Section 2.3.4.

Sulfite ion forms stable complexes with many metal ions, especially those in Periodic Group VIII (Lyons and Nickless, 1968). Ihe formation of the stable complex dichlorosulfitomercurate ion is the basis of the West-Gaeke method for determining SO_2 in the air (see Chapter 3).

Ihe physical properties of dissolved SO_2 and its water-association products are well known.

2.3.2.2 SO_3 and H_2SO_4--Knowledge of the properties of SO_3 and H_2SO_4 are important for the design of samplers and monitors, and for understanding the behavior of ambient particles, fogs, and rain.

SO_3 has a high affinity for water and is not present at significant concentrations in the atmosphere. Eree SO_3 molecules have a high affinity for water molecules and water droplets and quickly react to form H_2SO_4 water solution droplets. Ihe vapor pressure of SO_3 over H_2SO_4

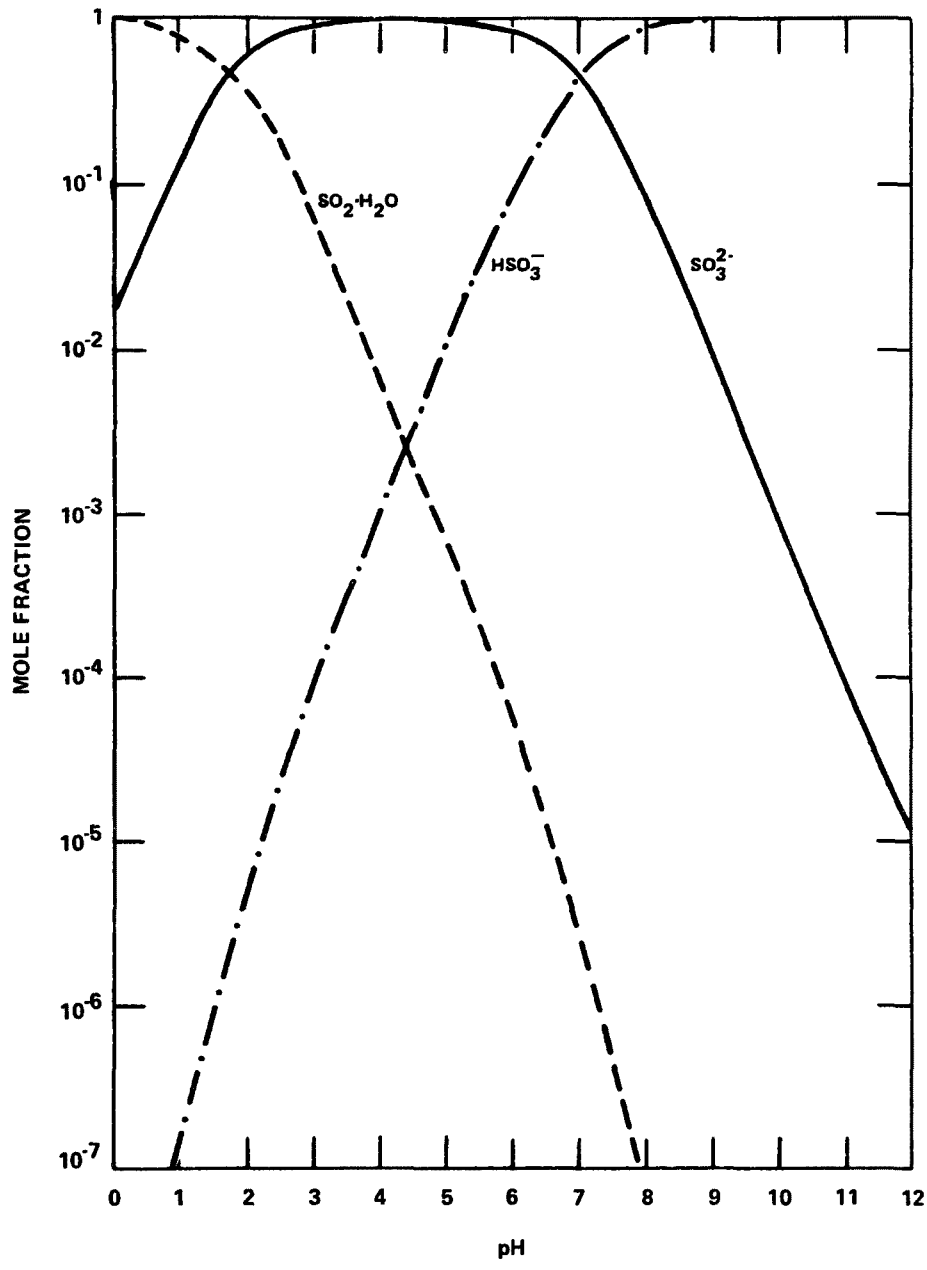

Figure 2-3. The distribution of species for the $SO_2 \cdot H_2O$-HSO_3^--SO_3^{2-} system as a function of pH.

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water solutions is extremely low; the vapor pressure of H_2O over H_2SO_4 water solution is an important parameter governing nucleation of particles and the size and pH of water droplets in the atmosphere. (See the discussion in Section 2.4.4.)

H_2SO_4 is the only important strong sulfur oxy acid in the troposphere. Its solution properties are well known. H_2SO_4 is a strong dibasic acid that reacts with water:

$$H_2SO_4 \rightarrow H^+ + HSO_4^-$$

$$HSO_4^- \rightarrow H^+ + SO_4^{2-}$$

For water systems likely to be present in the troposphere, the first dissociation can be considered to be complete. The pK_A of the second dissociation is ~2 (Robinson and Stokes, 1970). Thus, for pH >3, the H_2SO_4 - H_2O system can adequately be described in terms of H^+ and SO_4^{2-}; for lower pH's, it is often necessary to consider the presence of HSO_4^-

Sulfuric acid is not considered to be a strong oxidizer (Cotton and Wilkerson, 1967). Dilute H_2SO_4 solution is an important medium for organic reactions; however, the significance of this role in the troposphere has not been reported.

Most sulfate salts are soluble; the only important exceptions in the troposphere are $CaSO_4$ and $PbSO_4$. The properties of tropospheric aerosols are influenced by NH_4HSO_4 and $(NH_4)_2SO_4$ (see Section 2.4.4).

2.3.3 Gas-Phase Chemical Reactions of Sulfur Dioxide

The chemical transformation of sulfur dioxide in the atmosphere has been studied extensively over the past 20 years. Recent reviews, Calvert et al. (1978), Middleton et al. (1980) and Möller (1980), which consider analysis of laboratory and field data as well as theoretical studies, indicated that SO_2 oxidation may proceed through both gas and liquid phase reactions. The oxidation of SO_2 in the atmosphere is of considerable importance, in that it represents a major pathway for particle production through the formation of sulfates. The SO_2 oxidation process, though not completely understood mechanistically, has been demonstrated to proceed via four pathways: homogeneous gas phase reactions; heterogeneous gas-solid interface reactions; and catalyzed and uncatalyzed liquid phase reactions. Homogeneous gas phase reactions are by far the most extensively studied and best understood quantatively.

The homogeneous gas-phase chemistry of oxidation in the clean and the polluted troposphere is reviewed in this section. The status of our knowledge is presented for the elementary oxidation reactions of SO_2 and the importance of volatile organic and nitrogen oxides as generators of free radical oxidizers. This review will show that the photochemical oxidation of SO_2 is potentially a significant pathway for tropospheric sulfate formation. The three most important oxidizers of SO_2 are: (1) hydroxyl radical HO; (2) peroxy radical, HO_2, and (3) methoxy radical, CH_3O_2. At this time, only the reaction rate constant for HO is well established. The pathways of formation of the oxidizer radicals for the unpolluted troposphere can be explained in terms of the photochemistry of the NO-CH_4-CO-O_3 system. In polluted atmospheres, volatile organics and oxides of nitrogen act together to produce additional

*
radicals and accelerate overall radical production. There is also evidence that a dark reaction among O_3, alkenes, and SO_2 is effective in oxidizing SO_2.

2.3.3.1 Elementary Reactions--The elementary chemical reactions of SO_2 in air have been the subject of intense investigation. Studies prior to 1965 have been critically reviewed by Altshuller and Bufalini (1971), and more recently by Calvert et al. (1978). The review of Calvert et al. (1978) systematically examined the rate constants and significance of SO_2 elementary reactions known to occur in the troposphere; identified as generally unimportant reactions were: photodissociation, photoexcitation, reaction with singlet delta oxygen [$O_2(^1\Delta_g)$], reaction with oxygen atom [$O(^3P)$], reaction with ozone (O_3), reaction with nitrogen oxides (NO_2, NO_3, N_2O_5), reaction with tert-butylperoxy radical [$(CH_3)_3CO_2$], and reaction with acetylperoxy radical ($RCOO_2$). The only SO_2 reactions in the troposphere that were identified as important were those due to hydroxyl radical (HO), peroxy radical (HO_2), and methoxy radical (CH_3O_2). The rate constants recommended by Calvert et al. (1978) for these three reactions are given in Table 2-4. More recent work is in conflict with the rate constants for HO_2 and CH_3O_2 that have been recommended by Calvert et al. (1978). Graham et al. (1979) and Burrows et al. (1979) have reported rate constants for the HO_2 reaction that are much lower than that recommended by Calvert et al. (1978); these more recent results are shown in Table 2-4. Also, Sander and Watson (1981) have reported a rate constant for the CH_3O_2 reaction that is much lower that that recommended by Calvert et al. (1978); that value is given in Table 2-4. The reasons for the discrepancies for these two rate constants are unknown, and there is no basis to recommend preferred values.

Although the dark reaction of $SO_2 + O_3$ is too slow to be important in the troposphere, the addition of alkenes greatly enhances the oxidation rate. The experimental work of Cox and Penkett (1971a,b; 1972) and McNelis et al. (1975) has been reviewed and reevaluated by Calvert et al. (1978). The reaction system is too complex to discuss here, but Calvert et al. (1978) report results of their calculations for total alkenes = 0.10 ppm, [O_3] = 0.15 ppm, and [SO_2] = 0.05 ppm; they estimated that the disappearance rate of SO_2 is 0.23 and 0.12% h^{-1} at 50 and 100% relative humidity (25°C). The reaction mechanism for the O_3 + alkene + SO_2 system is not known, but studies by Niki et al. (1977) and Su et al. (1980) indicate that the reactive species may be the biradical, formed by the decomposition of the original molozonide.

Summary: The status of our knowledge of the gas-phase tropospheric oxidation reactions is:

1. Three reactions have been identified as being potentially important.
   a. HO radical. The rate constant appears to be well-established.
   b. HO_2 radical. The rate constant is not well-established.
   c. CH_3O_2 radical. The rate constant is not well-established.
2. The $SO_2 + O_3$ + alkenes reaction may be an important dark reaction.

TABLE 2-4. RATE CONSTANTS FOR HYDROXYL, PEROXY, AND METHOXY RADICALS

Reaction	Second order rate constant, $cm^3 mole^{-1} s^{-1}$	Source
$HO + SO_2 \rightarrow HOSO_2$ $\rightarrow H_2SO_4$	$(1.1 \pm 0.3) \times 10^{-12}$	Calvert et al. (1978)
$HO_2 + SO_2 \rightarrow HO + SO_3$ $\rightarrow H_2SO_4$	$>(8.7 \pm 1.3) \times 10^{-16}$	Calvert et al. (1978)
	$<1 \times 10^{-18}$	Graham et al. (1979)
	$\leq 2 \times 10^{-17}$	Burrows et al. (1979)
$CH_3O_2 + SO_2 \rightarrow CH_3O + SO_3$ $\rightarrow H_2SO_4$	$(5.3 \pm 2.5) \times 10^{-15}$	Calvert et al. (1978)
	5×10^{-17}	Sander and Watson (1981)

2.3.3.2 Tropospheric Chemistry of SO_2 Oxidation--The chemistry of the clean troposphere and its mathematical simulation have been studied extensively by Levy (1971), Wofsy et al. (1972), Crutzen (1974), Fishman and Crutzen (1977), Chameides and Walker (1973, 1976) and Stewart et al. (1977).

The photochemistry of the unpolluted troposphere develops around a chain reaction sequence involving NO, CH_4, CO and O_3. The photochemical reaction chain sequence in the troposphere is initiated by hydroxyl radicals (HO) formed from the interaction of $O(^1D)$, the product of photolysis of ozone in the short end portion of the solar spectrum, with water.

$$O_3 + h\nu(\lambda \leq 310 \text{ nm}) \rightarrow O(^1D) + O_2 \qquad (2\text{-}1)$$

$$O(^1D) + H_2O \rightarrow 2HO \qquad (2\text{-}2)$$

The HO produced reacts with CH_4 and CO present in the clean troposphere, resulting in the generation of peroxy radical species, HO_2, CH_3O_2.

$$HO + CH_4 \rightarrow CH_3 + H_2O \qquad (2\text{-}3)$$

$$HO + CO \rightarrow H + CO_2 \qquad (2\text{-}4)$$

$$CH_3 + O_2 + M \rightarrow CH_3O_2 + M \qquad (2\text{-}5)$$

$$H + O_2 + M \rightarrow HO_2 + M \qquad (2\text{-}6)$$

*

The peroxy radicals in turn participate in a chain propagating sequence which convert nitric oxide (NO) to nitrogen dioxide (NO_2) and in the process produces additional hydroxyl and peroxy radical species.

$$CH_3O_2 + NO \rightarrow CH_3O + NO_2 \qquad (2\text{-}7)$$
$$HO_2 + NO \rightarrow HO + NO_2 \qquad (2\text{-}8)$$
$$CH_3O + O_2 \rightarrow HO_2 + H_2CO \qquad (2\text{-}9)$$
$$H_2CO + h\nu(\lambda \leq 370\ nm) \rightarrow H + HCO \qquad (2\text{-}10)$$
$$HCO + O_2 \rightarrow HO_2 + CO \qquad (2\text{-}11)$$

The major chain terminating steps include:

$$HO + NO_2 + M \rightarrow HONO_2 + M \qquad (12\text{-}12)$$
$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \qquad (12\text{-}13)$$
$$H_2O_2 + HO \rightarrow H_2O + HO_2 \qquad (12\text{-}14)$$

The reaction sequence for O_3 production involves converting NO to NO_2 at a rate sufficiently high to maintain a NO_2/NO ratio to sustain the observed background levels of O_3.

$$HO_2 + NO \rightarrow NO_2 + HO \qquad (2\text{-}8)$$
$$NO_2 + h\nu \rightarrow NO + O \qquad (2\text{-}15)$$
$$O + O_2 + M \rightarrow O_3 + M \qquad (2\text{-}16)$$
$$NO + O_3 \rightarrow NO_2 + O_2 \qquad (2\text{-}17)$$
$$HO + CO \rightarrow H + CO_2 \qquad (2\text{-}4)$$

In general, reactions (15) through (17) govern the ozone concentration levels present in the sunlight irradiated well-mixed atmosphere at any instant and to a first approximation the steady state relationship, Leighton (1961),

$$\frac{(NO_2)\ k_{15}}{(NO)\ k_{17}} = (O_3)$$

provides an accurate estimate of ozone given the ratio of $(NO_2)/(NO)$ and k_{15}/k_{17}. The photolytic rate constant k_{15} is directly related to the integrated actinic solar flux over the wavelength range 290 - 430 nm.

The paths for ozone destruction in the troposphere include the reaction sequence

$$HO_2 + O_3 \rightarrow HO + 2O_2 \qquad (2\text{-}18)$$
$$HO + O_3 \rightarrow HO_2 + O_2 \qquad (2\text{-}19)$$

Hydroxyl radical abundances predicted by the tropospheric photochemical models, 10^5 to 10^6 molec - cm^{-3}, are in qualitative agreement with recent measurements by Davis et al. (1976), Perner et al. (1976), and Campbell et al. (1979) and inferred HO levels based on measured trace gas abundances in the troposphere by Singh (1977).

*

In the case of the chemistry of polluted atmospheres, extensive discussions on the mechanism of photochemical smog and its computer simulation have been presented by Demerjian et al. (1974), Calvert and McQuigg (1975), Niki et al. (1972), Hecht et al. (1974) and Carter et al. (1979).

Perturbations introduced by man's emissions on the photochemical oxidation cycle within the atmosphere are predominately due to two classes of compounds, volatile organics and nitrogen oxides. The reaction chain sequence discussed earlier for the clean troposphere has now been immensely complicated by the addition of scores of volatile organic compounds which participate in the chain propagating cycle. Figure 2-4 depicts a schematic of the polluted atmospheric photooxidation cycle. The addition of volatile organic compounds in the atmosphere introduces a variety of new peroxy radical species.

In its simplest form the photochemical oxidation cycle in polluted atmospheres is governed by the following basic features. Free radical attack on atmospheric VOCs is initialized by a select group of compounds which are for the most part activated by sunlight. Formaldehyde and nitrous acid, in particular, show high potential as free radical initiators during the early morning sunrise period. After initial free radical attack, the VOCs decompose through paths resulting in the production of peroxy radical species (HO_2, RO_2, $R'O_2$, etc.) and partially oxidized products which in themselves may be photoactive radical-producing compounds. The peroxy radicals react with NO, converting it to NO_2, and in the process produce hydroxy/alkoxy radical species (OH, RO, R'O, etc.). Alkoxy radicals can be further oxidized, forming additional peroxy radicals and partially oxidized products, thereby completing the inner cyclical loop reaction chain process illustrated in Figure 2-4; or they may attack, as would be the major path for hydroxyl radical, the VOC pool present in the polluted atmosphere, thereby completing the outer loop reaction chain process. The resultant effect in either case is the conversion of NO to NO_2 with a commensurate oxidation of reactive organic carbon.

The complex mixture of organic compounds present in the polluted atmosphere react at different rates dependent upon their molecular structure, the result being varying yields of free radical species, ozone, NO_2, PAN and other partially oxidized organic products as a function of VOC composition and VOC-NO_x levels.

Hydroxyl radical (HO) reactions seem to be the dominant mechanism by which hydrocarbons, nitrogen dioxide and sulfur dioxide are consumed in the atmosphere (Niki et al., 1972; Demerjian et al., 1974; Calvert et al., 1978). Interestingly enough, this highly reactive transient species, quite contrary to its organic free radical counterparts, does not show appreciable change in concentration with atmospheric VOC and NO_x variation, a result readily explainable upon review of the free radical production and consumption sources. In the case of hydroxyl radicals, ambient concentration conditions which enhance its production tend to also consume the radical at an equivalent rate. The result is a faster cycling in the VOC-NO_x oxidation chain (that is, increased chain lengths) but very little perturbation in the HO steady state concentration. In contrast, organic free radicals, mainly peroxy species, are

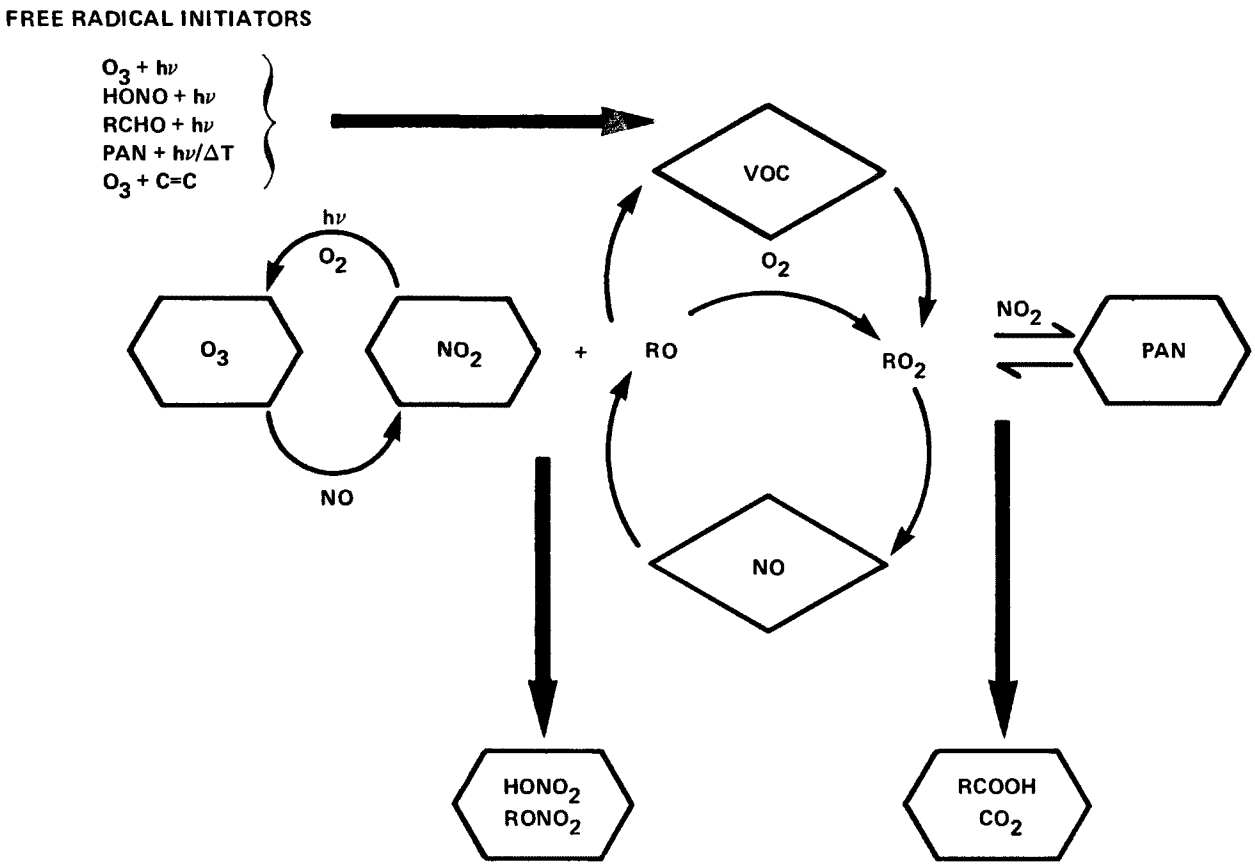

Figure 2-4. Schematic of the polluted atmospheric photooxidation cycle.

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consumed by alternate pathways which are less competitive and result in increased steady state concentration.

Applying this basic knowledge of the photochemistry of the lower atmosphere, Calvert et al. (1978) determined theoretical rates of SO_2 oxidation via attack of various free radical species whose concentrations were estimated from computer simulations of the chemical reaction mechanisms for clean and polluted atmospheres.

Based on limited rate constant data for the SO_2-free radical reactions, Calvert determined that the hydroxyl radical dominated the rate of SO_2 oxidation in the clean troposphere, while in polluted atmospheres the rate of SO_2 oxidation showed equivalent contributions from hydroxyl, hydroperoxy (HO_2) and methylperoxy (CH_3O_2) radicals. Figure 2-5 depicts the estimated time dependent rates of SO_2 oxidation by free radical species in a polluted air mass. Recent laboratory measurements suggest that the rate of reaction of SO_2 with HO_2 and CH_3O_2 may not be as great as estimated by Calvert et al. (1978) (see discussion in Section 2.3.3.1). Typical rates of SO_2 oxidation were of the order of 1.5 percent/h and 4.0 percent/h for clean and polluted atmospheres, respectively, during July at mid-northern latitudes, the major difference in rates being a result of higher concentration levels of free radicals in the hydrocarbon rich polluted atmospheres. In a similar manner, Altshuller (1979) predicted the rates of homogeneous oxidation of sulfur dioxide to sulfate in the clean troposphere using concentration predictions of the pertinent free radicals from a two dimensional global model by Fishman and Crutzen (1978). A sample result from this study showing the latitudinal and seasonal dependence of the rate of SO_2 oxidation is presented in Figure 2-6; the variability in rate being predominantly due to availability of u.v. solar intensity which derives the free-radical production process. The solar radiation dependence of SO_2 conversion rate has also been observed in field measurements within power plants plumes, Husar et al. (1978), but should be viewed cautiously in light of the complicating factors introduced by the dispersion and local chemistry of the primary source emissions.

The most important impact on SO_2 homogeneous gas phase reactions has come from recent experimental determinations of the reaction rate constants of SO_2 with HO_2 by Graham et al. (1979) and by Burrows et al. (1979) and SO_2 with CH_3O_2 by Sander and Watson (1981). As a result of these recent determinations, HO_2 and CH_3O_2 must be considered as questionable contributing sources to the oxidation of SO_2 in the atmosphere. Therefore, in the theoretical estimates of SO_2 oxidation rates, by Calvert et al. (1978), and by Altshuller (1979), only the hydroxyl radical portion of the contribution is now accepted as established, in view of these recent experimental rate constant determinations. This results in maximum established SO_2 oxidation rates of the order of 1.5 percent/h for both clean and polluted atmosphere during July at mid-northern latitudes, a factor of 2.5 less than previous theoretical estimates for polluted atmospheres. The revised rate is equivalent to a diurnally averaged rate of the order 0.4 percent/hr. Field measurements on the rates of SO_2 oxidation, discussed in Chapter 6, indicate that maximum SO_2 oxidation rates of the order of 10 percent/h are typical of many

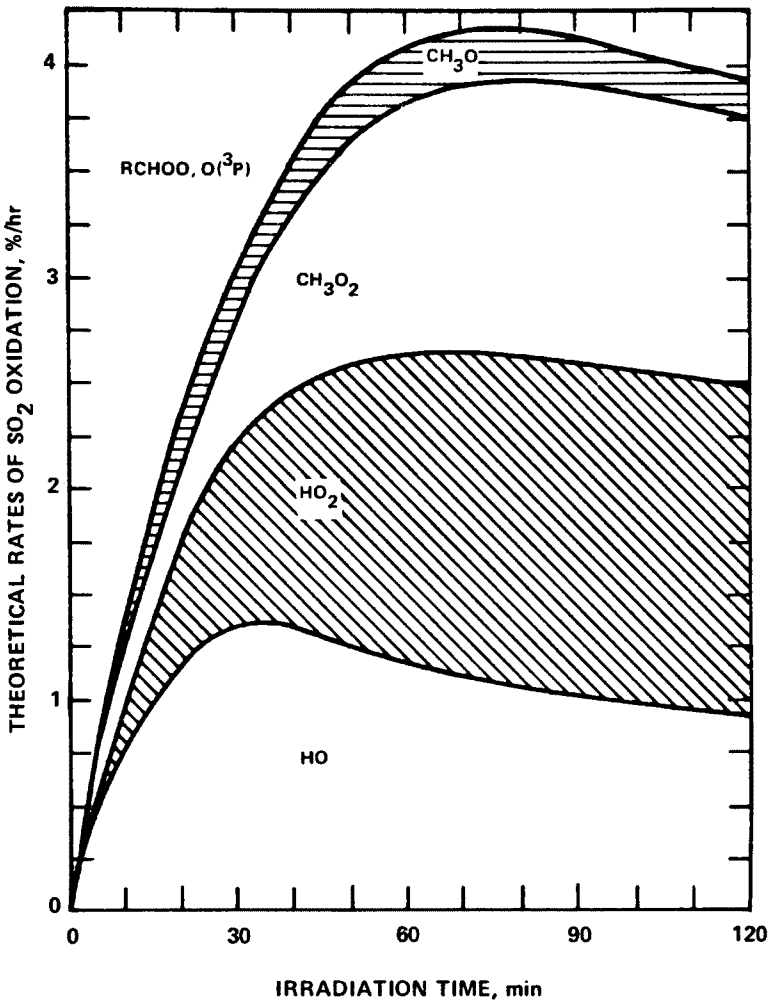

Figure 2-5. The theoretical rate of reaction (percent per hour) of various free-radical species on SO_2 is shown for a simulated sunlight-irradiated (solar zenith angle of 40°) polluted atmosphere. The initial concentrations (in ppm) were as follows: SO_2, 0.05; NO, 0.15; NO_2, 0.05; CO, 10; CH_4, 1.5; CH_2O, 0; CH_3CHO, 0. The relative humidity was 50 percent, and the temperature was 25° C.

Note: The rate constants for HO_2 and CH_3O_2 radical reactions with SO_2 are not well established. See Table 2-4 and its discussion.

Source: Calvert et al. (1978).

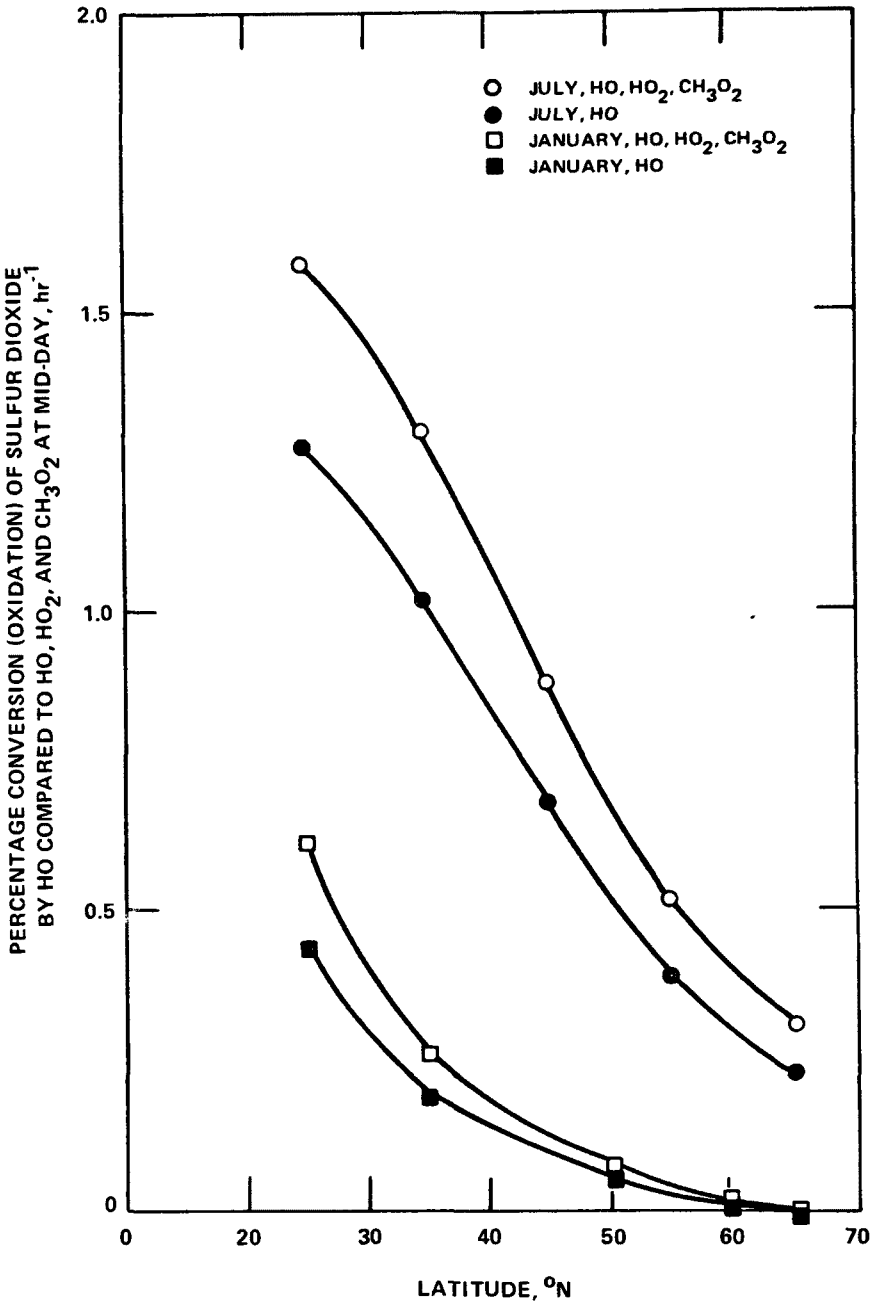

Figure 2-6. Percentage conversion at mid-day of sulfur dioxide to sulfate by HO and by HO, HO_2, and CH_3O_2 radicals as function of °N latitude in summer and winter.

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atmospheric pollution scenarios. Our present knowledge of homogeneous SO_2 gas-phase reactions does not sufficiently account for the rates observed. Smog chamber studies have demonstrated that some species other than HO radical oxidizes SO_2 (Kuhlman et al., 1978; McNelis et al., 1975). Alternate homogeneous gas reaction oxidation pathways are being studied (Su et al., 1980), but certainly the role of heterogeneous and liquid phase SO_2 oxidation pathways should not be overlooked in attempts to resolve this discrepancy.

Summary. The status of our knowledge of SO_2 oxidation in the troposphere is:

1. HO radical dominates the gas-phase oxidation of SO_2 in the clean troposphere. A typical rate is on the order of $1.5\%h^{-1}$ at noon during July at mid-northern latitudes.

2. HO radical accounts for about $1.2\%h^{-1}$ of the SO_2 oxidation in the polluted troposphere. The combined contribution of HO_2 and CH_3O_2 radical reactions may be as great as about $2.8\%h^{-1}$, but their rate constants are not well-established.

2.3.4 Solution-Phase Chemical Reactions

The knowledge of the reactions of the aqueous $SO_2 \cdot H_2O$-HSO_3^- -andSO_3^{2-} system is important to understanding the processes of H_2SO_4 formation in tropospheric particles, mists, fogs, and rain. This section reviews the oxidation reaction of dissolved SO_2 species, including the auto-oxidation, metal-ion catalyzed oxidation, carbon catalyzed oxidation, and reactions with the dissolved oxidants NO_2, O_3, and H_2O_2.

The state of knowledge of aqueous oxidation rates of dissolved SO_2, HSO_3^-, and SO_3^{2-} is inadequate for simple systems and is extremely poor (or non-existent) for complex systems that include dissolved nitrogen and carbon compounds. Unfortunately, most of the studies are not definitive because the investigators: (1) did not provide sufficient descriptions of experimental procedure (especially the purification of the water and reagents), (2) did not select a proper reactor design, and (3) worked at concentration levels that were orders of magnitude greater than possible for ambient atmospheric aqueous systems. Trace quantities (at the part-per-billion level) of catalytic metal ions are capable of enhancing the reaction velocities by orders of magnitude over the auto-oxidation rate, while similar trace quantities of organics inhibit the rate. The characteristics of the chemical reactor govern the range of the half-life that can be investigated and may influence the observed rate of oxidation. Two-phase air-water reactors (e.g., bubblers and supported droplets) may have reaction characteristics that are dependent upon: (1) the mass transfer rate of the reactants through the air-water interface, and (2) the mixing rates within the gas and water phases (Carberry, 1976; Freiberg and Schwartz, 1981). Unless an adequate characterization of the two-phase reactor was performed, it is not recommended that the implied elementary rate constant be accepted. Supported droplets may suffer from an additional problem: radical chains are efficiently terminated at liquid-solid interfaces, thereby reducing the observed rate. Therefore, supported droplet measurements are not defensible unless it is established that the oxidation is not a free-radical mechanism. Several notable reviews of the oxidation of dissolved SO_2 and its hydration products in simple systems have been published recently (Schroeter, 1963; Hegg and Hobbs, 1978).

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This review will show that:

1. The auto-oxidation (uncatalyzed) reaction is very slow compared to the other reactions

2. Mn(II) and Fe(III) are significant catalysts for the oxidation. The kinetic rate expression is in doubt for the Mn(II) reaction, but that for Fe(III) is in agreement among several independent investigators.

3. The catalytic effectiveness of these ions is unknown: Cu(II), V(V), V(IV), Ni(II), Zn(II), and Pb(II).

4. Elemental carbon (soot) with a water film is a potentially effective oxidation catalyst.

5. Dissolved HNO_2 and O_3 oxidation rates are known and appear to be too low to be effective.

6. The kinetics of the dissolved H_2O_2 oxidation of dissolved SO_2 species are known and appear to be effective for forming sulfate in particles, mists, fogs and rain.

2.3.4.1 <u>S(IV)-O_2 - H_2O System</u>--The simple S(IV) - O_2 auto-oxidation has been the subject of numerous investigations, most of which are listed in Table 2-5. The mechanism for the auto-oxidation is not firmly established. However, the behavior of the system is best explained as a modification to the scheme of Bäckström (1934), taking into account the recent results of Schmidkunz (1963) and Hayon et al. (1972):

Chain initiation

$$SO_3^{2-} + M^+ \rightarrow \cdot SO_3^- + M \qquad (2\text{-}20)$$

(M^+ = trace concentration of metal ion or reactive wall)

Chain propagation

$$\cdot SO_3^- + O_2 \rightarrow \cdot SO_5^- \qquad (2\text{-}21)$$

$$\cdot SO_5^- + SO_3^{2-} \rightarrow \cdot SO_4^- + SO_4^{2-} \qquad (2\text{-}22)$$

Oxidation

$$\cdot SO_4^- + SO_3^{2-} \rightarrow SO_4^{2-} + \cdot SO_3^- \qquad (2\text{-}23)$$

Termination

$$\cdot SO_4^- + \text{inhibitor} \rightarrow \qquad (2\text{-}24)$$

$$\text{radical} + \text{radical} \rightarrow \qquad (2\text{-}25)$$

Brimblecombe and Spedding (1974b) propose an alternative scheme that does not include the $\cdot SO_4^-$ radical-ion; in their scheme, equation (2-22) is replaced by:

$$\cdot SO_5^- + SO_3^{2-} \rightarrow \cdot SO_3^- + SO_5^{2-} \qquad (2\text{-}26)$$

$$SO_5^{2-} + SO_3^{2-} \rightarrow 2\ SO_4^{2-}. \qquad (2\text{-}27)$$

and equation (2-24) is absent.

Hegg and Hobbs (1978) have discussed most of the investigations identified in Table 2-5, and they summarized the rate expressions, rate constants, and important features of the studies. The observations can be classified into three types of rate expressions:

TABLE 2-5. INVESTIGATIONS OF SO_2 - O_2 AQUEOUS SYSTEMS

Investigators	Type of system	Comment*
Bigelow (1898)	Bubbler	1,2,3
Titoff (1903)	Bulk	2,3
Lumiere and Seyewetz (1905)	Bulk	2,3
Milbaur and Pazourek (1921)	Bulk	2,3
Reinders and Vles (1925)	2-phase bulk	1,2,3
Haber and Wansbrough-Jones (1932)	Bulk	2,3
Vol'fkovick and Belopol'skii (1932)	Bulk	2,3
Bäckström (1934)	Theoretical	
Fuller and Crist (1941)	Bubbler	1
Riccoboni et al. (1949)	Bulk	2,3
Abel (1951)	Theoretical	
Winkelmann (1955)	Bulk	2
van den Heuvel and Mason (1962)	Supported droplet	1,3
Schroeter (1963)	Bubbler	1
Schwab and Strohmeyer (1965)	Bulk	2
Rand and Gale (1967)	Bulk	2,3
Scott and Hobbs (1967)	Theoretical	
McKay (1971)	Theoretical	
Miller and de Pena (1972)	Supported droplets	1
Brimblecombe and Spedding (1974a)	Bubbler	1
Bielke et al. (1975)	Supported droplet	1,3
Horike (1976)	Bubbler	1,3
Larson (1976)	Bubbler	1
Huss et al. (1978)	Bulk	1,3
Larson et al. (1978)	Bubbler	1

*1. Incompletely characterized 2-phase system; results cannot be considered to be reliable.
2. Purity of water is uncertain; results cannot be considered to be reliable.
3. Rate expression not reported.

*

1. The type first reported by Fuller and Crist (1941),

$$\frac{d\left[SO_4^{2-}\right]}{dt} = \left\{k_1 + k_2\,[H^+]^{0.5}\right\}\left[SO_3^{2-}\right] \qquad (2\text{-}28)$$

2. The type first reported by Winkelmann (1955),

$$\frac{d\left[SO_4^{2-}\right]}{dt} = k_1\left[SO_3^{2-}\right] \qquad (2\text{-}29)$$

3. The type observed by Beilke et al. (1975).

$$\frac{d\left[SO_4^{2-}\right]}{dt} = k_1\,[H^+]^{-0.16}\left[SO_3^{2-}\right] \qquad (2\text{-}30)$$

It is presently unresolved as to which type of rate expression is correct. Doubt is cast on "type 3" found by Beilke et al. (1975) because of the use of a plastic vessel that could have introduced trace organic inhibitors into the system. All of the other studies (yielding "types 1 and 2") were performed with two-phase systems whose mass transfer properties were insufficiently reported.

The auto-oxidation is inhibited by trace concentrations of organic species. The classes of organic species capable of serving as inhibitors include alcohols, glycols, aldehydes, ketones, phenols, amines, and acids. Bäckström (1934) first demonstrated that the inhibition of sulfide oxidation can be expressed as:

$$\frac{d\left[SO_4^{2-}\right]}{dt} = \left\{A/(B + m)\right\} k_1\left[SO_3^{2-}\right] \qquad (2\text{-}31)$$

where

k_1 = the uninhibited rate constant

A,B = constants that are functions of the inhibitor

m = molar concentration of the inhibitor

The influence of inhibitors on the rate has been extensively studied by Schroeter (1963), and more recently by Altwicker (1979). According to Schroeter (1963), A and B are usually on the order of 10^{-5} molar, which means that inhibitor concentrations greater than 10^{-6} molar are effective. The form of the rate equation (Equation 2-31) suggests that the mechanism involves a bimolecular reaction between an inhibitor molecule and a radical in the chain.

In summary, our status of knowledge of the auto-oxidation reaction is:

1. The reaction is very slow.
2. The rate is extremely sensitive to the presence of catalysts and inhibitors.
3. The rate is first order in sulfite.
4. No reaction mechanism has been satisfactorily demonstrated to account completely for the observations of the more reliable studies (e.g., the dependence of the rate on $[H^+]^{0.5}$ found by Fuller and Crist, 1941 and by Larson et al., 1978).

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2.3.4.2 S(IV) - catalyst - O_2 - H_2O System--It is well-established that some metal cations catalyze the oxidation of HSO_3^- and SO_3^{2-}. Of particular interest to the issue of atmospheric sulfate formation in particles, mist, fog, and rain is possible catalytic activity of: Mn(II), Fe(III), Cu(II), Ni(II), and V(IV). General features of the catalyzed reaction include: (a) inhibition by oxidizable organic molecules, (b) inhibition by metal ion-complexing molecules (inorganic and organic), (c) exhibition of an induction time of several seconds to several minutes, (d) detection of metal ion - S(IV) complexes, (e) no dependence of rate on dissolved O_2 concentration, (f) dependence of the rate on the inverse of the initial H^+ concentration (i.e., the rate is independent of pH change after the reaction has been initiated). While the catalytic reaction mechanisms are unknown, they are thought to be a modification of the initiation step of the auto-oxidation free radical mechanism (Equations 2-20 through 2-25); instead of M^+ being a trace concentration ($<10^{-9}$ M) of metal ion or a reactive wall, it is a reagent present at concentrations $>10^{-6}$ M. The rate expressions for the various catalysts have different forms, suggesting different types of initiation mechanisms (e.g., simple redox reactions or the formation of stable, reactive complexes). The agreement between independent investigators is generally poor, indicating the likelihood of mass transfer limitations of the rate or the presence of contaminants. A large percentage of the investigations were conducted with two-phase reactors for which the mass transfer characteristics were not adequately reported; therefore, those results must be considered to be unreliable for estimating the elementary rate constant and for determining the reaction order. Also, the results for investigations using supported droplets may be biased due to radical chain termination at the liquid-solid interface.

The Mn(II) catalyzed reaction kinetics have been investigated for over 75 years; the studies pertinent to the formation of sulfate in the troposphere are presented in Table 2-6. One of the first critics of Mn(II) catalysis studies was Titoff (1903), who remarked: "In Bigelow's (1898) work the reaction occurred between two phases, and the retardation could be determined by a change in the boundary layer or by a decrease in the solution rate of oxygen." Unfortunately, that comment applies to all but three of the Mn studies in Table 2-6, which are: Hoather and Goodeve (1934), Neytzell-de Wilde and Taverner (1958), and Coughanowr and Krause (1965). It is odd that each of these investigators did not present rate expressions and rate constants derived from their data, and instead left to the reader the task of extracting that information. Estimates of their rate expressions are presented in Table 2-7. There is agreement that the Mn (II) catalyzed rate is independent of dissolved O_2, SO_2, HSO_3^-, and SO_3^{2-} concentrations.

Clearly, Hoather and Goodeve (1934) and Coughanowr and Krause (1965) are in good agreement. However, Neytzell-de Wilde and Taverner (1958) observed a first-order dependence on [Mn(II)]. There appears to be no basis to discount any of the three investigations, yet it appears that serious errors may have been made. There is a slight preference for the expression for the results of Neytzell-de Wilde and Taverner (1958) because: (1) they measured the rate of disappearance of S(IV) by direct chemical means, and (2) the period of observation

TABLE 2-6. INVESTIGATIONS OF SO_2 - MANGANESE - O_2 AQUEOUS SYSTEM

Investigators	Type of system	Comment
Titoff (1903)	Bulk	2
Johnstone (1931)	Bubbler	1,2
Hoather and Goodeve (1934)	Bulk	2
Bassett and Parker (1951)	Bulk	2
Johnstone and Coughanowr (1958)	Supported droplet	1,2
Neytzell-de Wilde and Taverner (1958)	Bulk	2
Johnstone and Moll (1960)	Free droplets	2
Coughanowr and Krause (1965)	Bulk and flow	2
Bracewell and Gall (1967)	Bubbler	1
Matteson et al. (1969)	Free and supported droplets	3
Cheng et al. (1971)	Supported droplets	1

1. Incompletely characterized 2-phase system; results cannot be considered to be reliable.
2. Rate expression not reported.
3. Results are biased due to continued reaction (supported) droplets on filter of sampler; rate expression cannot be considered to be reliable.

TABLE 2-7. RATE EXPRESSION FOR THE MANGANESE-CATALYZED OXIDATION

Expression[a,b,c]	pH	Investigators
$\frac{d[SO_4^{2-}]}{dt} \cong 44\ [Mn(II)]^{1.7}\ [S(IV)]^0\ [H^+]^0$	3-4	Adapted from Hoather Goodeve (1934)
$\frac{d[SO_4^{2-}]}{dt} \cong 1.7 \times 10^{-5}\ [Mn(II)]\ [S(IV)]^0\ [H^+]_o^{-1}$	~2.2	Adapted from Neytzell-de Wilde and Taverner (1958)
$\frac{d[SO_4^{2-}]}{dt} \cong 8\ [Mn(II)]^2\ [S(IV)]^0$	~3-4	Adapted from Coughanowr and Krause (1965); dependence on pH not reported

[a]The units are: liter, mole, second.

[b]Concentrations shown with zero power (e.g., $[S(IV)]^0$) indicate that the investigators found the rate to be independent of those species. Note that any concentration to the zero power is equal to unity.

[c]The term $[H^+]_o^{-1}$ indicates that the rate is dependent only on the inverse of the initial H^+ ion concentration; changes in H^+ concentration after the reaction is in progress do not affect the rate.

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(10-100 minutes) of the experimental runs were sufficiently long that it is reasonable that the rate of oxidation was measured after the establishment of the radial chains, and not during the induction period.

The Fe(III) catalyzed reaction studies that are pertinent to the formation of sulfate in the troposphere are identified in Table 2-8. The only studies not using two-phase systems (subject to mass transport limitations) are those of Neytzell-de Wilde and Taverner (1958), Karraker (1963), Brimblecombe and Spedding (1974a), and Fuzzi (1978). Hegg and Hobbs (1978) have pointed out that Karraker (1963) did not investigate the catalyzed oxidation in which dissolved O_2 is the oxidant, but instead the redox system associated with the couple $Fe(III) + e^- \rightarrow Fe(II)$ in an oxygen-free system. Thus, Karraker's work is not considered applicable. Neytzell-de Wilde and Taverner (1958) reported that the sulfate formation rate was second order for [S(IV)], but Karraker (1963) has re-analyzed their data and has shown instead that the order is unity. As noted for the Mn(II) system, Neytzell-de Wilde and Taverner (1958) did not present a rate expression and constant for the Fe(III) system; an estimate derived from their paper is presented in Table 2-9. Brimblecombe and Spedding (1974a) have reported a rate expression and constant measured at a constant pH = 4; unfortunately, they used a plastic reaction vessel, which could have released organic inhibitors into the system, causing the rate to be diminished. (At pH = 4, their rate is 0.25 of that of Neytzell-de Wilde and Taverner, 1958, and 0.1 of that of Fuzzi, 1978.) Fuzzi (1978) did not note the similarity of his observations and those of Neytzell-de Wilde and Taverner (1958), especially the dependence of the rate on the <u>initial</u> inverse H^+ concentration for pH $\leq$ 4.0. Fuzzi's (1978) rate expression has been modified by incorporating the dependence on $[H^+]_0^{-1}$ and is presented in Table 2-9. Note that Fuzzi's (1978) modified rate constant is 2.5 times greater than that of Neytzell-de Wilde and Taverner (1958), which is good agreement for this type of measurement; these two studies appear to be the most definitive for the Fe(III) system, and there is no basis to prefer one over the other. Fuzzi (1978) has clearly demonstrated the change in the reaction order of [S(IV)] from 1 to 2 as pH increases from 4 to 5. The change in kinetics is due to the formation of colloidal $Fe(OH)_3$ for pH > 4, which provides an explanation for the disagreement among earlier investigators. Because of the formation of the $Fe(OH)_3$ colloid, it is unlikely that a meaningful Fe(III) catalyzed rate expression for use in tropospheric sulfate formation can be stated for conditions in which pH > 4.

The Cu catalyzed reaction kinetics have been described in the early work of Titoff (1903). The pertinent investigations are identified in Table 2-10. As with the Mn and Fe studies, most of the Cu studies were performed with incompletely characterized systems. Fuller and Crist (1941) point out that the prior work is unreliable because of the likely presence of contaminants. However, the investigations of Fuller and Crist (1941) were carried out in a two-phase reactor whose mass transfer characteristics are not completely described; no one has since conducted a study that is more definitive of this system. The reagent concentrations used by Barron and O'Hern (1966) are orders of magnitude too large, and the pH range (>8) used by Mishra and Srivastava (1976) is not applicable. For that reason, no rate expression can

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TABLE 2-8. INVESTIGATIONS OF SO_2 - IRON - O_2 AQUEOUS SYSTEM

Investigators	Type of system	Comment
Reinders and Vles (1925)	Bulk	2
Bassett and Parker (1951)	Bulk	2
Higgins and Marshall (1957)	Bulk	2
Johnstone and Coughanawr (1958)	Support droplet	1
Junge and Ryan (1958)	Bubbler	1,2
Neytzell-de Wilde and Taverner (1958)	Bulk	2
Johnstone and Moll (1960)	Free droplets	2
Danilczuk and Swinarski (1961)	Bulk	2
Karraker (1963)	Bulk	3
Bracewell and Gall (1967)	Bubbler	1
Brimblecombe and Spedding (1974a)	Bubbler	1
Brimblecombe and Spedding (1974b)	Not reported	4
Freiberg (1974)	Theoretical	
Lunak and Veprek-Siska (1975)	Flow	5
Barrie and Georgii (1976)	Supported droplet	1
Fuzzi (1978)	Bulk	

1. Incompletely characterized 2-phase system; results cannot be considered to be reliable.
2. Rate expression not reported.
3. O_2-free system; results not applicable to tropospheric SO_2 oxidation.
4. Insufficient details reported to determine if the results should be considered to be reliable.
5. Photochemical initiation.

TABLE 2-9. RATE EXPRESSION FOR THE IRON-CATALYZED OXIDATION

Expression[a,b]	pH	Investigators
$\frac{d[SO_4^{2-}]}{dt} \cong 0.04\,[Fe(III)]\,[S(IV)]\,[H^+]_o^{-1}$	~2	Adapted from Neytzell-de Wilde and Taverner (1958)
$\frac{d[SO_4^{2-}]}{dt} = 100\,[Fe(III)]\,[S(IV)]$	4	Brimblecombe and Spedding (1974a)
$\frac{d[SO_4^{2-}]}{dt} \cong 0.1\,[Fe(III)]\,[S(IV)]\,[H^+]_o^{-1}$	≤ 4	Adapted from Fuzzi (1978)

[a]The units are: liter, mole, second.

[b]The term $[H^+]_o^{-1}$ indicates that the rate is dependent on the inverse of the initial H^+ ion concentration; changes in H^+ concentration after the reaction is in progress do not affect the rate.

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TABLE 2-10. INVESTIGATIONS OF SO_2 - COPPER - O_2 AQUEOUS SYSTEMS

Investigators	Type of system	Comment
Titoff (1903)	Bulk	2
Reinders and Vles (1925)	Bulk	2
Alyea and Bäckström (1929)	Bulk	2
Johnstone (1931)	Bubbler	1
Albu and Grof von Schweinitz (1932)	Bulk	2
Fuller and Crist (1941)	Bubbler	1
Riccoboni et al. (1949)	Bulk	2
Bassett and Parker (1951)	Bulk	2
Higgins and Marshall (1957)	Bulk	2
Johnstone and Coughanowr (1958)	Supported droplet	1
Junge and Ryan (1958)	Bubbler	1
Barron and O'Hern (1966)	Flow	
Bracewell and Gall (1967)	Bubbler	1
Cheng et al. (1971)	Supported droplet	1
Veprek-Siska and Lunak (1974)	Flow	2
Barrie and Georgii (1976)	Supported droplet	1
Huss et al. (1978)	Bulk	2
Mishra and Srivastava (1976)	Flow	

1. Incompletely characterized 2-phase system; results cannot be considered to be reliable.
2. Rate expression not reported.

be recommended as reliable for use in calculating sulfate formation rates due to Cu catalysis in the troposphere.

Vanadium catalysis has been reported in only one study (Bracewell and Gall, 1967); a bubble reactor was used, and its mass transfer characteristics were inadequately reported. Therefore, no rate expression can be recommended as reliable. However, Bracewell and Gall (1967) did observe qualitatively that V(V) was orders of magnitude less effective than Mn and Fe. Most likely, V(V) catalysis is unimportant for sulfate formation in the troposphere. Likewise, there are no definitive studies for Cr(III), Ni(II), Zn(II), and Pb(II), but it appears from the qualitative work of Bracewell and Gall that these catalytic reactions are unimportant.

Barrie and Georgii (1976) have demonstrated qualitatively that Mn(II) and Fe(III) exhibit a synergistic rate for the catalysis of S(IV) oxidation. Their rate expression cannot be considered to be reliable since they used a supported droplet.

In summary, our status of knowledge of the homogeneous metal ion catalysis systems is:

1. S(IV) oxidation rates are significantly increased by Mn(II) and Fe(III). There is serious doubt regarding the rate expression for Mn(II), but the agreement among independent studies is much better for Fe(III).

2. These systems are presently inadequately characterized: Cu(II), V(V), V(IV), Ni(II), Zn(II), and Pb(II).

3. There are no quantitative studies of metal ion-metal ion synergism.

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4. The ability of atmospheric organic compounds to inhibit the catalysis is unknown.

5. All studies have been performed in the absence of HCO_3^-; however, the reactions

$$\cdot SO_4^- + HCO_3^- \rightarrow HCO_3 + SO_4^{2-}$$

$$\cdot OH + HCO_3^- \rightarrow HCO_3 + OH^-$$

may be important. It is possible that such reactions may occur, and if so, they would prevent the oxidation radical chain from establishing since HCO_3 is not a powerful oxidizer (Hoigné and Bader, 1978).

6. In general, the rate expressions for catalytic oxidation to form sulfuric acid are not well-established.

2.3.4.3 S(IV) - Carbon Black -O_2 - H_2O--The catalysis of the oxidation of dissolved SO_2 by carbon particles suspended in the water has been studied by Chang et al. (1979) and by Eatough et al. (1979). It was found by Chang et al. (1979) that the oxidation rate of dissolved SO_2 species was:

$$-\frac{d[S(IV)]}{dt} = k[C]\,[O_2]^{0.69}[S(IV)]^0 \exp(-E_a/RT) \qquad (2\text{-}32)$$

with an activation energy of E_a = 11.7 kcal/mol over the pH range of 1.45 to 7.5 for the carbon studied, which was Nuchar-190. (The investigators demonstrated that Nuchar-190 behaved similarly to soot from acetylene and natural gas flames.) An average value of $k = 1.17 \times 10^5$ $mol^{0.3} \times liter^{0.7}$/g-sec was reported. The kinetics have been interpreted in terms of the rate-limiting step being the formation of an activated complex between molecular oxygen and the carbon surface (Chang et al., 1979; Eatough et al., 1979).

Chang et al. (1979) have estimated that for 10 μg of their fine carbon soot suspended in 0.05 g of liquid water and dispersed in 1 m^3 of air, the atmospheric sulfate production would be about 1 μg/hr. Heavy hydrocarbons are adsorbed on the surfaces of atmospheric soots and may inhibit the carbon-surface catalyzed oxidation of dissolved SO_2. At this time, it remains to be demonstrated that the laboratory soots used by Chang et al. (1979) correspond to those present in the atmosphere or that the suspension of soot at ambient levels (<10 μg/m^3) in aerosols, cloud droplets, or rain is similar to the laboratory system.

2.3.4.4 S(IV) - Dissolved Oxidants - H_2O--Hydrogen peroxide, ozone, and nitrogen dioxide may be important in the oxidation of SO_2 in aqueous aerosols and fogs. Although these compounds do not demonstrate high reactivity toward SO_2 in air, their reactivity is enhanced in the liquid phase. Again, caution is advised in accepting the results of studies of two-phase systems in which the investigators have not completely accounted for the possibility of the mass transport limitation of the oxidation rate. Therefore, only the recent results for single-phase systems are discussed here.

Martin et al. (1981) have used a stopped-flow reactor to investigate the kinetics of oxidation of aqueous SO_2 species by aqueous NO, NO_2^-, and NO_3^-. Over the pH range of 0.6 to 3.2,

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they found for NO and NO_3^- that the disappearance of S(IV) species is:

$$-\frac{d[S(IV)]}{dt} = k\ [NO \text{ or } NO_3^-]\ [S(IV)] \qquad (2\text{-}33)$$

$$k \leqq 0.01 \text{ mole } l^{-1}s^{-1}.$$

However, for the same conditions, the reaction with NO_2^- is rapid and the formation of SO_4^{2-} can be expressed as:

$$\frac{d[SO_4^{2-}]}{dt} = k_1[H^+]^{0.5}\ [HNO_2 + NO_2]\ [SO_2 \cdot H_2O + HSO_3^-] \qquad (2\text{-}34)$$

$$k_1 = 142 \text{ (liter/mole)}^{1.5}s^{-1}$$

The NO_2^- is reduced quantitatively in this reaction to N_2O. Martin et al. (1981) also observed that this reaction is not catalyzed by Fe(III), Mn(II), or VO^{2+}. It is unlikely that tropospheric nitrous acid (HNO_2) concentrations are high enough for this reaction to be important for H_2SO_4 formation.

The oxidation of dissolved SO_2 by ozone has been investigated with stopped-flow systems. Penkett (1972) and Penkett et al. (1979) have interpreted their work in terms of a decomposition of ozone to initiate a free-radical chain reaction involving OH, HSO_3, and HSO_5 radicals, after Backstrom (1934). Penkett et al. (1979) suggested that the rate expression is

$$\frac{d[SO_4^{2-}]}{dt} \cong k[HSO_3^-]\ [O_3]\ [H^+]^{-1} \qquad (2\text{-}35)$$

where $k \cong 71 \text{ sec}^{-1}$. Erickson et al. (1977) reported the fractional contributions of the oxidation of the three sulfur oxide species by ozone at various pH values; their rate expressions are

$$\frac{d[SO_4^{2-}]}{dt} = k_1[SO_2 \cdot H_2O]\ [O_3] \qquad (2\text{-}36)$$

$$\frac{d[SO_4^{2-}]}{dt} = k_2[HSO_3^-]\ [O_3] \qquad (2\text{-}37)$$

$$\frac{d[SO_4^{2-}]}{dt} = k_3[SO_3^{2-}]\ [O_3] \qquad (2\text{-}38)$$

where $k_1 = 590$ liter/mol·sec, $k_2 = 3.1 \times 10^5$ liter/mol·sec, and $k_3 = 2.2 \times 10^9$ liter/mol·sec.

Penkett et al. (1979) used a stopped-flow reactor to determine the kinetics of oxidation of dissolved SO_2 species by hydrogen peroxide. It was found that the rate of sulfate formation is given by

$$\frac{d[SO_4^{2-}]}{dt} = k[H_2O_2]\ [HSO_3^-]\ [H^+] + k_a[H_2O_2]\ [HSO_3^-]\ [HA] \qquad (2\text{-}39)$$

where $k \cong 2.6 \times 10^7$ liter^2/mol^2·sec, with k and k_a being the third-order rate constants for the catalysis by free protons and proton-donating buffers (HA), respectively. At pH $\leq$ 4, it

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is found that $k/k_a \geq 3200$. Therefore, the second term is probably not important for acid aerosols and fogs. It is of great significance that the reaction rate increases as the solution becomes more acidic, which is in contrast to aqueous oxidation by metal ions and by ozone. The activation energy and the effect of ionic strength on the reaction have been measured by Penkett et al. (1979). Dasgupta (1980) has criticized the presentation of Penkett et al. (1979); use of the rate expression (equation 2-39) takes into account Dasgapta's (1980) points. Martin and Damschen (1981) have found that

$$\frac{d[SO_4^{2-}]}{dt} = k[H_2O_2]\ [SO_2 \cdot H_2O]/\{0.1 + [H^+]\} \qquad (2\text{-}40)$$

where $k = 7.2 \times 10^4 s^{-1}$; their expression is applicable over the range 0<pH<5 and is in good agreement with Penkett et al. (1979).

In summary, our status of knowledge of the formation of H_2SO_4 by dissolved oxidants is:

1. The oxidation rates are known for NO and NO_3^- and are too low to be important.
2. The oxidation rate is known for NO_2^-, but the tropospheric concentration of HNO_2 is probably too low for this reaction to be important.
3. The oxidation rate is known for O_3, but it is expected to be usually unimportant.
4. The oxidation rate for H_2O_2 is known and appears to be potentially a highly effective reaction for formation of H_2SO_4 in the troposphere. This rate could possibly be enhanced by metal ions, but no studies have been reported.
5. Organic oxidizers may be important, but no studies have been reported.

2.3.4.5 <u>The Influence of NH_3</u>--It has been recognized for several decades that NH_3 may influence the formation rate of H_2SO_4 in aqueous particles, mist, fog, and rain. Hegg and Hobbs (1978) have reviewed the studies of the NH_3 influence. They have called attention to a misunderstanding in the literature: NH_3 is commonly reported incorrectly to be a "positive catalyst" for the oxidation of dissolved SO_2. In the strict sense of the definition of "catalyst," the term cannot be applied to the role of NH_3. The observed enhancement by NH_3 of the oxidation rates of the auto-oxidation, metal-ion oxidation, and the O_3 oxidation is due to its action to raise and maintain a high pH. The following process occurs to raise and maintain a higher pH through the conversion of NH_3 to NH_4^+:

1. Ambient gaseous $NH_{3(g)}$ dissolves in the water,
   $NH_{3(g)} \rightleftarrows NH_{3(aq)}$
2. The dissolved $NH_{3(aq)}$ reacts with H^+, which raises the pH
   $NH_{3(aq)} + H^+ \rightleftarrows NH_4^+$.

Therefore, the ambient pathways of auto-oxidation, Mn(II)- and Fe(III)- catalyzed oxidation, and O_3 oxidation would have their rates enhanced by absorption of NH_3. However, the ambient pathways of H_2O_2 and HNO_2 would have their rates retarded by NH_3 absorption. The rate for soot would not be influenced.

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NH_3 can play other important roles. Reinders and Vles (1925) observed qualitatively that Cu(II) was complexed by NH_3 and rendered non-catalytic. At high pH's (>9) such that $NH_{3(aq)}$ is the dominant form, NH_3 may be oxidized by O_3 and free-radicals (Hoigne and Bader, 1978).

In summary, the role of NH_3 is explained in terms of its influence on the pH of the water system; NH_3 is not a catalyst.

2.3.5 Surface Chemical Reactions

Industrial emissions of solid particles (e.g., fly ash) and fugitive dust (e.g., wind-blown soil and minerals) provide a solid-surface that may chemisorb SO_2 and yield sulfate ions. The work reviewed in this section will include investigations of the SO_2 oxidation on the surfaces of: metal oxides, fly ash, charcoal, and soot. Although reaction kinetics have not been identified, two general types of processes have been: a capacity-limited reaction for SO_2 removal and a catalytic SO_2 oxidation process. The initial contact of SO_2 with the solid produces a rapid loss of SO_2 from the gas phase; the reaction rate decreases with time. For the capacity-limited reaction, the rate slowly approaches zero; for the catalytic process, the rate levels off for a time and then approaches zero. The latter phenomenon is attributed to a pH decrease caused by sulfuric acid formation.

Urone et al. (1968) and Smith et al. (1969) found a number of solids to be effective in removing SO_2. In Urone's studies, SO_2 was admitted to a flask containing a powder that was allowed to react with no mixing, and the product and remaining SO_2 were determined. Only the average reaction rates can be calculated from these experiments; more importantly, with this experimental procedure the rates may be diffusion-limited. The highest rate determined was for SO_2 with ferric oxide; the value was >75 percent per minute. Other materials found to be slightly less reactive than ferric oxide were magnetite, lead oxide, lead dioxide, calcium oxide, and aluminum oxide. The rate for the ferric oxide experiment was for 20 mg of ferric oxide in a 2-liter flask; the ferric oxide concentration would thus be 10^7 $\mu g/m^3$. Assuming a direct proportionality between rate and particle concentration, the SO_2 removal rate in the atmosphere would be calculated to be 0.04 percent per hour for 100 $\mu g/m^3$ of particles with the same reactivity as ferric oxide. However, since the mass transfer characteristics of the reactor were not reported, these results cannot be considered reliable for estimating rates.

Smith et al. (1969) did not focus on sulfate formation kinetics; instead, they illustrated through a novel experiment the ability of solid particles to adsorb SO_2 and to release SO_2 during passage through a tube with a wall that adsorbes SO_2. They measured the number of SO_2 monolayers absorbed on suspended Fe_3O_4 as function of SO_2 partial pressure. (The monolayer coverage data reported in their Table I are in error by a factor of 100 to large; e.g., the number of monolayers at 1.13 ppm should be 0.38×10^{-2}.)

Chun and Quon (1973) measured the reactivity of ferric oxide to SO_2, using a flow system involving a filter containing suspended particles. They determined a removal rate constant of 9.4×10^{-3} ppm^{-1} min^{-1} ($-d\ln \theta/dt$), where θ is the fraction of surface sites available for reaction. Extrapolating this to an atmospheric particle concentration of 100 $\mu g/m^3$ with an

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equivalent reactivity and an SO_2 concentration of 0.1 ppm, the data project an atmospheric removal rate of 0.1 percent per hour.

Stevens et. al. (1978) report total iron concentrations in six U.S. cities ranging between 0.5 and 1.3 $\mu g/m^3$. Other species such as manganese, copper, or vanadium had total concentrations usually below 0.1 $\mu g/m^3$. Thus actual ambient air concentrations are a factor of approximately 50 times less than that assumed by the authors in the above papers. A reactive particle concentration of 2 $\mu g/m^3$ would yield a predicted SO_2 removal rate of no more than 0.002 percent per hour. Therefore, surface reactions are probably not important except in sources prior to or immediately after emission.

The most comprehensive study to date on SO_2 removal by pure solids was made by Judeikis (1974) and Judeikis et al. (1978), who used a tubular flow reactor in which solids were supported on an axial cylinder to measure reactivities of MgO, Fe_2O_3, Al_2O_3, MnO_2, PbO, NaCl, charcoal, and fly ash. They found that the rates of SO_2 removal diminished with exposure until the solids completely lost ability to react with SO_2. The relative humidity was important in determining the total capacity for SO_2 removal, but not the initial rate of uptake; total capacity increased as relative humidity increased. The capacity for SO_2 could be extended by exposure to NH_3. This type of behavior is consistent with the formation of H_2SO_4 on the surfaces.

Because of the ubiquitous nature of carbonaceous matter in ambient air particulate samples, various workers have studied the SO_2 removal rate by carbon. A comparison of the results is rather difficult because of the varieties of carbon available for study, such as activated charcoal, graphite, acetylene flame products, and combustion products of diesel oil and heating oil. We cite here a few investigations that deal with the gas-solid reaction of SO_2 with carbon.

Novakov et al. (1974) performed laboratory experiments that showed that graphite and soot particles oxidize SO_2 in air. The soot exposed to humidified air produced more SO_4^{2-} than that exposed only to dry air. They also observed for downtown Los Angeles a strong correlation between the concentrations of ambient carbon and SO_4^{2-}, which supports their hypothesis that carbon (soot) oxidation of SO_2 is the major pathway for SO_4^{2-} formation. (See discussion in Section 2.3.4.3).

Tartarelli et al. (1978) studied the interaction of SO_2 with carbonaceous particles collected from the flue ducts of oil-burning power stations. They concluded that the amount of adsorption is increased by the presence of oxygen and water in the gas stream. Reaction rates were not determined in this study.

Liberti et al. (1978) studied the adsorption and oxidation of SO_2 on various particles, including soot from an oil furnace and various atmospheric particulate samples. They concluded that the main interaction between the SO_2 and particulate matter is adsorption, with most catalytic reactions occurring at high temperatures, near the combustion source. Their

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experiments with atmospheric particulate samples led them to the conclusion that any heterogeneous nonphotochemical sulfate formation is strongly dependent on the reactivity of the particle surface, and hence the history (aged, freshly emitted), of the aerosol.

In summary, the status of our knowledge of surface reactions is:

1. The reactions are capacity-limited. Those that involve catalysis in liquid films can be extended by the absorption of NH_3.

2. The initial rates may be large, but quickly approach zero.

3. Except for the carbon (soot) reaction, solid surface reactions do not appear to be effective pathways for H_2SO_4 formation in the troposphere.

2.3.6 Estimates of SO_2 Oxidation

It is of interest at this point to compare the rates of SO_2 oxidation by the more important reactions identified in the previous sections of Chapter 2. The important reactions for gas-phase and aqueous-phase oxidation are listed in Table 2-11, and rates of SO_2 oxidation for an assumed set of conditions are present. These calculations ignore the non-homogeneous nature of the troposphere and assume that all of the reactants are well-mixed. (The more general case is treated in Chapter 6.)

TABLE 2-11. ESTIMATES OF SO_2 OXIDATION RATES IN WELL-MIXED TROPOSPHERE

Reaction	Rate, % h^{-1}			Discussion Section	Comments
I. Gas phase					
HO radical	0.3 - 1.3			2.3.3.2	1
HO_2 radical	0.4 - 2.0			2.3.3.2	1,2
CH_3O_2 radical	0.3 - 1.5			2.3.3.2	1,2
II. Aqueous phase, pH:	1	3	5		
Mn(II) catalysis	1E-1	1E+1	1E+3	2.3.4.2	2,3,4
Fe(III) catalysis	5E-5	5E-1	5E+3	2.3.4.2	3,5
C (soot) catalysis	3E+1	3E+1	3E+1	2.3.4.3	6
O_3 (40 ppb)	2E-8	2E-6	2E-4	2.3.4.4	3,7
O_3 (120 ppb)	6E-8	6E-6	6E-4	2.3.4.4	3,7
H_2O_2 (1 ppb)	2E-2	3E-2	3E-2	2.3.4.4	3,8
H_2O_2 (10 ppb)	2E-1	2E-1	3E-1	2.3.4.4	3,8

NOTE: "E" denotes "exponential to 10th power;" e.g., 3E-1 = 3 X 10^{-1}

1. Typical range for daytime at northern midlatitudes during the summer.
2. This reaction rate is not well established; see discussion section.
3. Assumed that liquid water volume of aerosol = 50 x $10^{-12} m^3/m^3$, $[SO_2]_g$ = 10 ppb (or 27 $\mu g/m^3$).
4. Assumed that Mn(II) mass concentration = 20 ng/m^3; also, the Mn(II) is assumed to be uniformly dissolved in the liquid water of the aerosol ([Mn(II)] = 8.9 x 10^{-3}M). Rate calculation used the expression of Neytzell-de Wilde and Taverner (1958); see Table 2-7.

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5. Assumed that Fe(III) mass concentration = 2 $\mu g/m^3$; also, the Fe(III) is assumed to be uniformly dissolved in the liquid water of the aerosol ([Fe(III)] = 0.9 M). Rate calculation used the expression of Neytzell-de Wilde and Taverner (1958); see Table 2-9.
6. Assumed that C mass concentration = 10 $\mu g/m^3$ and behaves as the soots studied by Chang et al. (1979), whose expression was used for this calculation (Equation 2-32).
7. Rate calculation was based on Equation 2-35.
8. Rate calculation was based on Equation 2-39.

For this comparison, it has been assumed that the SO_2 concentration is 10 ppb for all of the reactions, and that the liquid water content of the aerosol is 50×10^{-12} m^3/m^3.

The gas-phase rates have been calculated based on the discussion material presented in Section 2.3.3.2. The aqueous-phase rates have been calculated based on the discussion material presented in Sections 2.3.4.2-4. Several of the assumptions made do not have any basis, namely:

1. The ambient mass concentration of 20 ng/m^3 for Mn is reasonable, but: (a) it is not known if the predominate form is Mn(II), and (b) it is unlikely that Mn is uniformly distributed and dissolved.

2. Likewise, the ambient concentration of 2 $\mu g/m^3$ for Fe is reasonable, but: (a) it is not known if Fe(III) is the predominate form, and (b) it is unlikely that Fe is uniformly distributed and dissolved.

3. There is no basis to assume that the rate equation observed for laboratory-generated carbon (soot) applies to atmospheric carbon.

4. The rates for the HO_2 and CH_3O_2 reactions recommended by Calvert et al. (1978) are not well established.

It is very likely that the rates estimated for Mn(II) catalysis, Fe(III) catalysis, and C (soot) catalysis are gross over-estimates. Also, the HO_2 and CH_3O_2 rates may be too high.

Uncritically accepting all of the rates, at a pH = 3, and $[H_2O_2]$ = 10 ppb, the SO_2 conversion rate would exceed 40% h^{-1}. However, if only the well-established rates are considered, the SO_2 conversion rate becomes ~1.1% h^{-1}.

In summary, our status of knowledge of SO_2 oxidation pathways is:

1. The gas-phase reaction rate of HO and the aqueous-phase reaction of H_2O_2 are well established, but are expected to account for only about 1.1% h^{-1} (under the conditions given in Table 2-11).

2. The Mn(II), Fe(III), and C (soot) catalyzed reactions have sufficient rates to dominate SO_2 oxidation in the troposphere, but we do not have confidence that the assumptions discussed above are reasonable.

2.4 PHYSICS AND CHEMISTRY OF PARTICULATE MATTER

Knowledge of the physics and chemistry of particulate matter is necessary for design of satisfactory samplers and monitors, understanding the relationships between sources and

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effects, and understanding important processes in the troposphere that involve chemical transformations and removal.

In Section 2.2, the global cycle and annual budget for sulfur were presented to aid in establishing the goals and limitations of this document's treatment of sulfur oxides. That discussion is insufficient in that particulate matter is related to cycles of numerous elements and their interactions. Among the more important cycles of elements are: sulfur, nitrogen, carbon, hydrogen, boron, oxygen, sodium, aluminum, silicon, phosphorous, chlorine, potassium, calcium, vanadium, manganese, iron, mercury, and lead. Since it is beyond the scope of this document to deal with the details of these cycles, a perspective of the problem can be obtained from a budget estimate of the particulate mass injected into the troposphere. The estimate by Hidy and Brock (1971) of the daily particulate mass emitted or formed in the troposphere is presented in Table 2-12. On a global basis, the anthropogenic contribution is about 6 percent; however, the non-homogeneous distribution and the type of emissions pose serious problems. (See Chapter 4 for a discussion of sources in the United States.) Figure 2-2 showed the general inter-relations of pathways, processes, and properties of sulfur oxides and particulate matter and effects. Section 2-3 treated the SO_2 physical properties and chemistry (including transformation chemistry), which are indicated in Figure 2-2. Section 2.4 will discuss the physics and chemistry of particulate matter that are related to particle properties, single particle dynamics of motion, formation and growth, and aerosol system dynamics.

The budget in Table 2-12 indicates that secondary particulate matter formation dominate the rates. The importance of this type of source will be made evident in the discussions in Section 2.4.

2.4.1 Definitions

The field of aerosol science spans chemistry, physics, engineering, meteorology, and the biological sciences. Unfortunately, the lack of communication between workers in these diverse disciplines has impeded the unification of their ideas. One of the results has been a lack of universally accepted definitions of the terms "aerosol" and "particle" and the terms for classification of aerosol systems. For the purpose of this document, the definitions are made to be consistent with the general usage by atmospheric scientists.

Particle -- any object having definite physical boundaries in all directions, without any limit with respect to size (Cadle, 1975). In practice, the particle size range of interest is used to define "particle." In atmospheric sciences, "particle" usually means a solid or liquid subdivision of matter that has dimensions greated than molecular radii (~10 nm); there is also not a firm upper limit, but in practice it rarely exceeds 1 mm.

Aerosol -- a disperse system with a gas-phase medium and a solid or liquid disperse phase (Fuchs, 1964). Often, however, individual workers modify the definition of "aerosol" by arbitrarily requiring limits on individual particle motion or surface-to-volume ratio (e.g., see Hidy and Brock, 1970). Aerosols are formed by (a) the suspension of particles due to grinding or atomization, or (b) condensation of supersaturated vapors (Fuchs, 1964).

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For the purpose of this document, an aerosol is not the halocarbon vapor used as the propellent in pressured cans (commonly referred to as "aerosol cans" and "aerosol bombs"). The improper use of the term "aerosol" by marketers of foams, gels, sprays, etc., has caused the lay public to associate incorrectly environmental issues of suspended particulate matter with the issue of halocarbon impact on the stratospheric ozone layer. In the context of this document, the usage of the term "aerosol" is not related to the impact of halocarbons on stratospheric ozone layer.

TABLE 2-12. ESTIMATE OF TROPOSPHERIC PARTICULATE MATTER PRODUCTION RATES[a]

Source	% by weight of total[b]
A. Natural sources	
1. Primary	
Wind-blown dust	9.3
Sea Spray	28
Volcanoes	0.09
Forest fires	3.8
2. Secondary	
Vegetation	28
Sulfur cycle	9.3
Nitrogen cycle	14.8
Volcanoes (gases)	0.009
SUBTOTALS	94
B. Manmade sources	
1. Primary	
Combustion and industrial	2.8
Dust from cultivation	0.009
2. Secondary	
Hydrocarbon vapors	0.065
Sulfates	2.8
Nitrates	0.56
Ammonia	0.028
SUBTOTALS	6
TOTAL	100

[a]Source: Hidy and Brock (1970)
[b]Production rate = 10.7×10^6 metric tons/day

Traditionally, workers in various scientific fields have classified the aerosol systems to reflect their origin, physical state, and range of particle size. The meanings of these classifications are not universally accepted; however, the following definitions are consistent with general usage by atmospheric scientists.

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Particulate Mass -- a generic classification in which no distinction is made on the basis of origin, physical state, and range of particle size (Dennis, 1976). (The term "particulate" is an adjective, but it is commonly used incorrectly as a noun.)

Dust -- dispersion aerosols with solid particles formed by comminution or disintegration without regard to particle size (Fuchs, 1964; Dennis, 1976; Hidy and Brock, 1970). Typical examples include (a) natural minerals suspected by the action of wind and (b) solid particles suspended during industrial grinding, crushing, or blasting.

Smokes -- dispersion aerosols containing both liquid and solid particles formed by condensation from supersaturated vapors (Fuchs, 1964; Hidy and Brock, 1970). Generally, the particle size is in the range of 0.1 μm to 10 μm. A typical example is the formation of particles due to incomplete combustion of fuels.

Fumes -- dispersion aerosols containing liquid or solid particles formed by condensation of vapors produced by chemical reaction of gases or sublimation (Dennis, 1976). Generally, the particle size is in the range 0.01 μm to 1 μm. Distinction between the terms "smokes" and "fumes" is often difficult to apply.

Mists -- suspension of liquid droplets formed by condensation of vapor or atomization; the droplet diameters exceed 10 μm and in general the particulate concentration is not high enough to obscure visibility (Hidy and Brock, 1970).

Fogs -- same as "mists," but the particulate concentration is sufficiently high to obscure visibility (Hidy and Brock, 1970). [Dennis (1976) proposes alternate definitions that distinguish "mists" and fogs" on the basis of particle size.]

Haze -- an aerosol that impedes vision (Dennis, 1976) and may consist of a combination of water droplets, pollutants, and dust (Hidy and Brock, 1970).

Smog -- a combination of "smoke" and "fog." Originally this term referred to episodes in Great Britain that were attributed to coal burning during persistent foggy conditions (Chambers, 1968). In the United States "smog" has become associated with urban aerosol formation during periods of high oxidant concentrations.

Smaze -- a combination of "smoke" and "haze" (Corn, 1968).

Cloud -- a free aerodisperse system of any type having a definite size and form and without regard to particle size (Fuchs, 1964).

Primary Particles (or Primary Aerosols) -- dispersion aerosols formed from particles that are emitted directly into the air and that do not change form in the atmosphere (NAS, 1977). Examples include windblown dust and ocean salt spray.

Secondary Particles (or Secondary Aerosols) -- dispersion aerosols that form in the atmosphere as a result of chemical reactions, often involving gases (NAS, 1977). A typical example is sulfate ions produced by photochemical oxidation of SO_2.

In addition to classifying aerosol systems by their properties (origin, physical state, size), systems are classified according to the performance characteristics of the sampler or analyzer. Some of the more common classifications used are the following:

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Aitken nuclei -- those particles and ions measured by means of an instrument in which water vapor is made to condense on particles by supersaturating the vapor (White and Kassner, 1971). In order to eliminate condensation of light ions, the supersaturation should not exceed 270% (White and Kassner, 1971). The term "condensation nuclei" is often used synonymously with the term "Aitken nuclei."

Total Suspended Particulate (TSP) Mass -- the particulate mass that is collected by the Hi-Volume Sampler. (The system is classified in terms of the operational characteristics of the sampler. See the discussion in Chapter 3.)

Coarse and Fine Particles -- these two fractions are usually defined in terms of the separation diameter of a sampler. For the dichotomous sampler (see Chapter 3), the separation diameter is usually set to be 2.5 μm. Thus, for the dichotomous sampler, the "coarse particles" are those with diameters greater than 2.5 μm and that are collected by the sampler; the "fine particles" are those with diameters less than 2.5 μm and that are collected by the sampler. (NOTE: seperation diameters other than 2.5 μm have been used.)

Additional definitions that relate to particulate size, particle size distributions, and particle motion will be provided in the context of the material discussed in the following Sections.

2.4.2 Physical Properties of Gases and Particles

It is necessary to know the physical properties of the gases and particles of an aerosol system in order to understand the behavior of the system. Such knowledge is necessary for the design of particle samplers, understanding the effects of aerosols (e.g., loss of visual quality), understanding aerosol processes (such as coagulation, growth, deposition), and modeling the effects and dynamics of aerosols.

2.4.2.1 Physical Properties of Gases--An aerosol consists of two principal components: the gas-phase medium and the solid or liquid disperse phase. The behavior of aerosol systems can be described in terms of the behavior and interaction of these two components.

For tropospheric aerosols, the gas of interest is "air." The molecular and fluid properties of air are well established and will not be reviewed here (see Hirschfelder et al., 1954; Bird et al., 1960). The fluid motion of air, especially laminar flow, is adequately understood. Presently, turbulent flow is formulated in statistical descriptions, and often the flow fields in complex geometry cannot be satisfactorily predicted. This limitation in theory has seriously affected our ability to describe the tropospheric microscale motion of particles with diameters greater than 10 μm; specific problems include the performance of particle samplers and the formulation of particle dry deposition.

In summary, the status of knowledge of the properties of air is:

1. The physical properties are adequately known.
2. Laminar flow of air is adequately understood.
3. Turbulent flow must be described in terms of a random fluctuating component; this limitation seriously affects our ability to describe particle motion, especially for particles with diameters greater than 10 μm.

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2.4.2.2 Physical Properties of Particles--The physical properties of particles that influence behavior have been recognized to be divided into three types (Billings and Gussman, 1976): physical configuration, bulk material properties, and surface properties. The specific properties within these three types that are important for characterizing tropospheric particles are discussed in detail.

2.4.2.2.1 Physical configuration. The shape, structure, and density are physical configuration properties that are very important parameters in the equations of motion for particles.

The shape of particles is highly variable. Tropospheric particles have been reported to have the following types of shapes: spherical, irregular, cubical, flake, fibrous, and condensation flocs. The shape of particles has been observed to be related to source type, as shown in Table 2-13.

The physical dimensions of particles are usually expressed in terms of an equivalent statistical diameter; for such a measure to be meaningful for non-spherical particles, it must be applied as an average to a statistically significant number of particles (Cadle, 1975). For sizing collected particles, the most widely used "diameters" for irregular particles are:

TABLE 2-13. PARTICLE SHAPES AND SOURCE TYPES[a]

Shape	Examples
Spherical	Smoke, pollen, fly ash
Irregular	Mineral
Cubical	Cinder
Flakes	Mineral, epidermis
Fibrous	Lint, plant fiber
Condensation flocs	Carbon, smoke, fume

[a]Whitby et al., 1957.

1. Martin's diameter -- the distance between opposite sides of the particle, measured crosswise of the particle and on a line bisecting the projected area. (For examples, see Cadle, 1975; McCrone and Delly, 1973.)

2. Feret's diameter -- the distance between two tangents on opposite sides of the particle. (For examples, see Cadle, 1975; McCrone and Delly, 1973.)

3. The maximum horizontal intercept -- the longest diameter from edge to edge of the particle, parallel to the reference line (McCrone and Delly, 1973).

4. The projected area diameter (British Standard method) -- found by comparing the projected area of the particle with the areas of reference circles on an ocular graticule (McCrone and Delly, 1973).

Historically, these four "diameters" are of interest in powder technology; they possess a deficiency in their usefulness for applications relating to particle dynamics. They describe

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the shape in terms of one or two dimensions (i.e., projected surface area). The dynamics of particle motion are formulated in terms of the diameters of spheres (which is a three-dimensional shape). The relation between the "diameters" measured for projected surface areas of irregular particles and the "diameter" meaningful for particle motion is not obvious. For regular-shaped particles (e.g., cubes, cylinders, oblates), Fuchs (1964) has derived dynamic shape factors that permit their representation as equivalent spheres.

The density (mass per unit volume) of particles is an important parameter that affects motion and behavior. The density of particles that are spheres, cubes, and other regular geometries is the same as the density of the bulk material. However, many particles are agglomerates of smaller particles of various composition. Such agglomerates have a large percentage of their volume as voids or pores that are filled with air. Such a structure has the appearance of a cluster of grapes. The sum of the volume of the small solid/ liquid particles plus the void volume is defined as the "apparent" volume of the agglomerate. The "apparent density" of agglomerates is defined as the ratio of solid/liquid mass to the apparent volume (Fuchs, 1964), and it is often factors of 2-10 times lower than the density of mass that excludes the pore volume (Hesketh, 1977).

Because of the large number of tropospheric particles that are irregular or agglomerates and have unknown density, it has become common practice to represent the shape, structure and density of particles in terms of dynamically equivalent spheres of unit density. Hence, the following definition:

Aerodynamic diameter -- the diameter of a sphere of unit density (1 g/cm^3) that attains the same terminal velocity at low Reynolds number in still air as the actual particle under consideration.

2.4.2.2.2 Bulk material properties. The bulk material properties that affect aerosol behavior include chemical composition, vapor pressure, hygroscopicity and deliquescence, and index of refraction. These properties are of interest because they control (a) the physical state and growth, and (b) the scattering and absorption of light by tropospheric particles.

The chemical composition of tropospheric particles will be discussed briefly in Section 2.4.5 and in more detail in Chapter 5. It is sufficient to point out here that the particles with diameters less than approximately 2.5 μm contain most of the SO_4^{2-}, NO_3^-, H^+, and NH_4^+ and interact with H_2O vapor much more strongly than larger particles (Meszaros, 1971; Charlson et al., 1978).

The most important systems are those of H_2SO_4, NH_4HSO_4, $(NH_4)_2SO_4$. These systems have been characterized recently by Charlson et al. (1978), Tang et al. (1976), Tang and Munkelwitz (1977), and Tang (1980a). Charlson et al. (1978) used an apparatus in their studies that measured the light scattering coefficient of the aerosol as a function of the relative humidity. They obtained good agreement between theory and experiment in observing the hygroscopic behavior of H_2SO_4. However, they did not observe the predicted deliquescence points of NH_4HSO_4 and $(NH_4)_3H(SO_4)_2$. They speculated that these transitions were not observed because the salt

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particles may have exhibited hysteresis and formed supercooled solutions (Orr et al., 1958). Tang (1980a) used a system in which the salt aerosol was first dried, and then passed through a controlled humidity chamber; the particles were sized with a single-particle optical analyser. His data on deliquescence points and hygroscopic growth agreed well with theory, and he concluded that for the NH_4HSO_4-H_2O systems that the equilibrium size of mixed-salt droplets may be adequately predicted from bulk solution properties. (The Kelvin effect, which may limit growth, is discussed in Section 2.4.4.) Tang (1980a) has described the equilibrium deliquescence points and hygroscopic behavior for the complete H_2O-$(NH_4)_2SO_4$-H_2SO_4 system. He also demonstrated the hysteresis phenomenon for $(NH_4)_2SO_4$ particles; as the particles were subjected to decreasing relative humidity, solid crystals did not form at the deliquescence point (79.5% RH), but formed at about 30% RH (in agreement with the observations of Orr et al., 1958).

The influence of NO_3^- is an important consideration. Tang (1980b) has performed detailed qualitative calculations of the partial pressures of NH_3 and HNO_3 over the NH_3-HNO_3-H_2SO_4-H_2O system at 24°C. He studied the effects of relative humidity and pH on these partial pressures and deduced that: (1) the HNO_3 partial pressure depends strongly on both the relative humidity and droplet pH, and (2) the NH_3 partial pressure varies only slightly with humidity but inversely with H^+ concentration. Tang (1980b) remarked that the strong dependence of the HNO_3 partial pressure on relative humidity may affect the nitrate content of particles that are sampled, leading to biases in the determination of ambient NO_3^-.

Charlson et al. (1978) have reviewed the potential use of the difference in the indices of refraction for differentiating ambient particles of H_2SO_4 and $(NH_4)_2SO_4$. The ratio of backward hemispheric scattering to the total scattering was measured near St. Louis in 1973 during periods that were classified as H_2SO_4 or $(NH_4)_2SO_4$ dominated events. However, the absolute value of the backward/total scatter did not agree with the predicted, which led Charlson et al. (1978) to deduce that the <u>refractive index</u> is too variable to be used as an analytical tool in differentiating the types of SO_4^{2-} systems.

In general, the status of our knowledge regarding the bulk material properties is:

1. Bulk material properties are adequate for describing the state of tropospheric particles.

2. However, there is a paucity of thermodynamic data to permit prediction of deliquescence and hygroscopic behavior and vapor pressures of multi-component systems, especially for relative humidities below about 90 percent.

2.4.2.2.3 <u>Surface properties</u>. The surface properties of particles provide a means of detection and measurement, collection, and may increase persistence of droplets in the atmosphere. Some of the more important surface properties are: electrostatic charging, adhesion, and the influence of surface films.

A number of identifiable mechanisms can lead to electrostatic charging of particles. These include contact charging, photionization, field emission charging, and gaseous ion capture. For the practical applications in the troposphere gaseous ion capture is the most

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important of these mechanisms. Contact charging also produces charging as in the triboelectric charging of dust as a result of dust rise by wind on the earth surface and by production of charged sea spray aerosols over the ocean.

Reviews of experiment and theory for gaseous ion capture by aerosol particles may be found in Bricard (1977) and Whitby and Liu (1966). Two recognized capture mechanisms are field charging and diffusion charging. Field charging denotes the process in which an ion is captured by a particle in the presence of an external electrical field. Diffusion charging is a process in the absence of an external electrical field. Field charging of aerosol particles is utilized in particle control technology in the operation of electrostatic precipitators. Diffusion charging is employed in classification or sizing of aerosol particles according to their electrical mobility.

The rate of gaseous ion capture by an aerosol particle depends upon a number of parameters including the particle size and shape, the dielectric coefficient of the particle, the number of charges already on the particle, and the mean free path and mobility of the gaseous ion, plus, for field charging, the external electrical field strength.

The charging of an aerosol has been shown to be a stochastic process by Biosdron and Brock (1970). Inherent difficulties in the use of particle charging as an aerosol detection method has been shown by Marlow (1978a and 1978b) and by Porstendorfer and Mercer (1978). These studies indicate that the polydispersity of the aerosol, the dielectric coefficient of the particles, and humidity in the presence of trace gases lead to uncertainties in aerosol particle charges.

Particles are removed from the troposphere by diffusion to or impaction against surfaces; particles also collide with each other and stick together. The forces of adhesion that hold particles to surfaces and to each other include electrostatic forces, capillary forces in the presence of a liquid, and London van der Walls forces. In general, for uniform conditions, the efficiency of particle removal from surfaces by air flow decreases as the particle size decreases for dry, solid particles (Corn, 1976). While the types of forces are known, the magnitude of these forces usually cannot be predicted precisely.

The influence of surface films on aqueous droplets has been recognized for many years (Bradley, 1955; Eisner et al., 1960). Chang and Hill (1980) have reviewed some of the studies on droplet stabilization by surface films. They have also demonstrated that the products of the reaction between O_3 and 1-decene in humid air produces a species that adsorbs on water droplets and retards the evaporation rate. Chang and Hill (1980) suggest that photochemical reactions may produce similar products that would retard the evaporation of urban fogs, and perhaps extend their duration by hours. However, they report no kinetic data. Eisner et al. (1960) investigated the kinetics of evaporation of droplets with fatty alcohols on the surface. They were able to increase the lifetime of an evaporating 10-μm droplet only by a factor of about 250, which corresponds to about 2.5 minutes. (Another likely cause of stable fogs is the formation of supercooled droplets.) At this time, the influence of photochemically produced organic condensates on the kinetics of droplet evaporation is not known.

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2.4.3 Dynamics of Single Particles

The behavior of atmospheric aerosols depends upon the physical properties of the suspending gas, the particles, gas-particle interactions, particle-particle interactions, and the fluid motion of the gas. Knowledge of these properties and interactions is essential to our understanding of atmospheric phenomena, our ability to formulate predictive models of pollutant particle concentrations and effects, and our ability to sample and measure particles. In this section, the conditions will be presented for which aerosol systems can be described in terms of the dynamics of single particles.

According to Hidy and Brock (1970), particles may be considered to be independent of each other and the dynamics of single particles may be applied if the conditions in Table 2-14 are satisfied. If coagulation or deposition is an important process, and the system satisfies all but the last condition, they refer to the system as being in the "quasi-single particle regime." As is seen in Table 2-14, the conditions for the "single particle regime" are generally satisfied for the troposphere.

The dynamics of single particles include sedimentation, impaction, diffusion, coagulation, electrodynamics, and filtration (Fuchs, 1964; Hidy and Brock, 1970; Friedlander, 1977). In general, the dynamics can be described adequately for particles with diameters less than 10 μm. However, the motion of particles with diameters greater than 10 μm in a turbulent air stream cannot be predicted accurately. This deficiency in theory has adversely impacted our efforts to design adequate samplers for particles with diameters greater than 10 μm.

2.4.4 Formation and Growth of Particles

Particles are formed by two processes: (1) the grinding or atomization of matter, and (2) the nucleation of supersaturated vapors. The particles formed in the first process may be emitted directly into the atmosphere. However, the particles formed in the second process usually result from reactions of gases in the atmosphere to yield compounds with low vapor pressures, when such species reach sufficiently high supersaturation, they nucleate to form particles. The dynamics of nucleation have been extensively reviewed by Hidy and Brock (1970), who discuss two types:

1. Homogeneous nucleation, which is the formation of particles by the molecular agglomeration of supersaturated vapors in the absence of foreign particles and ions. Important examples include the formation of particles by: (a) H_2SO_4 molecules produced by the reaction of HO radical with SO_2, and (b) carboxylic acids formed by the reaction of O_3 and olefins.

2. Heterogeneous nucleation, which is the condensation of molecules of a supersaturated vapor onto foreign particles or ions. Important examples include: (a) the condensation of hydrocarbon vapors onto Pb halide and carbon particles during cooling of automobile exhaust, and (b) the condensation of H_2SO_4 molecules onto fly ash during the cooling of plumes from power plants burning fossil fuels.

Particle growth in the atmosphere occurs through gas-particle interactions, and particle-particle interactions (coagulation).

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TABLE 2-14. CONDITIONS FOR THE SINGLE-PARTICLE REGIME[a]

Conditions	Range in troposphere
1. $n_i/n_G \ll 1$ for all i	$\sim 10^{-13}$ to 10^{-19}
2. $\lambda_G n_i^{1/3} \ll 1$ for all i	$\sim 10^{-3}$ to 10^{-5}
3. $R_i n_j^{1/3} \ll 1$ for all i,j	$\sim 10^{-1}$ to 10^{-7}
4. $n_i^{1/3} L_{vi} \ll 1$ for all i	~ 0
5. $Q_i Q_j K/kT \ll 1$ for all i,j	$\sim 10^{-2}$ to 10^{-6}

[a] From Hidy and Brock (1970).

[b] n_i = number concentration of particles of type i
n_G = number concentration of air molecules ($\sim 10^{-19}$ cm^{-3})
λ_G = mean free path of air molecules ($\sim 10^{-5}$ cm)
R_i = radius of particle, cm
L_{vi} = characteristic distance (cm) associated with change in number concentration, temperature, and velocities
Q_i = electrostatic charge
K = Debye reciprocal length
k = Boltzmann' constant
T = temperature, °K

Gas-particle interactions include the absorption and the adsorption of pollutant gases, such as SO_2, NO_2, hydrocarbons, O_3 and H_2O_2, followed by their chemical reactions to yield products such as SO_4^{2-}, NO_3^-, and organics. Also included is the condensation of low-vapor pressure molecules formed in gas phase reactions, such as H_2SO_4, HNO_3, and organics. An important limitation on the accumulation of chemical species on submicrometric particles is the Kelvin-Gibbs effect. The vapor pressures of the solvent and solute (or surface-absorbed species) are increased as surface curvature is increased. For a condensing species being formed by gas-phase reactions, there will be a minimum particle-size for which condensation will not occur; this value is determined in part by the supersaturation reached by the species (Friedlander, 1977).

Nair and Vohra (1975) have used bulk vapor pressure data and the Kelvin-Gibbs equation to predict the growth behavior of H_2SO_4 droplets as a function of the degree of H_2O supersaturation. For example, a droplet with 10^{-17}g H_2SO_4 has a diameter of 0.02 μm at r.h. = 0 percent. At r.h. = 100 percent, its diameter increases by a factor of 3; droplets with greater dry mass

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of H_2SO_4 will grow without bound. However, this 10^{-17}g H_2SO_4 droplet and those smaller are prevented by the Kelvin-Gibbs effect from reaching the critical size needed for unbounded growth (a r.h. $\geq$ 102 percent is required for this mass). This effect is important because it prevents the dilution of H_2SO_4 acidity in particles below the critical growth diameter; such particles when inhaled could remain highly acidic.

Our status of knowledge of the formation and growth of particles is:

1. Fundamental problems remain regarding nucleation, condensation, diffusion, coagulation, and transport. However, our understanding is adequate to explain and predict the tropospheric behavior of particles with diameter less than 10 μm.

2. The dynamics of motion of particles with diameters greater than 10 μm are difficult to predict, especially in turbulent flow fields.

2.4.5 Characterization of Atmospheric Aerosol

Significant advances have been made in the past decade in regard to elucidating the nature of the tropospheric particle size, area, volume, and mass distribution functions and the chemical composition. This section will discuss general aspects of distribution functions, the observed behavior of tropospheric particle distributions, and chemical composition. Evidence will be presented for the existence of multi-modal mass distributions and the difference in composition of particles above and below 2.5 μm.

2.4.5.1 Distribution--The multimodal nature (to be discussed below) of tropospheric particle surface and mass distribution functions remained unrecognized until the early 1970s. The factors that caused it to remain dormant were the methods of presenting number size distribution data and mass distribution data.

Tropospheric particles are polydisperse. For reason of convenience, particle size, area, and volume (or mass) data are usually expressed in terms of a mathematical distribution function. Such functions are ordinarily characterized by two parameters. The fraction of the total number of particles having diameters which lie between D and dD is

$$dN = f(D)dD \qquad (2\text{-}41)$$

with the normalization condition

$$\int_0^\infty f(D)dD = 1. \qquad (2\text{-}42)$$

the curve representing the function f(D) is called the "number frequency distribution" or the "number differential" curve. Similarly, the area and volume frequency distributions are

$$dA = f(D^2)dD \qquad (2\text{-}43)$$

and

$$dV = f(D^3)dD \qquad (2\text{-}44)$$

where the proper normalization is taken into account.

*

Prior to the 1970s, atmospheric scientists employed two predominate types of frequency distributions [i.e., functional forms of f(D), $f(D^2)$, and $f(D^3)$]: they were (a) Junge's (1955) power law distribution for particle size, and (b) the log-normal distribution for mass.

Investigators that employed instrumentation that measured the particle size spectra usually reported their data in terms of Junge's (1955) power law, which is

$$\frac{dN}{dD} = AD^{-k} \qquad (2\text{-}45)$$

where A and k are constants. Clark and Whitby (1967) found that this power law was a reasonable fit to the number distribution, but it was an inadequate model of the surface and volume distribution.

Also, investigators that used cascade impactors that determined the mass distribution spectra usually reported their data in terms of the log-normal distribution (see Fuchs, 1964; Cadle, 1975). While multi-modal log-normal distributions can be recognized from standard plots of data on log-normal graph paper, three effects combined to mask the multi-modal character of urban particle mass distribution: (1) the cascade impactors had serious (and unknown) inlet biases against particles larger than about 5 μm, (2) the cascade impactors did not have operational characteristics that permitted mass fraction below about 0.2 μm, and (3) particle bounce distorts the mass distribution in cascade impactors. The warning of Fuchs (1964) that the log-normal distribution is an adequate model only if the particles are sampled perfectly and the sampler provides adequate fractionation points went unnoticed.

Whitby et al. (1972) were responsible for a major advance in recognizing that Junge's (1955) power law and the log-normal distribution function were inadequate models of experimental data for urban aerosols. Instead of seeking other functional forms to express the number, area, and volume distribution, they plotted dN/d log D, dA/d log D, and dV/d log D versus log D. The result is seen in Figure 2-7. This type of plot has a convenient feature: the area under the curve is proportional to the quantity (N, A, or V) between two diameters. The particle volume between the diameters D_1 and D_2 is:

$$V(D_1, D_2) = \int_{\log D_1}^{\log D_2} (dV/d \log D)\, d \log D \qquad (2\text{-}46)$$

For small values of Δ log D, Equation 2-43 becomes

$$V(D_1, D_2) = \overline{(\Delta V/\Delta \log D)} \times \Delta \log D \qquad (2\text{-}47)$$

where $\overline{(\Delta V/\Delta \log D)}$ is the average value in the interval between log D_1 and log D_2.

The peaks in the three types of distribution plots are called "modes". As is evident in Figure 2-7, there is usually one "number mode", one or two "surface modes", and two "volume modes" for urban aerosols; sometimes an additional mode is observed in the range from 0.005 to

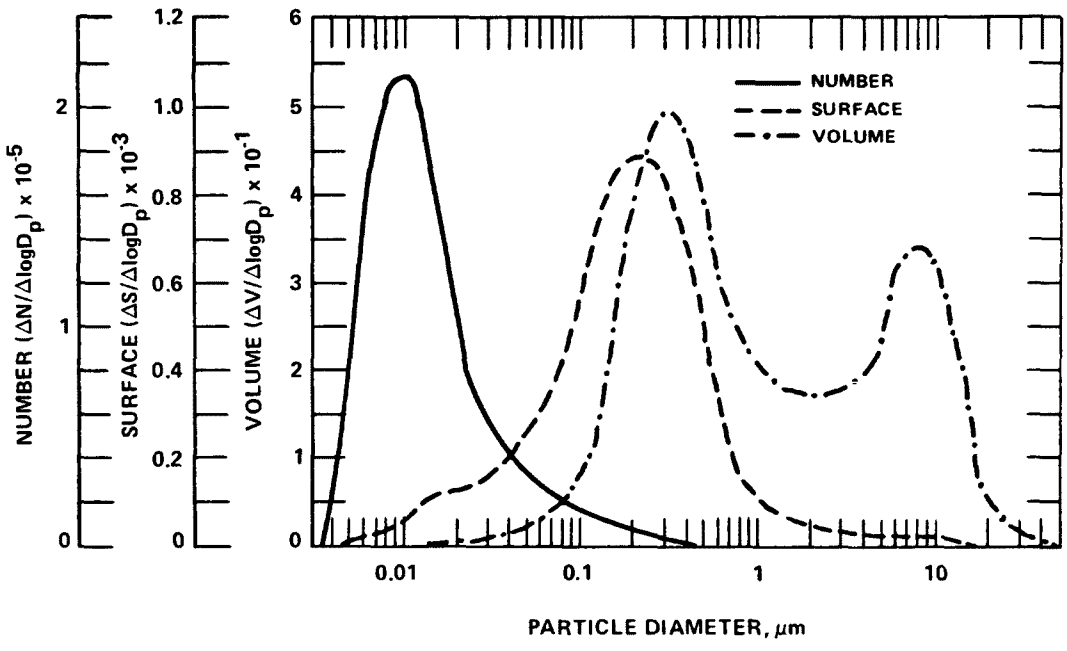

Figure 2-7. Frequency plots of number, surface, and volume distributions for 1969 Pasadena smog aerosol.

Source: Airborne Particles (NAS, 1977).

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0.05 μm. Because of the differences in chemical composition for particles with diameters greater and less than 2.5 μm, samplers have been devised to collect particles into these two fractions (called fine and coarse).

The fine volume fraction consists mainly of secondary particles that have been recognized as forming two modes: (1) the Aitken (or nuclei) mode, which is from 0.005 to 0.05 μm diameter, and (2) the accumulation mode, which is from 0.05 to 2 μm.

The multi-modal distributions are generally observed for urban aerosols, but may not be detected in other cases, such as marine environments or areas under the domination of a strong source.

In summary, the status of our knowledge of the size distribution of continental tropospheric particles is:

1. The particle volume (or mass) frequency function ($\Delta V/\Delta$ log D versus log D) is often multi-modal. The fine volume fraction may have two or more modes at ~0.02 and ~0.2 μm. The coarse fraction generally has one mode within the range ~5 - 50 μm.

2. The types of sources of particles that contribute to the fine and to the coarse fractions are well known.

3. The relative behavior of the particle volume frequency functions for the fine and for the coarse fractions often behave independently.

2.4.5.2 Composition of Particle--Upon the elucidation of the multi-modal behavior of particle distributions through the use of the forms $\Delta N/\Delta$ log D, $\Delta S/\Delta$ log D, and $\Delta V/\Delta$ log D, it was recognized that: (1) the chemical composition of the particles above a diameter of about 2.5 μm is different from that below. Evidence will be presented in this section to show that secondary particles containing SO_4^{2-}, NO_3^-, NH_4^+, H^+ and organics are found in the fine fraction, while primary particles consisting of minerals are usually found in the coarse fraction.

TABLE 2-15. CLASSIFICATION OF MAJOR CHEMICAL SPECIES ASSOCIATED WITH ATMOSPHERIC PARTICLES

Fine fraction	Coarse fraction	Both fine and coarse fractions	Variable
$SO_4^=$, C (soot), organic (condensed vapors), Pb, NH_4^+, As, Se, H^+	Fe, Ca, Ti, Mg K, $PO_4^=$, Si, Al organic (pollen, spores, plant parts)	NO_3^-, Cl^-	Zn, Cu, Ni, Mn Sn, Cd, V, Sb

From: Lee and Goranson (1976); Patterson and Wagman (1977); Durham et al. (1975); Rahn et al. (1971); Akselsson et al. (1975); Hardy et al. (1976); Gladney et al. (1974); Lundgren and Paulus (1975); Lee et al. (1968); Lee et al. (1972).

*

Investigations of the chemical composition of the fine and coarse particles for urban aerosols indicate that chemical species may be distributed primarily in the fine or coarse fraction, or both, as is shown in Table 2-15. The major components of the fine fraction of urban particles are SO_4^{2-}, NH_4^+, NO_3^-, Pb compounds, elemental C (soot), and condensed organic matter.

2.4.5.2.1 Elemental Carbon (Soot) and Organics. The carbon in fine particles consists of an elemental component (such as graphite or soot) and an organic component of low volatility. There are significant differences in the optical properties of elemental and organic carbon components. Elemental carbon is formed during the combustion of fossil fuels and is emitted as primary particles (~0.1 μm), which strongly absorb light. The organic component consists of primary hydrocarbons emitted in combustion exhaust and of secondary organics formed by photochemical reactions. These primary hydrocarbons and secondary organic vapors either nucleate or condense on existing aerosols. They do not strongly absorb light, but do contribute to light scattering in urban hazes.

There are only limited data on the mass ratio of elemental/(primary + secondary organics) for a few cities. Appel et al. (1978, 1979) found for a four-day period in July 1975 in Pasadena, Pomona, and Riverside that elemental carbon was the most abundant carbon species; also, the secondary organic carbon was usually twice that of primary hydrocarbons. Of the secondary organics, hexanedioic and pentanedioic acids were among the most abundant products; most likely they were oxidation products of cyclohexene and cyclopentene emitted by motor vehicles. The composition of the organic component retained on filters varied with the length of the sampling period. The retention of less polar organics (e.g., hydrocarbons) was favored by longer sampling time, apparently because of absorption of such organics on previously collected material. From total carbon, benzene soluble organics, and hydrogen analyses of fine particles collected in Denver in Nov. 1971, it was estimated that the elemental carbon was 2.3-3.6 $\mu g/m^3$ for the episode days observed; from measured Pb concentration as a tracer, it was suggested that in Nov. 1973 in Denver the elemental carbon in fine particles was 1.7-4.4 $\mu g/m^3$ (Durham et al., 1979). Also, for Denver in Nov. 1973, Pierson and Russell (1979) estimated from Hi-Vol samples the total elemental carbon to be 2.9-27.6 $\mu g/m^3$.

Although atmospheric measurements of carbon-containing particles are less complete than those of sulfates, available results suggest that carbon-containing particles in many locations, both urban and nonurban, are the second most abundant fine-particle species after sulfates. At some western urban locations where SO_x emissions have been small, carbon-containing aerosols have made the largest contribution to fine-particle mass. The concentration of primary carbonaceous particles is likely to have been even higher in the past in the Eastern United States when coal was more widely used as a fuel. With the possible growing use of industrial coal and wood combustors for home heating, carbonaceous particle concentrations are likely to increase.

The National Academy of Sciences (Grosjean, 1977) has extensively reviewed the methods of primary and secondary organic particle identification, and the physical and chemical aspects

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of their formation. Primary organics emitted into the atmosphere by industrial sources, motor vehicles, agriculture activities, and natural sources include: linear and branched alkanes and alkenes, substituted benzenes and styrenes, quinones, acridines, quinolines, phenols, cresols, pthlalates, fatty acids, carbonyl compounds, polyaromatic hydrocarbons, terpenes and pesticides. Secondary organic particles are formed by the oxidation reactions of the primary organics, ozone, and nitrogen oxides. Typical products that have been identified are: aliphatic organic nitrates, dicarboxylic acids, benzoic and phenylacetic acids, and terpene products such as pinonic acid (Grosjean and Friedlander, 1975; Miller et al., 1972; Schuetzle et al., 1975). By using computer-controlled high-resolution mass spectrometry and thermal analysis Schuetzle et al. (1975) and Cronn et al. (1977) obtained diurnal variations of primary and secondary organics from two-hour size-resolved samples.

In an attempt to understand the atmospheric oxidation pathways that yield secondary organic particles, simple mixtures have been investigated in laboratory chamber studies. As discussed in more detail in the National Academy of Sciences report (Grosjean, 1977), the following trends have been observed by chamber researchers: (a) Most paraffins do not generate aerosols during irradiation, (b) acetylenes do not form aerosols, (c) all other unsaturated compounds with six or more carbon atoms can form organic aerosols, (d) cyclic olefins and diolefins form more aerosol than their 1-alkene analogs, (e) conflicting results have been reported on the aerosol-forming ability of aromatics, (f) carbonyl compounds do not generate aerosol, and (g) mechanical stirring inhibits particle formation. Cyclic olefins are the most efficient class of organic particle precursors, due mainly to their high gas-phase reactivity and their ability to form non-volatile dicarboxylic acids.

The chemical composition of organic particles generated in smog chambers is not well established for suspected important aerosol precursors. Functional group analyses for the products of olefins, benzene and benzene substituted compounds, and terpenes that have reacted with ozone show that the bulk consists of highly oxygenated compounds, which include carbonyls, carboxylic acids, and nitrate esters. Only a few studies of species identification have been reported. Detailed aerosol product identification has been reported for the ozone-1-butene reaction (Lipeles et al., 1973); the NO_x-toluene, NO_x-cyclohexene, and NO_x-α-pinene photo-reactions (Schwartz, 1974), and the NO_x-cyclopentene, NO_x-cyclohexene, and 1-7-octadiene photo-reactions (Grosjean, 1977). Good agreement was indicated by Grosjean (1977) with Schwartz (1974) for the NO_x-cyclohexene photo-reaction, except that Grosjean observed hexanedioic acid to be the major product (not reported by Schwartz). It is significant that most of the polyfunctional compounds identified (see the cited papers and the NAS report for details) have also been identified as important constituents in ambient aerosols.

The secondary particles formed from alkenes having seven or more carbons (cyclic olefins, diolefins, and terpenes) grow into the light-scattering range and produce appreciable visibility reduction. For example, particles formed from cyclic olefins and diolefins have particle sizes between 0.1 and 0.3 μm. For such systems, the gas-to-particle conversion process

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consists of the formation of supersaturation in the gas phase and subsequent condensation on preexisting particles.

The rates of conversion of precursor organic vapors to organic particles in Los Angeles have been estimated to average 1 to 2 percent per hour. This moderate rate of conversion is consistent with the observation that organics account for an important fraction of the fine particles under conditions of intense photochemical activity, while only a small part of the precursor organic vapors are converted to particulate matter.

2.4.5.2.2 Nitrates. Nitrogen oxide gases are oxidized in the atmosphere to yield HNO_3, which accumulates as nitrate in both fine and coarse particles. Because the topics related to the transport of nitrogen oxides and their transformation to gaseous and particulate nitrates are discussed in the Air Quality Criteria for Oxides of Nitrogen (to be published, 1981), they will not be repeated here. (These topics include visibility, environmental transport and transformation, and acidic precipitation.) Atmospheric nitrates most likely result from photochemical reactions involving the oxidation of NO and NO_2 to yield HNO_3 and organic nitrates (Demerjian et al., 1974). The measurement of ambient nitrate particles has been recognized to be subject to significant sampling errors, which are discussed in Chapter 3.

2.4.5.2.3 Summary. In summary, the status of our knowledge of the chemical composition of the fine and coarse mass fractions is:

1. The composition of the coarse fraction of continental tropospheric particles is dominated by primary minerals.

2. The composition of the fine fraction of continental tropospheric particles is dominated by secondary particles that consist mainly of SO_4^{2-}, NO_3^-, NH_4^+, H^+, and organics, plus primary elemental soot.

3. The fine fraction is acidic, and the coarse fraction is basic.

4. The chemical pathways for forming organics and NO_3^- particles are not fully understood.

2.4.6 Modeling of General Aerosol Systems

Qualitatively, the processes that affect the composition and concentration of tropospheric aerosols are understood. For the urban atmosphere, Middleton and Brock (1977) have presented this relationship which applies at some arbitrary point in the urban atmosphere:

$$U = -A + B + C + D + E + F + G \qquad (2\text{-}48)$$

where

U = rate of change in composition or concentration of some size fraction of urban aerosol;

A = rate of change due to advection;

B = rate of change due to convection and dispersion

C = rate of change due to coagulation;

D = rate of change due to accretion and condensation;

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E = rate of change due to homogeneous nucleation;

F = rate of change due to input of primary sources;

G = rate of change due to gravitational sedimentation.

with processes occurring at surfaces, such as deposition, appearing as boundary conditions. Analogous relationships also describe the alteration of other characteristics of the various size fractions making up the urban aerosol. Equations, such as Equation 2-48, for the aerosol are coupled to relate relationships for the various chemical species participating in the aerosol growth processes.

This approach has been applied to the calculation of dust concentrations in Phoenix (Suck et al., 1978); however, the lack of knowledge of the significant chemical pathways for the formation of SO_4^{2-}, NO_3^-, and organics hinder its general application to urban areas.

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CHAPTER 3. TECHNIQUES FOR THE COLLECTION AND ANALYSIS OF SULFUR OXIDES, PARTICULATE MATTER, AND ACIDIC PRECIPITATION

3.1 INTRODUCTION

The 1970 Air Quality Criteria documents for sulfur oxides and particulate matter (SO_x and PM) provided a reasonably thorough review of measurement techniques available at that time. Subsequent advances in measurement technology for these pollutants have resulted in several new techniques and more information on the quality of data collected by older methods. This chapter provides a review and, where possible, a critical assessment of both the earlier techniques used in historical monitoring efforts and the newer techniques on which much of the information gathered in the next few years will be based. Discussion of the methods is intended to be a brief explanation of the underlying principle of the method, the applicability to intended use, and the quality of the aerometric data produced. References to figures and tables in the Appendix of this chapter or to the open literature are provided for more detail.

Selection of methods for this review was primarily based on frequency of usage of a method in past or current studies. These include routine monitoring applications used in demonstrating compliance with air quality standards; in support of effects studies, especially epidemiology; and in examining long-term trends for the evaluation of control strategy effectiveness. More widely used research measurement methods that appear promising as routine monitoring methods or that have been used to collect important ancillary data, such as particle size distributions for aerosols, are also discussed but in less detail.

Measurement techniques for SO_x, PM, and acidic precipitation are intimately related to the chemical and physical properties of the substances measured. Since such properties of SO_x and PM are discussed in detail in Chapter 2, and in Chapters 6-8 for acidic precipitation, only the measurement methods per se are discussed in this chapter. Chemical analysis methods for PM and acidic precipitation for constituents such as sulfates are described following the sections on methods of sample collection. The relationship of particles to visibility and their related measurements are discussed in Chapter 9.

Discussion of each sampling and analytical method covered in this chapter includes a general method description, a discussion of the utility and applicability of the method, and a critical assessment of the method capabilities where information is available. The capabilities described include the accuracy, precision, measurement range, sensitivity to interferences, and reliability. The last parameter (reliability) is strongly influenced by competency of the operator and completeness of accepted procedure documents. It is often difficult to quantify these factors, except in very specific cases, and apply the conclusions to the general utility of the method. Hence an assessment of the quality of historical data based on reliability of the method alone is virtually impossible. Many important earlier studies did not collect certain quality assurance information now shown (Von Lehmden and Nelson, 1977) to be important in field monitoring. In other cases, supporting data were

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collected, but are no longer available. Therefore the critical assessment of the methodology will consider those areas which apply to the general utility of the method, except in cases where specific problem areas were quantified in the open literature for a selected study.

3.2 MEASUREMENT TECHNIQUES FOR SULFUR DIOXIDE

3.2.1 Introduction

Atmospheric sulfur oxides originate from both natural and manmade sources. Sulfur dioxide (SO_2) is the predominant sulfur oxide in the atmosphere, together with smaller amounts of sulfuric acid (H_2SO_4) and sulfate salts. This section discusses techniques that have commonly been used for determination of atmospheric concentrations of SO_2.

Manual methods for determination of SO_2 are those in which sample collection, preparation, and analysis, or some combination thereof, are performed manually. Automated methods are those in which sample collection and analysis are performed continuously and automatically. Devices using such methods are generally referred to as continuous analyzers.

This section focuses on a brief description of each method with emphasis on measurement principle and method characteristics such as detection limits and interferences. Sample collection and method calibration are discussed for both manual and automated methods. Among the manual methods, those most widely used are discussed first. Sulfation methods are presented last only because they measure "sulfation rate" rather than ambient SO_2 concentration *per se*. The discussion of automated methods follows a semi-chronological order, with earlier continuous analyzers described first. Much of the descriptive information in the section is based on a review by Tanner, Forrest, and Newman (1978). Also discussed in this section are various continuous analyzers designated by EPA as equivalent methods for the measurement of SO_2 in the atmosphere to determine compliance with National Ambient Air Quality Standards (NAAQS).

3.2.2 Manual Methods

3.2.2.1 Sample Collection--A number of methods use aqueous solutions for collection of sulfur dioxide. The efficiency of mass transfer of sulfur dioxide from air to the solution phase depends on the gas-liquid contact time, diffusion coefficients of sulfur dioxide in the gas and liquid phases, bubble size, concentration of sulfur dioxide, and solubility of sulfur dioxide in solution. Calvert and Workman (1960) describe a method to predict the efficiency of various bubbler designs in collecting sulfur dioxide. Their method is predominantly qualitative, but it can serve as a useful guide. The more efficient designs include that of Wartburg et al. (1969); the Greenberg-Smith impinger (Smith et al., 1961); midget impingers (Jacobs et al., 1957); Drechsel bottles (British Standards Institution, 1963); and packed columns (Bostrom, 1966), which are useful where low flow rates are involved. In using such devices, care must be taken to prevent carryover of solution at high flow rates and to compensate for solvent losses by evaporation.

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Collection efficiency depends in part on the solution in which sulfur dioxide is actively dissolved and stabilized. One current method involves stabilization of sulfur dioxide as the sulfite anion in an aqueous solution of sodium or potassium tetrachloromercurate, with which the sulfite anion complexes. To prevent conversion of sulfite to sulfate, the temperature of the collecting solution must be maintained below 20°C. Failure to maintain temperature control of samples during collection, shipment, and storage leads to underestimation of sulfur dioxide levels in the atmosphere, particularly during summer months. Another approach involves collection in aqueous solution and conversion to the sulfate anion by oxidizing agents such as hydrogen peroxide. Although stabilization of sulfur dioxide as the sulfate anion can be effective, some of the soluble sulfate in the atmospheric aerosol is collected (unless removed by a particle filter) and added to the sample; thus, discrimination between sulfur dioxide and sulfate may be impossible.

Several methods employ alkaline solutions for the absorption of sulfur dioxide. Although their collection efficiency is quite high, alkaline solutions rapidly oxidize the collected sulfite anion to sulfate unless some means are available for the direct complexation and stabilization of the sulfite anion.

Another collection technique involves the use of filter papers or tapes impregnated with an alkaline reagent such as potassium hydroxide, triethanolamine, or potassium carbonate, together with small amounts of glycerol as an humectant (Lodge et al., 1963; Huygen, 1963; Pate et al., 1963; Forrest and Newman, 1973). The collected sulfur dioxide is supposed to be maintained as a sulfite, but it may be oxidized to sulfate. Although laboratory tests have shown that such oxidation can be negligible, field tests have produced very erratic results. Particulate matter collected from air passing through the filter contains traces of transition metal ions, which promote rapid oxidation of sulfite to sulfate. Prefilters should be used to eliminate particulate matter. Oxidation of the collected sulfite to sulfate prior to analysis is also recommended. Alternatively, an analytical technique that measures both sulfite and sulfate may be employed.

Some of the earlier methods for estimating ambient SO_2 concentrations (sulfation methods) are based on the reaction of sulfur dioxide with lead peroxide to form lead sulfate (Wilsdon and McConnell, 1934). The sulfur dioxide is stabilized in the form of a sulfate, eliminating the problem of oxidative conversion. However, any particulate matter containing sulfate species which come in contact with the collection surface will lead to errors.

Occasionally, samples of ambient air are collected in a gas-tight syringe or other suitable container for later analysis. The reactivity of sulfur dioxide is a major problem, however. Natusch et al. (1978) have reported extensive adsorption losses of SO_2 on thick-walled Mylar® laminates, Tygon®, Teflon®, and stainless steel container walls.

3.2.2.2 Calibration--The relationship between true pollutant concentration and the measured value by any method is determined by calibration. For methods that measure relative exposure to sulfur species (e.g., sulfation methods), no calibration is usually attempted. The use of

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uniform reagents, equipment, and procedures is essential with these methods in order to compare exposure data over time and space. Those methods that involve direct collection of an air sample for later analysis or collection of the SO_2 in an air sample by absorption or adsorption require calibration of both the sample volume measurement and the analytical measurement.

Devices used for sample volume measurement are generally calibrated against reliable volume standards. The analytical measurement is often calibrated statically using a known amount of the sulfite or sulfate anion in solution. Static calibration is a rapid and simple method for checking the analytical procedure, but does not subject the overall measurement method to scrutiny since the process of SO_2 collection is circumvented. Dynamic calibration of these methods has an advantage over the static approach by subjecting the total measurement to scrutiny, but it is time-consuming and therefore not used routinely. This approach, described in more detail in a later section (3.2.3) on automated methods, uses synthetic atmospheres containing the pollutant in known concentrations to define the response of the method.

3.2.2.3 Measurement Methods--The principal manual methods for determining sulfur dioxide in the air are discussed in this section.

3.2.2.3.1 Colorimetric method: pararosaniline. The West-Gaeke method is probably the most widely used colorimetric procedure for SO_2 determination in ambient air (West and Gaeke, 1956). It is also the basis of the EPA reference method for measurement of SO_2 in the atmosphere (U.S. Environmental Protection Agency, 1979). In the West-Gaeke method, air is bubbled into fritted bubblers containing 0.1 M sodium tetrachloromercurate (TCM) solution, which forms the stable dichlorosulfitomercurate ion with SO_2. The SO_2-TCM complex is reacted with bleached pararosaniline and formaldehyde to form red-purple pararosaniline methanesulfonic acid. The optical absorbance of the solution is measured spectrophotometrically at 560 nm and is, within limits, linearly proportional to the concentration of sulfur dioxide. The lower limit of detection of SO_2 in 10 ml of TCM absorbing solution is approximately 0.5 μg, representing a concentration of 13 μg SO_2/m^3 (0.005 ppm) in an air sample of 38.2 liters. Ozone, nitrogen dioxide, and heavy metals were negative interferents in early versions of this method.

An improved version of the West-Gaeke method was adopted by EPA in 1971 as the reference method for the determination of atmospheric SO_2 (U.S. Environmental Protection Agency, 1979). Several important parameters were optimized, resulting in greater sensitivity and reproducibility, as well as adherence to Beer's Law throughout a greater working range. In the EPA method, SO_2 is collected in impingers containing 0.04 M potassium tetrachloromercurate. A 20-minute wait before analysis allows ozone, a potential interferent, to decompose. Sulfamic acid is then added, followed by a 10-minute wait, to remove interference from nitrogen oxides. Interference by heavy metals is eliminated by use of phosphoric acid in the dye reagent and the disodium salt of ethylenediaminetetraacetic acid (EDTA) in the TCM absorbing solution. The complex is then reacted with a purified pararosaniline dye reagent and formaldehyde to form the colored pararosaniline methanesulfonic acid. Absorbance is measured at 548 nm.

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Accuracy depends on rigid control of many critical variables: pH, temperature, reagent purity, color development time, age of solutions, and concentrations of some atmospheric interferents (Scaringelli et al., 1967). Because temperature affects rate of color formation and color fading, a constant-temperature bath is recommended for maximum precision. Highly purified reagents, especially the pararosaniline dye, are vital for acceptable reproducibility. The precision of the EPA reference method analytical procedure was estimated using standard sulfite samples (Scaringelli et al., 1967) and reported to be 4.6 percent at the 95 percent confidence level. The lower limit of detection of SO_2 in 10 ml of TCM absorbing solution was 0.75 μg, representing a concentration of 25 μg SO_2/m^3 (0.01 ppm) in an air sample of 30 liters.

A collaborative study (McCoy et al., 1973) of the 24-hour EPA reference method procedure indicated the following: method repeatability (day-to-day variability within an individual laboratory) varies linearly with SO_2 concentration from ± 18 μg/m^3 (0.007 ppm) at concentration levels of 100 μg/m^3 (0.04 ppm) to ± 51 μg/m^3 (0.019 ppm) at concentration levels of 400 μg/m^3 (0.15 ppm); method reproducibility (day-to-day variability between two or more laboratories) varies linearly with SO_2 concentration from ± 37 μg/m^3 (0.014 ppm) at 100 μg/m^3 to ± 104 μg/m^3 (0.040 ppm) at 400 μg/m^3. The method has a concentration dependent bias which becomes significant at the 95 percent confidence level at the high concentration level. Observed values tend to be lower than the expected SO_2 concentration level.

Results of the above collaborative study and other investigations (Blacker et al., 1973; Bromberg et al., 1974; Foster and Beatty, 1974) suggest that pararosaniline methods tend to underestimate SO_2 concentrations by 5 to 20 percent. In the Bromberg study, simulated 24-hour bubbler samples were analyzed by 134 laboratories throughout the United States. Observed negative biases ranged from -3 percent for a 45 μg/m^3 sample to -16 percent for a 767 μg/m^3 sample, but reasons for the negative biases have not been determined. Based on the Bromberg study results, EPA recommended that intralaboratory quality control programs be upgraded and improved in laboratories that routinely analyze SO_2-TCM samples. EPA also recognized the need for and promoted development of standard reference samples for use in laboratory quality control programs.

More recent information on the reliability of pararosaniline analytical procedures has been obtained through EPA's ambient air audit program. In this program, freeze-dried mixtures of sodium sulfite and TCM are sent to participating laboratories for analysis. These simulated field samples represent ambient SO_2 concentrations ranging from about 10 to 200 μg/m^3. EPA audit results from 1976-1978 summarized in recent reports (Bromberg et al., 1979, 1980) indicate no apparent problems with bias (accuracy) in the analytical portion of the pararosaniline methods.

Subsequent to promulgation of the SO_2 reference method, effects of temperature on the method have been studied (Kasten-Schraufnagel et al., 1975; Sweitzer, 1975). One investigation (Fuerst et al., 1976) showed that collected SO_2-TCM samples decay at a temperature-dependent rate. Table 3-1 indicates that sample collection at 25°C results in a 1.1 percent

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loss in SO_2 during the 24-hour sampling period, but further exposure of the collected sample for 4 days at this temperature leads to a 10 percent loss in SO_2. Significant decay can occur during collection of ambient samples and during shipment and storage of collected samples when TCM solutions are exposed to temperatures above 20°C. Under typical field conditions temperature exposure is quite often extreme, especially during the summer months at sites with relatively little protection from the elements (e.g., rooftop locations).

TABLE 3-1. TEMPERATURE EFFECT ON COLLECTED SO_2-TCM SAMPLES (EPA REFERENCE METHOD)

		Percent SO_2 remaining			
			Days of Exposure		
°C	°F	At end of sampling	2	4	6
15	59	99.8	99.0	98.2	97.4
20	68	99.6	97.8	96.1	94.3
25	77	98.9	94.4	90.2	86.1
30	86	97.4	87.4	78.5	70.4
35	95	95.1	74.1	57.9	45.2
40	104	87.6	50.8	29.5	17.2

Source: Fuerst et al., 1976.

Measures to minimize these temperature effects have been investigated by Martin (1977), who recommends use of thermostatted shelters to house sampling equipment during sample collection. The temperature of samples during shipment can be controlled with cold-pack shipping containers. When samples are stored before being analyzed, refrigeration at 5°C minimizes further decay. Temperature control procedures are currently being incorporated in the EPA reference method.

Other sources of error in the pararosaniline method, common to all manual methods of this type (wet chemical), include spillage of absorbing reagent and collected samples during shipment, leakage in the sampling apparatus, and inaccurate sample volume measurements. These errors can generally be minimized by the application of standard quality control practices.

Under the provisions of EPA's "Ambient Air Monitoring Reference and Equivalent Methods" regulations (U.S. Environmental Protection Agency, 1979b), two additional manual pararosaniline methods have been designated as equivalent methods (U.S. Environmental Protection Agency, 1975). These methods are identified as:

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EQS-0775-001, "Pararosaniline Method for the Determination of Sulfur Dioxide in the Atmosphere - Technicon I Automated Analysis System."

EQS-0775-002, "Pararosaniline Method for the Determination of Sulfur Dioxide in the Atmosphere - Technicon II Automated Analysis System."

These methods employ the same sample collection procedure used in the EPA reference method and an automated analytical measurement based on the colorimetric pararosaniline method.

3.2.2.3.2 Titrimetric method: hydrogen peroxide. The British Standard Method uses a standard sampling instrument or 8-port valve for the measurement of smoke and sulfur dioxide (British Standards Institution, 1963). Air is drawn through a filter paper and into a Drechsel bottle containing ~0.3 percent hydrogen peroxide solution adjusted to pH 4.5. The hydrogen peroxide oxidizes the atmospheric SO_2 to sulfuric acid which is subsequently titrated with standard sodium borate using the mixed indicator of the British Drug House (grey at pH 4.5). The method is capable of measuring SO_2 concentrations from about 25 to 25,000 $\mu g/m^3$ (0.01 to 10 ppm) using a 24-hour sampling period.

Since the method measures total acidity rather than SO_2 specifically, any strong acids that are collected will produce positive errors. Normally the concentration of such substances is low relative to that of SO_2, and the measurement is generally accepted as a good approximation of the actual SO_2 concentration. Ammonia will neutralize the sulfuric acid and give negative errors. When the presence of ammonia is suspected, a portion of the absorbing solution can be analyzed for dissolved ammonia and the SO_2 measurement adjusted accordingly.

An instruction manual on the use of the hydrogen peroxide method in the British National Survey was issued in 1966 (Warren Spring Laboratory, 1966). The manual discusses the quality of the water used for reagent preparation and states that it need not be free of carbon dioxide. Martin and Barber (1971), however, reported that use of water rich in carbon dioxide can lead to significant negative errors in the method. During sample collection and subsequent standing, sufficient carbon dioxide can be evolved from the absorbing solution to cause low titers and, on some occasions, to result even in alkaline solutions. The instruction manual also discusses the problem of alkaline contamination in the glassware required in the method. The Drechsel bottles used during sample collection and sample storage bottles need to be preconditioned with absorbing reagent prior to use. Likewise, alkaline contamination in other glass parts of the sampling apparatus can lead to underestimation of ambient SO_2 levels.

Evaporation of absorbing reagent during sampling can result in overestimation of ambient SO_2 levels with the method (Fry, 1970). If evaporation occurs, the pH of the solution is lowered and a portion of the standard alkali added during the subsequent titration is required to compensate for this effect alone. The effect is likely to be more prevalent in the summer months and can lead to overestimation of SO_2 levels by up to about 15 $\mu g/m^3$. Fry reports that this source of error can be overcome either by making up the absorbing solution to its original volume prior to the titration or by making a mathematical correction to the titration result based on the final volume of absorbing solution after collection.

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Uncertainty in the titration end-point and rounding-off of the volume of alkali required in the titration to the nearest 0.1 ml each introduce errors of up to about ±5 $\mu g/m^3$ (Warren Spring Laboratory, 1975). Other potential sources of error in the method include inaccurate air sample volume measurements and conversion of ambient SO_2 to sulfate on the smoke filter used in the sampler.

The reproducibility of the hydrogen peroxide method based on results from five comparative studies using duplicate sampling apparatus has been reported by Warren Spring Laboratory (1962). The coefficients of variation were on the order of 15 to 20 percent for SO_2 concentrations ranging from about 15 to 250 $\mu g/m^3$ and 5 to 10 percent for concentrations ranging from about 100 to 800 $\mu g/m^3$. The same reagents and analytical apparatus were used to service all the samplers in each study, thus obviating a further potential source of error.

In a more recent investigation (Barnes, 1973), duplicate SO_2 measurements were obtained with the British Standard Method at a residential site where ambient levels were low (18 to 84 $\mu g/m^3$). Nineteen sets of observations were made from two samplers with a common inlet using the same supply of reagents and glassware and a further 18 using a separate supply for each. Differences in measured concentrations using the two samplers on individual occasions ranged up to 31 percent of the mean of the two separate values. However, most of these differences did not exceed 13 percent of the mean. Titration error was cited as the single most common source of variation between the samplers in these experiments. An error in titration of 0.1 ml would result in an error in the measured SO_2 concentration of 7 $\mu g/m^3$. When measuring low concentrations such errors could represent a difference of 100 percent from the true concentration. Barnes concludes from these observations that measurement of low SO_2 concentrations with the method require great care on the part of the operator, more than might be expected of most operators.

3.2.2.3.3 Iodimetric methods. Several iodimetric methods have been used for the determination of SO_2 in the atmosphere. In one version, an absorbing solution containing soluble starch, potassium iodide, dilute sulfuric acid, and standard 0.01 N iodine solution is prepared (Katz, 1950). SO_2 in the air sample reacts with this 8×10^{-5} N iodine solution to decolorize the blue iodine-starch complex. The reduction in color intensity is measured spectrophotometrically. The range of applicability is 25 to 2600 $\mu g\ SO_2/m^3$ (0.01 to 1 ppm), depending upon the volume and concentration of absorbent solution and the volume of air sampled. In a modification of this method, the excess iodine is titrated with a standard thiosulfate solution (Katz, 1969).

Oxidizing gases interfere to give low results; reducing agents interfere to give high results. Interference from high concentrations of nitrogen oxides or ozone can be removed by introducing hydrogen into the air sample and passing the mixture over a platinum catalyst at 100°C (Bokhaven and Niessin, 1966).

In another version, air is bubbled through a sodium hydroxide solution which absorbs SO_2 (Jacobs, 1960). After acidification of the solution, the liberated sulfurous acid is titrated

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with standard iodine solution, using starch as an indicator. Because sulfite oxidizes to sulfate in the alkaline absorbent solution, samples cannot be stored. Oxidizing agents, nitrogen dioxide, and ozone interfere, resulting in an underestimation of the SO_2 concentration. Hydrogen sulfide and reducing agents result in an overestimation. For an 850-liter air sample collected at 30 liters/minute, the lower limit of detection is 25 μg SO_2/m^3 (0.01 ppm) (Terraglio and Manganelli, 1962).

3.2.2.3.4 Impregnated filter paper methods. Filter papers, impregnated with alkali plus a humectant to keep them moist, will absorb SO_2 from air samples (Lodge et al., 1963; Huygen, 1963; Pate et al., 1963; Forrest and Newman, 1973). Two solutions commonly used to impregnate papers are a mixture of 20 percent potassium hydroxide and 10 percent triethanolamine, and a mixture of 20 percent potassium carbonate and 10 percent glycerol. The treated filters are inserted into filter holders, and air is aspirated through them. An untreated prefilter is generally recommended to remove particulate matter. Absorbed SO_2 can be extracted from the papers and determined colorimetrically by the West-Gaeke method. The alkali must be neutralized exactly to attain the proper acidity prior to color development. Alternatively, the extract solution may be treated with an oxidizing agent, such as hydrogen peroxide, to convert sulfite to sulfate, followed by a sulfate analysis (Johnson and Atkins, 1975; Forrest and Newman, 1973).

Efficiency for SO_2 absorption is better than 95 percent under average weather conditions, but decreases rapidly below 25 percent relative humidity and above 80 percent relative humidity. The error may be minimized by using two filter papers in series (Forrest and Newman, 1973). Elimination of glassware and reagents during sampling removes the possibility of spillage or breakage during transport. Sampled papers may be stored conveniently for long periods before being analyzed.

SO_2 may be sampled on Whatman no. 17 filter papers impregnated with tetrachloromercurate (TCM) solution containing mercuric chloride, sodium chloride, ethyl alcohol, and glycerol in water (Axelrod and Hansen, 1975). Sampled filters are extracted with TCM, and the West-Gaeke procedure generally follows. Capacity of the 47-mm filters is 13 mg of SO_2, after which collection efficiency decreases. Samples collected at very low relative humidities (10 percent) cannot be stored more than 1 day before exhibiting losses. Filters sampled at 40 percent relative humidity may be safely stored for 1 week. No interference is observed for nitrogen dioxide and hydrogen sulfide, but ozone at 175 $\mu g/m^3$ (0.09 ppm) causes negative errors.

A method that uses nondispersive x-ray fluorescence to measure ambient SO_2 collected on sodium carbonate impregnated membrane filters has been developed by Hardin and Shleien (1971). After collection the sample filter is irradiated with a one millicurie iron-55 source. The resulting 2.3 kev sulfur x-rays are counted by a proportional counter with a beryllium window. A minimum detectable quantity of 30 μg SO_2 can be detected by the counter, equivalent to 25 g/m^3 (0.01 ppm) using a collection time of one hour and a sampling rate of 20 liters/minute.

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Chlorine gas is collected to a significant degree and since its characteristic x-ray cannot be resolved from that of sulfur, it may interfere to produce elevated results if not removed prior to encountering the treated filter.

3.2.2.3.5 Chemiluminescence method. The basis for this method is the chemiluminescence produced when sulfite solution is oxidized (Stauff and Jaeschke, 1975). Ambient SO_2 is absorbed in 50 ml of tetrachloromercurate solution to form the dichlorosulfitomercurate ion. Five milliliters of 2×10^{-5} N $KMnO_4$ in 10^{-3} N H_2SO_4 is added. Oxidation of the absorbed sulfite is accompanied by a chemiluminescence, which is detected by a photomultiplier tube. The total light yield, measured by a photon counting system, is proportional to the oxidizable sulfite. By sampling 1 m^3 of air, 0.5 $\mu g/m^3$ (0.2 ppb) of SO_2 may be detected with an error of less than 10 percent.

3.2.2.3.6 Ion exchange chromatographic method. Small et al. (1975) have described an ion exchange chromatographic system which separates ionic species and effectively neutralizes the eluant allowing a conductometric measurement of the ion. A commercial instrument based on the above system is now available (Dionex Corporation, 1975) for use in trace anion analysis. In this system a strong base anion exchanger of low capacity, agglomerated onto a surface-sulfonated DVB resin, is used as the analytical column. This is followed by a high capacity, strong acid exchange column which converts the eluant - typically 0.003 M Na_2CO_3 + 0.024 M $NaHCO_3$ - into a non-conducting carbonic acid solution after which the separated ions are monitored with a high sensitivity, multi-range conductivity meter. Although the method is not totally free from ambiguity, careful selection of eluant and ion chromatographic exclusion steps can effectively separate ionic species of interest.

A method for collection and ion exchange chromatographic analysis of atmospheric SO_2 has recently been developed by EPA (Mulik et al., 1978). The method uses dilute (0.6 percent) hydrogen peroxide to collect the ambient SO_2. The resultant sulfate ion is analyzed by ion exchange chromatography. When a prefilter is used in the sampling train to remove aerosol sulfates, there are no apparent interferences. Collection efficiency is approximately 100 percent over the range of the method, 25 to 1300 $\mu g\ SO_2/m^3$ (0.01 to 0.5 ppm).

3.2.2.3.7 Sulfation methods. Sulfation methods are based on the reaction of gaseous SO_2 in air with lead peroxide (PbO_2) paste to form lead sulfate ($PbSO_4$). They are cumulative methods for estimating average concentrations over extended time periods. In the lead peroxide gauge method (Department of Scientific and Industrial Research, 1933) and the lead candle method (Wilsdon and McConnell, 1934), the paste is prepared by mixing PbO_2, gum tragacanth, alcohol, and water. The paste is applied to a piece of cotton gauze wrapped around a cylinder 10 cm round and 10 cm high. After drying, the cylinder is exposed to the atmosphere in a sheltered location. After exposure, the sulfated cylinder is treated with sodium carbonate solution and the resultant sulfate is then determined gravimetrically or turbidimetrically. Measurements with the method are reported as sulfation rates (mg SO_3/100 cm^2/day). In the sulfation plate method (Huey, 1968), a similar paste containing glass filter fibers is poured into a petri dish and, after drying, is exposed to the atmosphere and analyzed for sulfate.

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Sulfation methods have the advantage of being inexpensive, but their accuracy is subject to many physical and chemical variables and interferents. For example, the rate of sulfate formation is proportional to atmospheric SO_2 concentration up to 15 percent conversion of the lead peroxide (Wilsdon and McConnell, 1934). Reaction rate increases with temperature and with humidity. Other factors affecting rate of sulfation are wind velocity, purity of lead peroxide, and shape of the shelter (Bowden, 1964). Positive errors are contributed by hydrogen sulfide and sulfate aerosols. Methyl mercaptan is a potential negative interferent.

Huey et al. (1969) compared the sulfation plate method with the sulfation candle method at some 250 sampling sites nationwide. A correlation coefficient of 0.95 was obtained, confirming that both methods are measuring the same species. The results also indicated that sulfation plates are 10 percent less reactive than sulfation candles.

Various attempts have been made to correlate sulfation methods with more specific methods for estimation of SO_2 concentrations. In 1962, as part of the establishment of the British National Survey, measurements with the lead peroxide gauge were compared to simultaneous measurements with the hydrogen peroxide method (Warren Spring Laboratory, 1967). The correlation between 829 pairs of results from 20 sites over a period of four years was highly significant, showing that both methods were predominantly affected by the same pollutant, sulfur dioxide. However, the Warren Spring Laboratory concluded that there was no generally applicable conversion factor for relating lead peroxide and hydrogen peroxide results. The conversion from lead peroxide to hydrogen peroxide reading was not recommended except to give a rough indication of the levels of concentration concerned.

Stalker et al. (1963) compared the lead peroxide method and the pararosaniline method to measure sulfur dioxide at 123 stations in Nashville, Tennessee. The lead peroxide method was considered good for estimating mean SO_2 levels in communities during months with arithmetic mean concentrations of at least 65 $\mu g/m^3$ (0.025 ppm). The reliability of these mean estimates was estimated to be within ± 25 percent. However, seasonal effects were noted and the lead peroxide estimates of SO_2 (using an average conversion factor for sulfation rate to ppm of 0.031) during the spring season of low SO_2 levels were about twice as high as simultaneous 24-hour colorimetric measurements of SO_2.

Huey et al. (1969) compared ambient SO_2 measurements by conductometric, coulometric, and colorimetric methods with sulfation results. They concluded that sulfation data in mg SO_3/100 cm^2/day could be converted to SO_2 concentrations in ppm by multiplying by 0.03, and that 95 percent of the time this approximation from a single sulfation value will lie within a factor of about 3 of any single measurement using the other techniques.

3.2.2.3.8 Other manual methods. Other manual methods that have been used for the measurement of ambient concentrations of SO_2 include the barium perchlorate-thorin titrimetric method (Fritz and Yamamura, 1955), the barium sulfate turbidimetric method (Volmer and Frohlich, 1944), and the barium chloranilate colorimetric method (Bertolacini and Barney, 1957).

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3.2.3 Automated Methods

3.2.3.1 Sample Collection--In continuous sulfur dioxide analyzers sample collection is an integral part of the total automated measurement process. The sample line leading from the sample manifold to the inlet of the analyzer should be constructed of an inert material such as Teflon®. The sample line dimensions (length and internal diameter) should be selected to minimize the residence time without creating a significant pressure drop between the sample manifold and the analyzer inlet. The use of an inert particle filter at the inlet of the analyzer should depend on the analyzer's susceptibility to interference, malfunction, or damage due to particulate matter. Heavy loading of particulate matter on the filter may lead to erroneous SO_2 measurements; therefore, it may be necessary to change the filter frequently.

3.2.3.2 Calibration--The relationship between true pollutant concentration and the response of a continuous analyzer is best determined by dynamic calibration. In dynamic calibration, zero air and standard atmospheres containing known concentrations of SO_2 are introduced into the analyzer to define the analyzer response over the full measurement range. Dynamic calibration provides evidence that all components of the instrument are functioning properly.

Standard atmospheres required for calibration purposes may be generated using permeation tubes (O'Keeffe and Ortman, 1966), i.e., sealed Teflon® tubes containing liquified gas. Gas diffuses through the walls at a low, constant rate at constant temperature. The gas is then diluted with zero air at accurately known flowrates to obtain SO_2 concentrations over the required range. Permeation tubes with certified permeation rates are available from the National Bureau of Standards as Standard Reference Materials or from commercial suppliers. Dynamic calibration may also be carried out using known concentrations of SO_2 in high pressure cylinders. For stability purposes they are usually prepared in high concentrations and dynamically diluted to the desired level. Traceability of such standards to NBS SRMs may be established by the gas standard manufacturer or by the user.

Static calibration techniques are possible for several of the continuous SO_2 analyzers described below. Static calibration introduces a stimulus to measure instrumental response under no sample air flow conditions. Typical stimuli are electrical signals, solutions chemically equivalent to the pollutant, or solutions producing comparable physical effects upon properties by which the pollutant is detected such as optical density or electrical conductivity. Static calibration is a rapid and simple method for checking various components of the instrument, but does not subject total instrument performance to scrutiny.

3.2.3.3 Measurement Methods--The principal automated methods (continuous analyzers) for determining sulfur dioxide in the air are discussed in this section in a more-or-less chronological order, with earlier continuous analyzers described first.

3.2.3.3.1 Conductometric analyzers. Conductometric analyzers were the first commercially available instruments for continuously monitoring SO_2 in the atmosphere and are still used today. In their operation, air is brought into contact with an absorbing solution, which

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dissolves SO_2. The ions formed by SO_2 dissolution increase the conductivity, which is proportional to the concentration. The absorbent may be either deionized water or acidified hydrogen peroxide solution. When water is used, conductance is increased by formation and dissociation of sulfurous acid:

$$SO_2 + H_2O \rightarrow H_2SO_3 \rightarrow 2H^+ + SO_3^=$$

Hydrogen peroxide solution oxidizes SO_2 to form sulfuric acid:

$$SO_2 + H_2O_2 \rightarrow H_2SO_4 \rightarrow 2H^+ + SO_4^=$$

Conductance is measured by a pair of inert (platinum) electrodes within the cell. To increase accuracy, comparison is made to a reference cell, which measures conductance of unused absorbent. The response characteristics of conductometric analyzers are lower detection limits ranging from 0.005 to 0.04 ppm, lag times (time interval from change in input concentration to change in output signal) ranging from 5 to 200 seconds, and response times (time interval from change in input concentration to 90 percent of maximum output signal) ranging from 1 to 4 minutes (Lawrence Berkeley Laboratory, 1972).

The major disadvantage of conductometric analyzers is their susceptibility to interference by any species that either forms or removes ions from solution and changes the conductivity of the solution. The degree of interference depends on humidity, temperature, SO_2 concentration, and the particular instrument. The worst interferents are chlorine, hydrochloric acid, and ammonia (Rodes et al., 1969); nitrogen dioxide and carbon dioxide interfere to a lesser extent. Airborne particles, especially ocean-borne salt aerosols, are potentially damaging. Several methods have been used to minimize these problems. Chemical scrubbers which selectively remove gaseous interferents have been incorporated into some conductometric analyzers. Particle filters have also been employed.

3.2.3.3.2 Colorimetric analyzers. Colorimetric analyzers are based upon reaction of SO_2 with solutions of organic dyes to form colored species. Optical absorbance of the resulting solution, measured spectrophotometrically, is within limits linearly proportional to the concentration of the colored species in accordance with Beer's Law. Most instruments utilize improved versions of the manual pararosaniline method developed by West and Gaeke (1956). Automation of the West-Gaeke method *per se* does not ensure a practical continuous monitoring instrument since some solutions require daily preparation.

The response characteristics for some commercially available instruments are lower detection limits ranging from 0.002 to 0.01 ppm, lag times ranging from 0.6 to 25 minutes, and response times ranging from 5 to 30 minutes (Lawrence Berkeley Laboratory, 1972). Advantages of these instruments include good sensitivity and, with proper control, good specificity. Interferences by nitrogen oxides may be controlled by using a sulfamic acid reagent. Heavy metals may be complexed with EDTA in the scrubbing solution or with phosphoric acid in the dye solution. Ozone interference may be controlled by use of a delay coil downstream from the absorber to allow time for ozone to decay, but this results in longer lag and response times. Major disadvantages of these instruments are the need for reagent and pump tubing replacement and frequent recalibration.

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3.2.3.3.3 Coulometric and amperometric analyzers. Coulometric analyzers are based on the reaction of SO_2 with a halogen, formed directly by electrolysis of a halide solution. The current necessary to replace the depleted halogen is proportional to the amount of SO_2 absorbed in the solution, and hence to the SO_2 concentration in the air.

In one common coulometric system, an inner chamber, into which air is introduced, is contiguous with an outer chamber (Treon and Crutchfield, 1942). Both contain a solution of potassium bromide and bromine in dilute sulfuric acid. Potential difference between chambers, relative to a reference potential, is measured by the reference electrodes. As absorbed SO_2 reduces the Br_2 concentration in the inner chamber, the amplifier produces a current to restore the Br_2 content in the inner chamber until the potential difference is again zero. In a second system, the change in halogen concentration is detected as a current change rather than a potential difference. The cell is filled with a potassium iodide solution, buffered to pH 7. At the platinum anode, a constant current source continuously generates iodine, which is subsequently reduced at the cathode. An equilibrium concentration of iodine is established, and no current is generated at an activated-carbon bipolar reference electrode, connected in parallel. Reaction with SO_2 decreases the equilibrium concentration of iodine, which cannot transport the charge generated by the constant-current source. Part of the current is diverted through the reference electrode; this flow is proportional to the SO_2 concentration in the air sample. The response characteristics of coulometric analyzers are lower detection limits ranging from 0.002 to 0.05 ppm, lag times ranging from 2 to 120 seconds, and response times ranging from 2 to 5 minutes (Lawrence Berkeley Laboratory, 1972).

Interferent species are those able to oxidize halides, reduce halogens, or complex with either. They consist primarily of sulfur compounds (hydrogen sulfide, mercaptans, and organic sulfides and disulfides) with sensitivities comparable to or greater than that of SO_2. Other potential interferents, at lower sensitivities, are ozone, nitrogen oxides, chlorine, olefinic hydrocarbons, aldehydes, benzene, chloroform, other nitrogen- or halogen-containing compounds, and other hydrocarbons (deVeer et al., 1969; Schulze, 1966; Thoen et al., 1968; Washburn and Austin, 1952). Interferences can be minimized by selective filters, which are sometimes built into the instrument or offered as optional features. For example, a heated silver gauze filter is reported to remove hydrogen sulfide, ozone, chlorine, nitrogen oxides, carbon disulfide, ethylene, aldehydes, benzene, and chloroform, but will not remove mercaptans (Philips Electronic Instruments, undated).

The major advantage of a coulometric analyzer is minimal maintenance (reagent may need only monthly replacement; electrodes may require annual cleaning). Also, reagent consumption is negligible because of halide regeneration, and evaporated water is replaced by condensation from air or from a reservoir.

3.2.3.3.4 Flame photometric analyzers. The flame photometric detector (FPD) is based on the measurement of the band emission of excited S_2^* molecules during passage of sulfur-containing

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compounds through a hydrogen-rich (reducing) flame. The emitted light passes through a narrow-pass optical filter, which isolates the 394 nm S_2^* band, and is detected by a photomultiplier tube (PMT). Photomultiplier tube output is proportional to the square of the sulfur concentration; hence, an electronic system to "linearize" output is a desirable feature. Application of the FPD to the detection of SO_2 was first made by Crider (1965) and analyzers using FPD have been widely accepted for ambient SO_2 monitoring. The response characteristics of continuous flame photometric SO_2 analyzers are lower detection limits ranging from 0.002 to 0.010 ppm, lag times ranging from 1 to 5 seconds, and response times ranging from 10 to 30 seconds (Lawrence Berkeley Laboratory, 1972).

Although the FPD is insensitive to nonsulfur species, it will detect sulfur compounds other than SO_2. Particle filters will remove troublesome aerosol sulfates and selective filters may be used to reduce interference from other gaseous sulfur compounds; e.g., an H_2S filter is used on most commercial instruments. Interference by carbon dioxide can be minimized by maintaining ambient levels of CO_2 in the calibration and sample matrices.

Gas chromatographs with flame photometric detectors (GC-FPD) are also available commercially. GC-FPD can separate individual sulfur compounds and measure them individually (Stevens et al., 1971). However, the temporal resolution of GC-FPD data is limited by the chromatographic elution time of SO_2 and other gaseous sulfur compounds.

Disadvantages of FPD systems include the need for a source of compressed hydrogen and sensitivity to all sulfur compounds. Advantages of FPD systems include low maintenance, good sensitivity, very fast response, and good selectivity for sulfur compounds. No reagents are necessary other than compressed hydrogen.

3.2.3.3.5 Second-derivative spectrometric analyzers. The second-derivative spectrometer processes the transmission-versus-wavelength function of a spectrum to produce a signal proportional to the second derivative of this function (Hager and Anderson, 1970). The signal amplitude is proportional to the concentration of the gas in the absorption path. These instruments center on the shape characteristics rather than basic intensity changes of molecular band spectral absorption. The slope and curvature characteristics are often large, specific, and independent of intensity. Because these shape characteristics are large but specific to individual compounds, resolution of component gases is possible.

In the operation of a second-derivative spectrometer, radiant energy from a UV or visible source is directed into a monochromator, where it is dispersed by a grating to provide monochromatic light to the sample cell. The wavelength of this light (299.5 nm) is modulated with respect to time in a sinusoidal fashion by an oscillating entrance slit. The angular position of the grating sets the center wavelength coming out of the monochromator into the multipass cell. The sample is continuously drawn through the cell by a pump. Output from the photomultiplier tube is electronically analyzed to develop the second derivative of the absorbance.

Sensitivity is greatly enhanced over ordinary spectrometers because the output is an AC signal of known wavelength and phase, adaptable to high-gain electronic amplification. Uniqueness of the curvature of a given molecular band enables this type of instrument to be

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highly specific. A theoretical assessment by Ratzlaff and Natusch (1977) indicates that precision may be a problem with spectrometric techniques of this type. Measurements are independent of sample flow rate, but relatively high flow rates (4 liters/minute) are necessary to achieve reasonable response times. The response characteristics for one commercially available instrument are a lower detection limit of 0.01 ppm, lag time of 1 minute, and response time of 8 minutes (U.S. Environmental Protection Agency, 1979a).

3.2.3.3.6 Fluorescence analyzers. Fluorescence analyzers are based on detection of the characteristic fluorescence released by the sulfur dioxide molecule when it is irradiated by ultraviolet light (Okabe et al., 1973). This fluorescent light is also in the ultraviolet region of the spectrum, but at a different wavelength than the incident radiation. Wavelengths between 190 and 230 nm are used for excitation and the fluorescent wavelengths usually monitored are between 300 and 400 nm. In this region of the spectrum, there is relatively little quenching of the fluorescence by other molecules occurring in ambient air. The light is detected by a PMT that, through the use of electronics, produces a voltage proportional to the light intensity and SO_2 concentration. The fluorescent light reaching the PMT is usually modulated to facilitate the high degree of amplification necessary. Some analyzers mechanically "chop" the incident irradiation before it enters the reaction chamber. Other instruments electronically pulse the incident light source at a constant rate. The response characteristics of fluorescence analyzers are lower detection limits of 0.005 ppm, lag times of about 30 seconds, and response times of about 5 minutes (U.S. Environmental Protection Agency, 1979a).

Potential interferences to the fluorescence technique include any species that either quenches or exhibits fluorescence. Both water vapor and oxygen strongly quench the fluorescence of SO_2 at some wavelengths. Water vapor can be removed by a dryer within the instrument or the water interference can be minimized by careful selection of the incident radiation wavelength. The effect of oxygen quenching can be minimized by maintaining identical oxygen concentrations in the calibration and sample matrices.

Aromatic hydrocarbons such as naphthalene exhibit strong fluorescence in the same spectral regions as SO_2 and are major interferents. These aromatics must be removed from the sample gas stream by an appropriate scrubber upstream of the reaction chamber. The scrubbers may operate at ambient or elevated temperature. Certain elevated-temperature scrubbers, however, have the potential for converting ambient hydrogen sulfide (which normally does not interfere with the fluorescence technique) into SO_2. In these cases, the hydrocarbon scrubber must be preceded by a scrubber for H_2S.

3.2.3.3.7 Other automated methods. Other automated methods (continuous analyzers) that have been used for the measurement of ambient concentrations of SO_2 include: voltammetry (Chand and Marcote, 1971); correlation spectroscopy (Barringer Research, Ltd., 1969; Moffat et al., 1971); differential lidar (Johnson et al., 1973); and condensation nuclei formation (Environment One Corp.).

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3.2.3.4 EPA Designated Equivalent Methods--Under provisions of EPA's "Ambient Air Monitoring Reference and Equivalent Methods" regulations (U.S. Environmental Protection Agency, 1979b), several commercial continuous analyzers have been designated as equivalent methods for determining compliance with National Ambient Air Quality Standards for SO_2. These analyzers have undergone required testing and meet EPA's performance specifications for automated methods, summarized in Table 3-2. A list of SO_2 analyzers designated as of December 31, 1980, is given in Table 3-3. Information on designation of these analyzers as equivalent methods may be obtained by writing the Environmental Monitoring Systems Laboratory, Methods Standardization Branch (MD-77), U.S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711.

Review of performance data submitted in support of the designations listed in Table 3-3 indicates that these analyzers exhibit performance better than that specified in Table 3-2. For the analyzers tested, noise levels were typically 3 ppb or less. The zero drift results (12-and 24-hour) were all less than 5 ppb and typically less than 3 ppb. The span drift results (at 20 and 80 percent of the full scale range of 0 to 0.5 ppm) were all less than 5 percent and typically 2 to 3 percent. The precision results (at 20 and 80 percent of the full scale range of 0 to 0.5 ppm) indicate a typical precision of 1 to 2 ppb. Lag times were typically less than 1 minute. Response times (rise and fall times) for the various types of analyzers were typically as follows: flame photometric, 1 minute or less; fluorescence, 5 minutes; coulometric, 3 minutes; conductometric, 0.5 minute; second-derivative spectrometric, 8 minutes. For analyzers of the same type (e.g., flame photometric), interference test results for a given potential interferent were somewhat variable. The concentration of SO_2 during the tests was 0.14 ppm and the interferent concentrations were as indicated in Table 3-4. Interference equivalents of 5 ppb or less were obtained in each case except for the following: flame photometric--negative CO_2 interference equivalents of about 10 ppb were typical; coulometric--positive O_3 interference equivalents of about 8 ppb were typical.

As part of required equivalency testing by manufacturers, all continuous SO_2 analyzers designated by EPA as equivalent methods have demonstrated a consistent relationship with the reference method. A consistent relationship is demonstrated when the differences between (1) measurements made by the test analyzer and (2) measurements made by the reference method are less than or equal to the allowable discrepancy specifications prescribed in the equivalency regulations, when both methods simultaneously measure SO_2 concentrations in a real atmosphere. All of the equivalent methods listed in Table 3-3 have demonstrated this consistent relationship with the reference method and the observed differences between simultaneous measurements were generally well within the required specifications.

A comparison study using EPA designated equivalent methods for SO_2 was recently conducted by EPA in an urban-industrial-commercial area of Durham, North Carolina (U.S. Environmental Protection Agency, 1979a). Eight continuous SO_2 analyzers were compared over a period of 150 days under more or less typical air monitoring conditions. During the study, the analyzers

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TABLE 3-2. PERFORMANCE SPECIFICATIONS FOR EPA EQUIVALENT METHODS FOR SO_2 (CONTINUOUS ANALYZERS)

Performance parameter	Units	Specification
Range	ppm	0-0.5
Noise	ppm	0.005
Lower detectable limit	ppm	0.01
Interference equivalent		
Each interferent	ppm	±0.02
Total interferent	ppm	0.06
Zero drift, 12-and 24-hour	ppm	±0.02
Span drift, 24-hour		
20 percent of upper range limit	percent	±20.0
80 percent of upper range limit	percent	±5.0
Lag time	minutes	20
Rise time	minutes	15
Fall time	minutes	15
Precision		
20 percent of upper range limit	ppm	0.01
80 percent of upper range limit	ppm	0.015

Source: U.S. Environmental Protection Agency (1979b)

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TABLE 3-3. LIST OF EPA DESIGNATED EQUIVALENT METHODS FOR SO_2 (CONTINUOUS ANALYZERS)

Designation number	Manufacturer	Model	Measurement principle
EQSA-1275-005	Lear Siegler	SM1000	Second-derivative spectrometric
EQSA-1275-006	Meloy	SA185-2A	Flame photometric
EQSA-0276-009	Thermo Electron	43	Fluorescence
EQSA-0678-010	Philips	PW9755	Coulometric
EQSA-0876-011	Philips	PW9700	Coulometric
EQSA-0876-013	Monitor Labs	8450	Flame photometric
EQSA-0877-024	ASARCO	500,600	Conductometric
EQSA-0678-029	Beckman	953	Fluorescence
EQSA-1078-030	Bendix	8303	Flame photometric
EQSA-1078-032	Meloy	SA285E	Flame photometric
EQSA-0779-039	Monitor Labs	8850	Fluorescence
EQSA-0580-046	Meloy	SA700	Fluorescence
EQSA-1280-049	Lear Siegler	AM2020	Second-derivative spectrometric

TABLE 3-4. INTERFERENT TEST CONCENTRATIONS (PARTS PER MILLION)[a] USED IN THE TESTING OF EPA EQUIVALENT METHODS FOR SO_2

Analyzer type[b]	Hydrochloric acid	Ammonia	Hydrogen sulfide	Sulfur dioxide	Nitrogen dioxide	Nitric oxide	Carbon dioxide	Ethylene	Ozone	M-Xylene	Water vapor	Carbon monoxide
Flame photometric (FPD)	--	--	0.1	0.14[d]	--	--	750	--	--	--	20,000[c]	50
Gas chromatography-FPD	--	--	0.1	0.14[d]	--	--	750	--	--	--	20,000[c]	50
Spectrophotometric-wet chemical (pararosaniline reaction)	0.2	0.1[c]	0.1	0.14[d]	0.5	--	750	--	0.5	--	--	--
Electrochemical	0.2	0.1[c]	0.1	0.14[d]	0.5	0.5	--	0.2	0.5	--	20,000[c]	--
Conductivity	0.2	0.1[c]	--	0.14[d]	0.5	--	750	--	--	--	--	--
Spectrophotometric-gas phase	--	--	--	0.14[d]	0.5	0.5	--	--	0.5	0.2	--	--

[a]Concentrations of interferent listed must be prepared and controlled to ± 10 percent of the stated value.

[b]Analyzer types not listed will be considered by the administrator as special cases.

[c]Do no mix with pollutant.

[d]Concentration of pollutant used for test. These pollutant concentrations must be prepared to ± 10 percent of the stated value.

Source: U.S. Environmental Protection Agency (1979b)

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simultaneously measured ambient air sampled from a common manifold. The ambient sample was occasionally augmented with artifically generated pollutant to allow for analyzer comparisons at higher concentrations. A statistical comparison of hourly averages for each test analyzer with the average of the hourly averages (for corresponding hours) from the other test analyzers is presented in Table 3-5. Each test analyzer is identified in the table by manufacturer, model number, and measurement principle. The data clearly indicate that these continuous SO_2 analyzers are capable of excellent performance (high correlation with one another, small mean differences).

3.2.4 Summary

Methods for the measurement of sulfur dioxide can be classified as: (1) manual methods, which involve collection of the sample over a specified time period and subsequent analysis by a variety of analytical techniques, or (2) automated methods, in which sample collection and analysis are performed continuously and automatically.

In the commonly used manual methods, the techniques used for the analysis of the collected sample are based on colorimetric, titrimetric, turbidimetric, gravimetric, x-ray fluorescent, chemiluminescent, and ion exchange chromatographic measurement principles.

The most widely used manual method for the determination of atmospheric sulfur dioxide is the pararosaniline method developed by West and Gaeke. An improved version of this colorimetric method, adopted as the EPA reference method in 1971, is capable of measuring ambient SO_2 concentrations as low as 25 $\mu g/m^3$ (0.01 ppm) with sampling times ranging from 30 minutes to 24 hours. The method has acceptable specificity for SO_2, but collected samples are subject to a temperature-dependent decay which can result in an underestimation of the ambient SO_2 concentration. Temperature control during sample collection, shipment, and storage effectively minimizes this decay problem.

A titrimetric method based on collection of SO_2 in dilute hydrogen peroxide followed by titration of the resultant H_2SO_4 with standard alkali is the standard method used extensively in Great Britain. Although simple to perform, the method requires long sampling times (24 hours) and is subject to interference from atmospheric acids and bases. Additional sources of error with the method include evaporation of reagent during sampling, titration errors, and alkaline contamination of glassware.

Methods that employ alkali impregnated filter papers for the collection of SO_2 and subsequent analysis as sulfite or sulfate by a variety of techniques have been developed. Most of these methods involve an extraction step prior to analysis although nondispersive x-ray fluorescence has been used for the direct measurement of SO_2 collected on sodium carbonate impregnated membrane filters.

Two of the most sensitive methods now available use measurement principles based on chemiluminescence and ion exchange chromatography. In the first, SO_2 is absorbed in a tetrachloromercurate solution and subsequently oxidized with potassium permanganate. The oxidation

TABLE 3-5. COMPARISON OF EPA DESIGNATED EQUIVALENT METHODS FOR SO_2 (CONTINUOUS ANALYZERS)

Analyzer	Meloy SA185-2A	Monitor Labs 8450	Meloy SA285E	Thermo Electron 43	Beckman 953	Lear Siegler SM1000	Philips PW9755	Bendix 8303
Measurement principle	Flame photometry	Flame photometry	Flame photometry	Fluorescence	Fluorescence	Second derivative spectrometry	Coulometry	Flame photometry
Correlation coefficient	0.999	0.999	0.999	0.997	0.998	0.936	0.998	0.998
Mean difference[a] ppb	-3.695	-0.006	-0.251	-0.177	5.108	4.924	5.775	-3.278
Std. dev. of diff. ppb	3.925	4.555	3.243	8.300	6.901	20.712	4.631	4.392
Max. abs. diff. ppb	19.3	19.2	15.5	29.9	25.4	100.9	25.6	21.0
No. of abs. diff. >20 ppb	0	0	0	49	21	427	13	1
No of data pairs	3302	3186	3306	2170	1594	1820	3070	1984

[a]Between subject analyzer and average of other test analyzers (for corresponding hours)

Source: U.S. Environmental Protection Agency (1979a)

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of the absorbed SO_2 is accompanied by a chemiluminescence which is detected by a photomultiplier tube. The second uses ion exchange chromatography to determine ambient levels of SO_2 which have been absorbed into dilute hydrogen peroxide and oxidized to sulfate.

Sulfation methods, based on reaction of SO_2 with lead peroxide paste to form lead sulfate, have commonly been used to estimate ambient SO_2 concentration over extended time periods. The accuracy of sulfation methods is subject to many physical and chemical variables and interferents. Sulfation rate (mg SO_3/100 cm^2/day) is commonly converted to a rough estimate of SO_2 concentration (ppm) by multiplying the rate by the Huey factor (0.03).

Automated methods for measurement of ambient levels of sulfur dioxide have gained widespread use in the air monitoring community. Some of the earliest continuous SO_2 analyzers were based on conductivity and coulometry. These first generation analyzers were subject to interference by a wide variety of substances present in typical ambient atmospheres. However, more recent commercially available analyzers using these measurement principles exhibit improved specificity for SO_2 through the incorporation of sophisticated chemical and physical scrubbers. Early continuous colorimetric analyzers using West-Gaeke type reagents and having good sensitivity and acceptable specificity for SO_2 were fraught with various mechanical problems, required frequent calibration, and thus never gained widespread acceptance.

Continuous sulfur dioxide analyzers using the techniques of flame photometric detection, fluorescence, and second-derivative spectrometry have been developed over the past ten years and are commercially available from a number of air monitoring instrumentation companies. Flame photometric detection of ambient SO_2 is based on measurement of the band emission of excited S_2^* molecules formed from sulfur species in a hydrogen-rich flame. The FPD analyzers exhibit high sensitivity and fast response, but must be used with selective scrubbers or coupled with gas chromatographs when high specificity is required.

Fluorescence analyzers are based on detection of the characteristic fluorescence of the SO_2 molecule when it is irradiated by UV light. These analyzers have acceptable sensitivity and response times, are insensitive to sample flowrate, and require no support gases. They are subject to interference by water vapor (due to quenching effects) and certain aromatic hydrocarbons, and therefore must incorporate ways to minimize these species or their effects.

Second-derivative spectrometry is a highly specific technique for measurement of SO_2 in the air and continuous analyzers based on this principle are commercially available. The analyzers are insensitive to sample flowrate and require no support gases. Relatively high sample flowrates are required to achieve reasonable response times, and frequent realignment of the optics is necessary when the analyzers are used under typical field conditions. Excessive electronic noise and inherent lack of precision can be problems with these analyzers.

Continuous analyzers based on many of the above measurement principles (conductivity, coulometry, flame photometry, fluorescence, and second-derivative spectrometry) have been

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designated by EPA as equivalent methods for the measurement of SO_2 in the atmosphere. Testing of these analyzers by the manufacturers prior to designation has demonstrated adequate performance for use when an EPA reference or equivalent method is desired or required. Testing of these methods by EPA has verified their performance and has also demonstrated excellent comparability among these designated methods under typical monitoring conditions.

3.3 PARTICULATE MATTER (PM)

3.3.1 Introduction

As described in Chapter 2, particulate matter suspended in ambient air presents a complex multiphase system which consists of a spectrum of aerodynamic particle sizes from below 0.01 micron (μm) up to 100 μm and larger. As discussed in Chapter 2, fine particles below 2.5 μm tend to remain suspended in air unless removed by external processes such as rainfall. Coarse particles above 2 μm have appreciable settling velocities and tend to settle unless kept in suspension by high wind speeds or turbulence. The sources and characteristics of the particles in both size ranges are generally quite different, and depending on the objectives of the sampling, measurements are often made which consider only a selected size fraction. Samplers used to identify fine and coarse particle fractions typically are designed to have inlet and substage cutpoints that are as sharp as possible. Samplers used to simulate the deposition pattern of particles in the respiratory system have well defined but more gradual cutpoints. Lippmann (1970) summarized samplers and deposition patterns in the 1-10 μm range proposed by several organizations. As shown in Figure 3-1 these include models of the American Conference of Governmental Industrial Hygienists (ACGIH), (Ref: American Industrial Hygiene Associate 1970) British Medical Research Council (BMRC), and U.S. Atomic Energy Commission (called the "Los Alamos" curve). Miller et al. (1979) proposed a sampler cutpoint of 15 μm related to respiratory system deposition, but did not recommend a desireable cutpoint sharpness. Particle deposition in the respiratory system is discussed in more detail in Chapter 11.

The aerodynamic diameter is one of the most important physical parameters when considering particle deposition in the atmosphere or the respiratory system. Suspended particles are rarely spherical, and the ability to obtain a representative dimension equivalent to a diameter for a single particle is often difficult. As defined by Hesketh (1977) the aerodynamic diameter is not a direct measurement of size, but is the equivalent diameter of a spherical particle of unit density which would settle at the same rate. This definition inherently considers factors such as the density and shape of a particle without requiring their direct measurement. Aerodynamic diameters are used in this chapter unless stated otherwise. Sampling methods which utilize collection or separation techniques based on the inertia or settling properties of particles consider the aerodynamic size. In general all sampling methods which draw the particles into an inlet or opening perform an aerodynamic size segregation. Particles with unusual geometries such as long fibers, however, may not be separated as effectively as more spherical particles, since the orientation of the fiber at the point of separation has a substantial impact on the effective diameter.

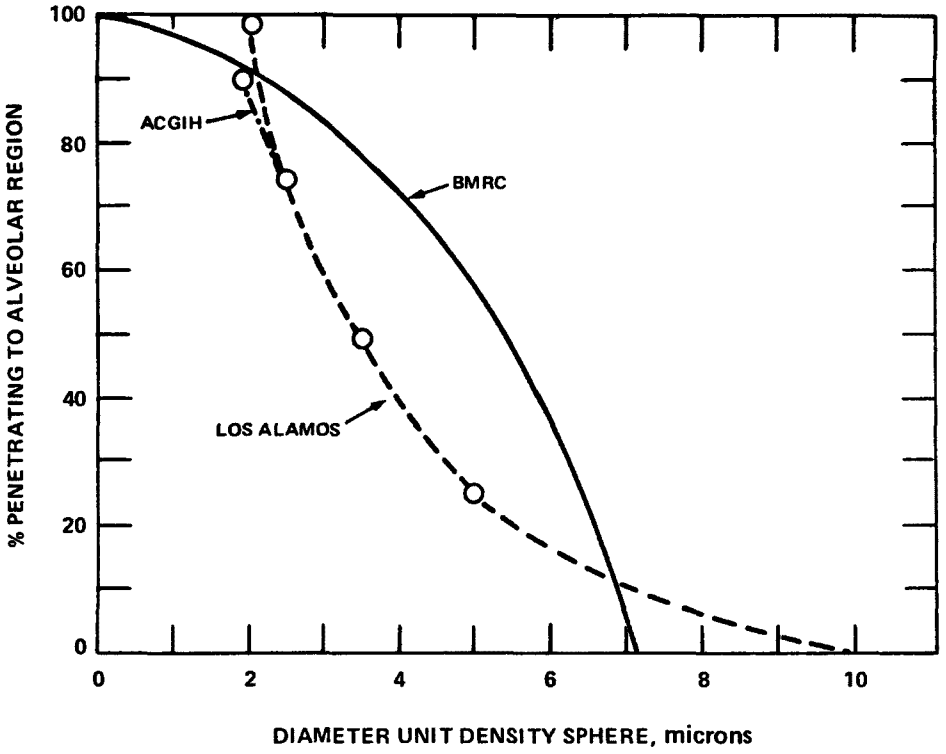

Figure 3-1. Respiratory deposition models used as patterns for sampler cutpoints.

Source: Lippmann (1970).

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As discussed in texts such as Fuchs (1964), there are several ways to examine particle size distributions. Separate distributions of volume, surface area, and number of particles as shown in Figure 3-2 can be measured to provide detailed information especially useful in studying particle transport and transformation. The particle size distribution by mass is perhaps the most important characteristic of an aerosol when considering the majority of current sampling methods. A mathematical integration of the mass distribution function over the effective aerodynamic collection range of the sampler directly provides the total mass collected per unit volume of air sampled. This information can be obtained indirectly from volume, surface area, or number distribution, but an estimate of the average particle density must be included in the calculations.

The most common aerosol measurement made in conjunction with health and welfare effect studies is the mass concentration measurement. Direct measurement of the mass concentration is made by collecting particles on a substrate such as a filter, gravimetrically determining the mass of the particles, and dividing the mass by the volume of air sampled. Ideally the particles reaching the substrate have been segregated by an efficient sampling mechanism which provides a defined portion of the ambient size distribution of particles to be collected. Airborne Particles (NAS, 1979) stated that ". . . integral methods used are always sensitive to the modification of the size distribution by the sampling inlets and transport lines used in the technique." This reference notes that Lundgren (1973), using special high efficiency samplers to produce mass size distributions as shown in Figure 3-3, showed that most mass sampling methods truncate the true ambient particle distribution, thereby giving concentrations less than those actually existing. If these less than perfect sampling efficiencies were constant for all conditions, the mass collected would always be a consistent proportion of the true ambient size distribution. As will be shown for selected methods, however, it has been determined that the efficiencies of many sampler inlets are substantially affected by wind speed, and in some cases wind direction. Some of the commonly used PM samplers which employ direct mass measurement techniques include the TSP Hi-Volume Sampler, the dichotomous sampler, cascade impactors, and cyclone samplers.

Mass concentrations of particles can be estimated using methodology which does not employ direct weighing. These indirect measurements utilize analytical techniques other than direct weighing for assessing integral properties of particles other than mass. Typically an empirical relationship with a gravimetric method is developed and pseudo-mass concentrations reported in lieu of the integral property measurement. Beta-ray attenuation by the particles on a filter and optical reflectance of the darkening of a filter by collected particles are examples of indirect measurement techniques. In situ methods which examine particles still suspended in the air stream include a wide variety of techniques such as the light scattering measurements of the integrating nephelometer and the size classification capability of optical particle counters.

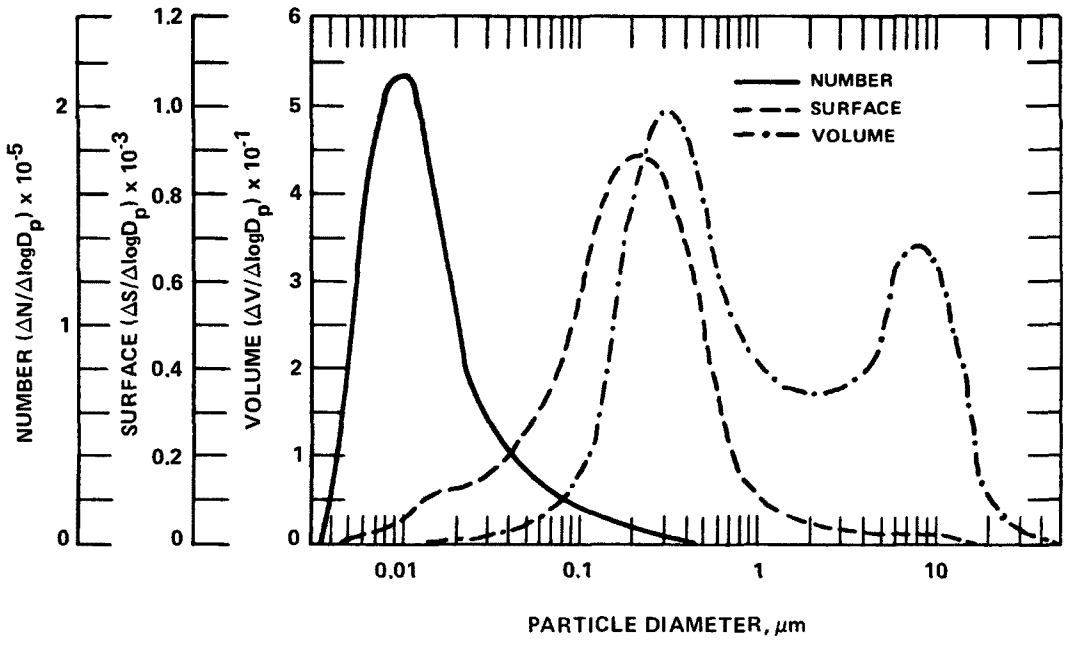

Figure 3-2. Plots illustrating the relationship of particle number, surface area, and volume distribution as a function of particle size.

Source: Whitby (1975).

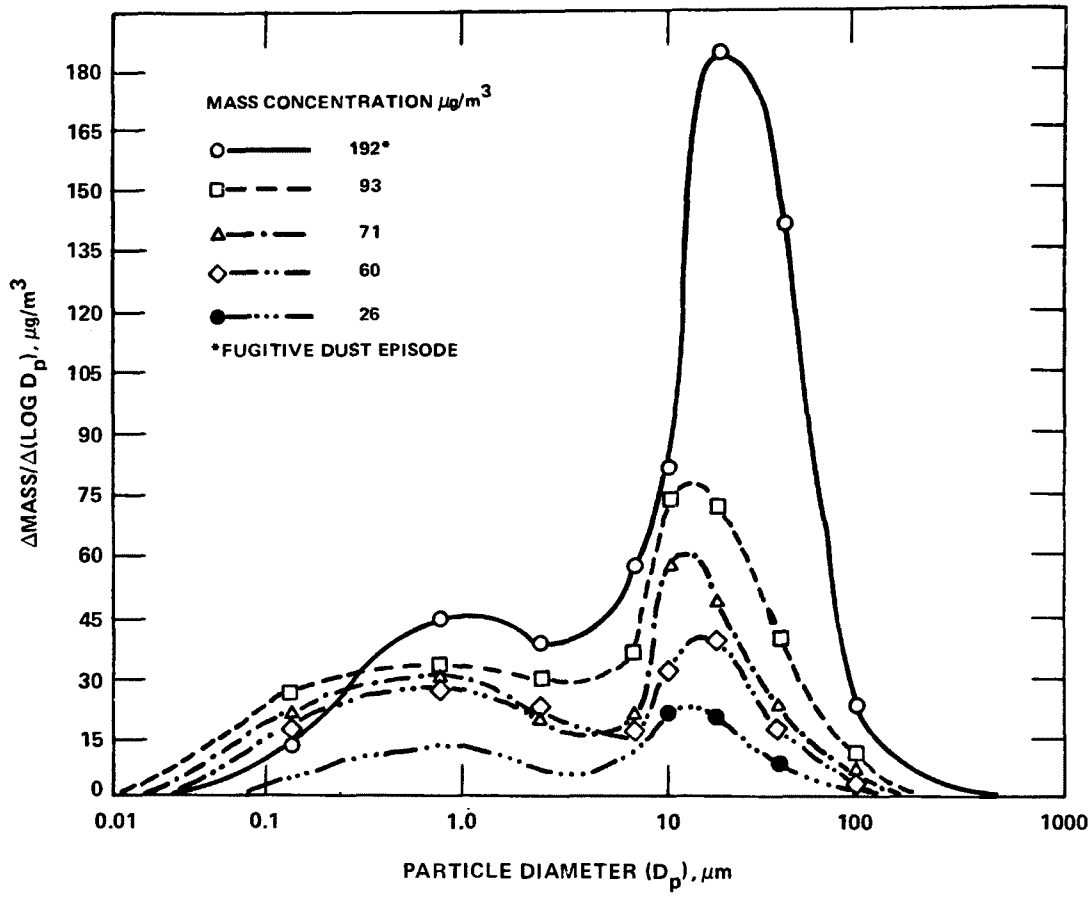

Figure 3-3. Typical ambient mass distribution data for particles up to 200 μm.

Source: Lundgren (1973).

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Analytical measurement of the chemical composition of particles can be strongly influenced by the sampling method. Surface measurements such as x-ray fluorescence spectroscopy require a filter which retains particles on the surface rather than allowing penetration as occurs into a fiber filter. The composition and impurities in the collection substrate can be critical, especially in the analysis of trace elements. Selected substrates can also interact with ambient gases to produce artifact particulate matter. Section 3.3.4 contains descriptions of the most common analytical methods and Section 3.3.5. briefly discusses particle morphology measurements by microscopic examination.

Measurement technology for aerosols has advanced significantly in the past 10 years, especially in the area of size specific measurements for larger particles. Before the advent of specially designed wind tunnels into which specific aerosol sizes and types can be injected, determination of sampling accuracy (effectiveness) under conditions similar to field sampling had rarely been attempted. For these tests effectiveness is defined as the percent of particles reaching the collection substrate of the sampler compared to results obtained by isokinetic sampling in the wind tunnel. Researchers such as McFarland and Ortiz (1979), Wedding et al. (1980), and Liu and Pui (1980) have designed and built such test facilities for characterizing aerosol samplers. From these tests it is now recognized that ambient wind speed and direction can have a profound effect on particle sizes reaching the point of collection or measurement within the sampler. Without knowledge of these and related sampler characteristics, an accurate interpretation of the aerometric data is impossible. This section describes important characteristics for commonly used sampler types, so that the utility of aerometric data discussed in subsequent chapters can be assessed.

3.3.2 Direct PM Mass Measurements

Techniques that employ direct gravimetric weighing of particles collected on a substrate are discussed here separately from those that use other approaches. Sampling techniques that fall into the first category are extractive rather than in situ, in that the particles are removed from the air stream for subsequent analysis. Typically the ambient air is drawn into an inlet, transported to the collection substrate, often after one or more stages of particle size separation, and then deposited on a substrate by either filtration or impaction. In addition to the effect of internal separation stages, the particle size range collected by a filtration sampler depends on other parameters such as inlet geometry, internal wall losses, and the efficiency of the filter material. The high-volume sampler defined by EPA in the previous Air Quality Criteria for Particulate Matter (National Air Pollution Control Administration, 1969) and in the reference method for TSP was considered to have captured all sizes of particles up to 100 μm (aerodynamic diameter). However, recent sampler characterization testing by Stevens and Dzubay (1975), Wedding et al. (1977), and McFarland and Rodes (1979) has shown that the gable roof used as an inlet and weather shield precludes efficient collection of particles larger than about 50 μm. As shown by the data of McFarland and Rodes in Figure 3-4, the sampling effectiveness of the high-volume sampler for large particles is substantially affected

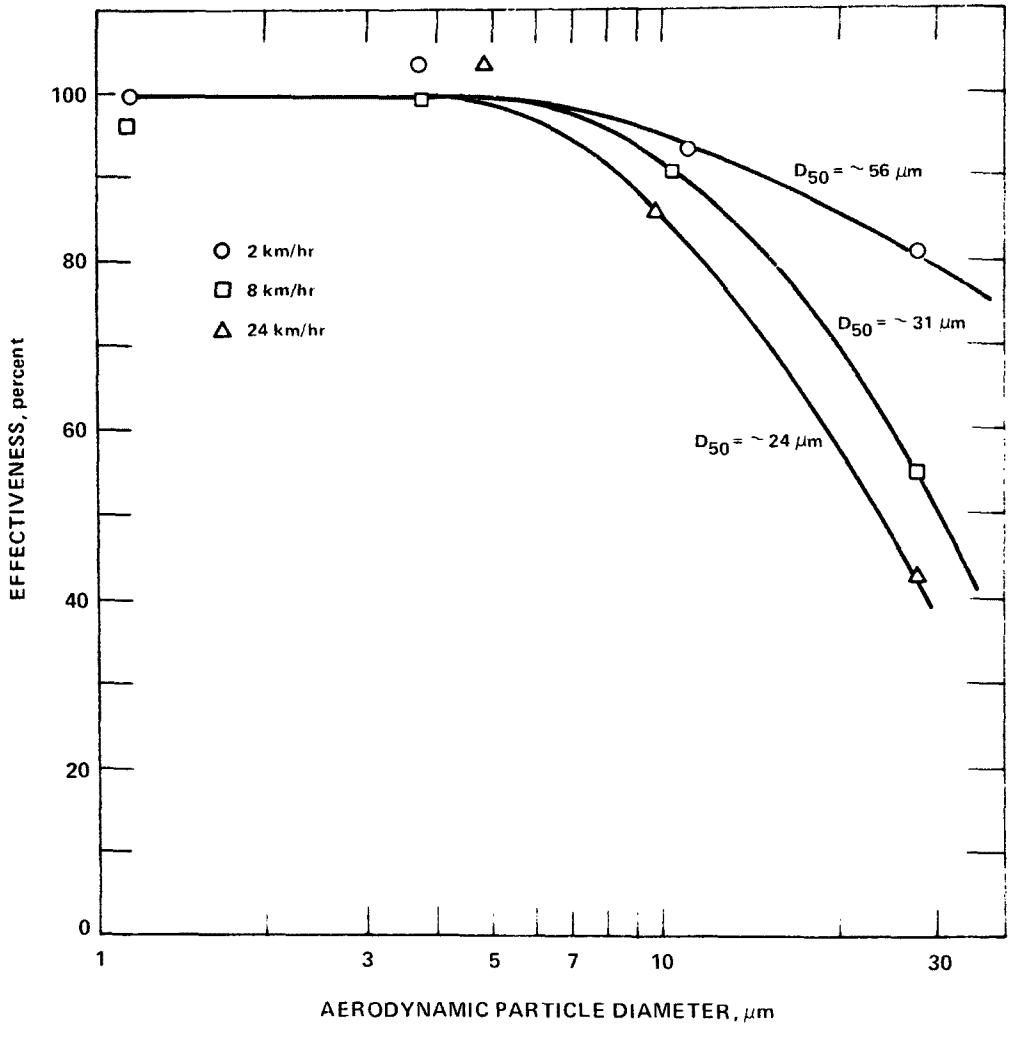

Figure 3-4. Sampling effectiveness of a Hi-Vol sampler as a function of wind speed.

Source: McFarland and Rodes (1979).

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by ambient wind speed. Lundgren (1973) has examined the mass distribution of large particles up to 200 μm in the atmosphere as shown in Figure 3-3. Comparison of high-volume sampler collection efficiency data in Figure 3-4 with these particle size distributions shows that the high-volume sampler does not provide a true measure of the large particles in the atmosphere. Because particle mass increases as a cube function of the diameter for particles with constant density, the sampling of large particles must be treated carefully when considering a broad size distribution.

Size-specific sampler inlets designed to limit the particles collected to a certain size range are a relatively new technology for particles larger than 10 μm. Since these larger particles are difficult to transport quantitatively, a sharp cutoff for large particles is not easily obtained except at high sampler flowrates using multiple stages of separation. The efficiency of a single stage inlet designed in 1977 (Stevens and Dzubay, 1978; see Figure A-1, appendix to this chapter) to provide a 15 μm cutoff for a low flowrate sampler operating at 1.0 m^3/hr, as tested by Wedding et al. (1977), is shown in Figure 3-5. Note that the D_{50} -- the particle size at which 50 percent of the particle mass is passed on to the filter -- for this inlet is very wind speed dependent and varies from 9 to 22 μm. More advanced inlets (see Appendix Figure A-2 for diagram) for this flowrate have been designed by Wedding (1980) and Liu et al. (1980) and have reduced wind speed sensitivities and sharper cutpoints as shown in Figures 3-6 and 3-7 respectively. The geometric standard deviations of the sampling effectiveness curves (a measure of the sharpness of the size cut-off and denoted as σ_g) for these inlets vary from approximately 1.2-1.5 as compared to an ideal step-function inlet with a σ_g of 1.0.

After particles pass through the sampler inlet they can be lost from the flowstream before collection or measurement by attraction to or impaction on the internal surfaces of the sampler. Minimizing internal loss, especially for larger particles, requires careful design of the sample transport system geometry as well as consideration of factors such as surface charge dissipation. Wedding et al. (1977) reported internal wall losses in a prototype size-specific sampler to exceed 40 percent for particles greater than 15 μm. Loo et al. (1979) reported that recent improvements in the dichotomous sampler reduced internal particle losses to less than a few percent.

3.3.2.1 Filtration Samplers--The most commonly used methodology for direct gravimetric measurement involves collection of the particles suspended in a known volume of ambient air on a preweighed filter. The size distribution of particles reaching the filter are affected by the characteristics of the inlet, the transport system, and the separation stages, operating at the sampler design flowrate. The performance of a sampler is also substantially affected by the filter characteristics. The efficiency of the filter media used can influence the total mass collected if very small particles are not retained on the filter, or if very large particles bounce from the filter to subsequent stages. The collection efficiencies over a range of particle sizes for a wide variety of filter materials, face velocities, and effective porosities have been determined by Liu et al. (1978) for clean filters and by John and Reischl

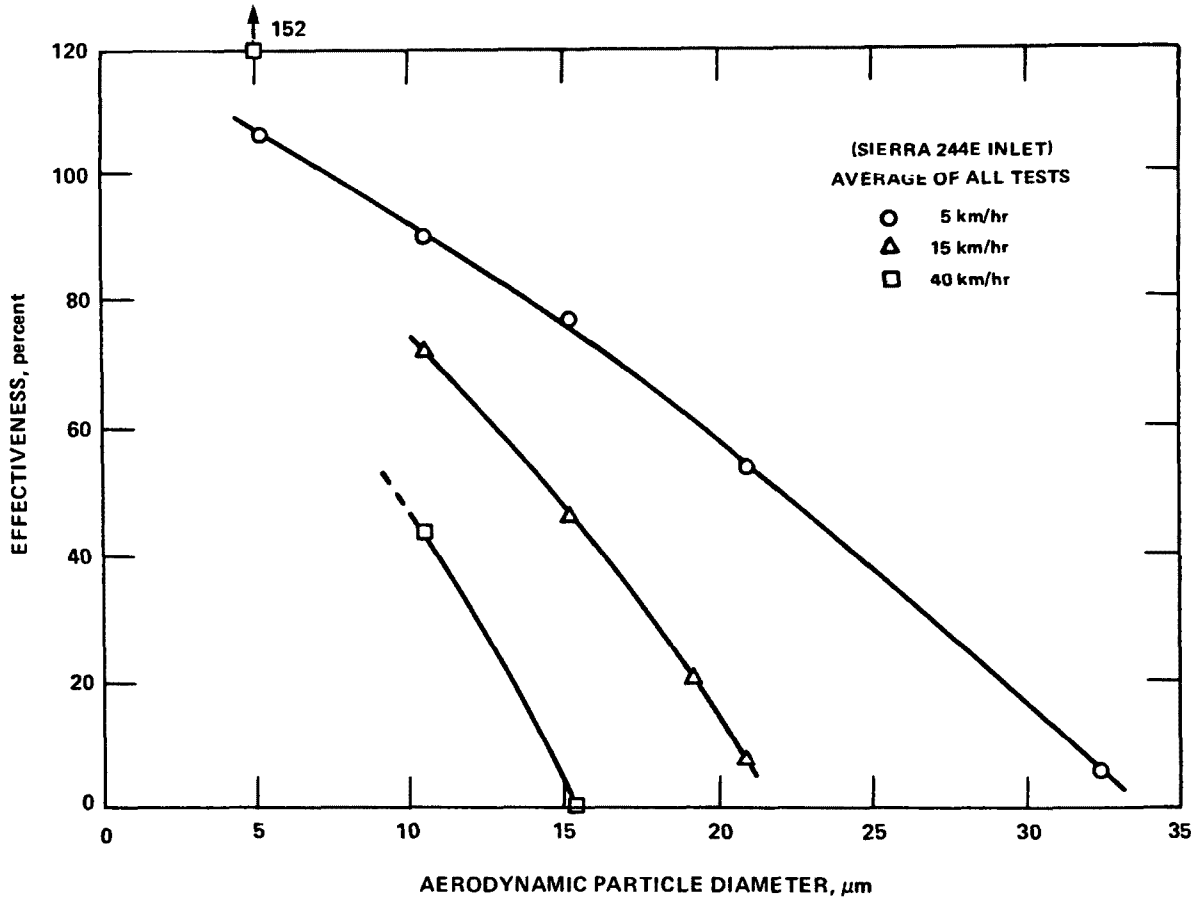

Figure 3-5. Sampling effectiveness of the dichotomous sampler inlet as a function of wind speed.

Source: Wedding et al., (1980).

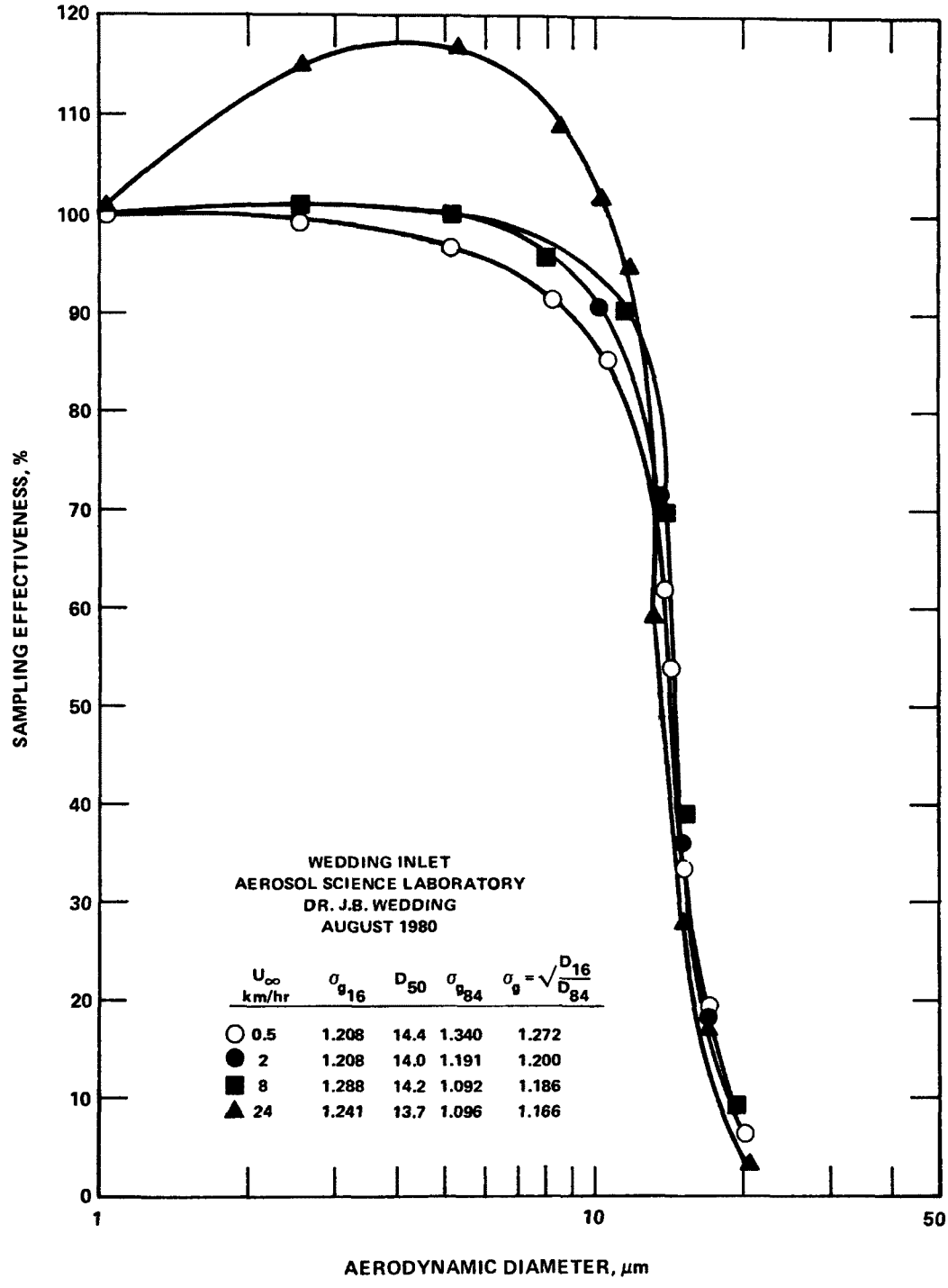

Figure 3-6. Sampling effectiveness of the Wedding IP inlet.

Source: Wedding (1980).

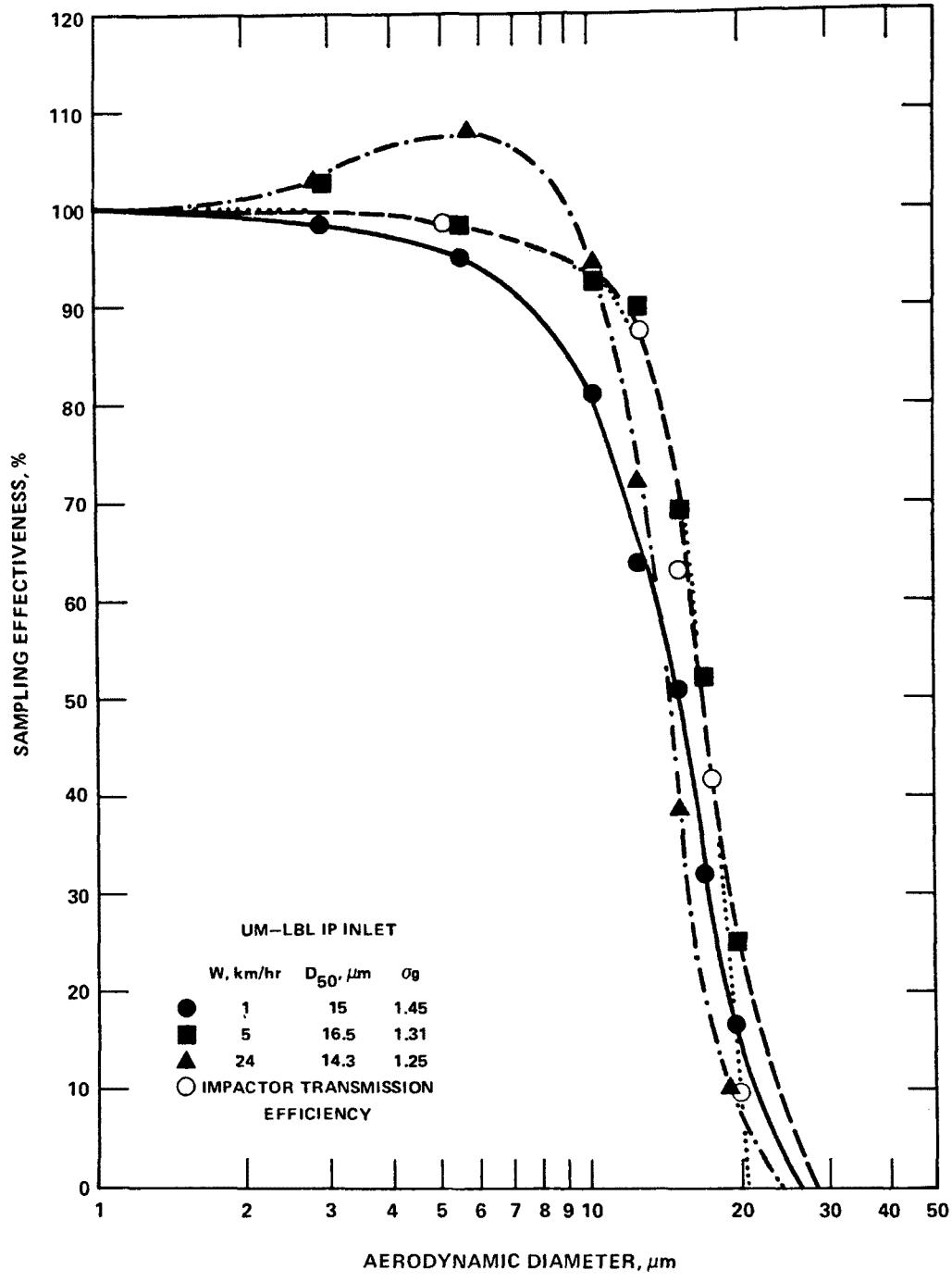

Figure 3-7. Sampling effectiveness of UM-LBL IP inlet.

Source: Liu et al. (1980).

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(1978) for exposed filters. Appendix Table A-1 tabulates selected fractional efficiency data for the commonly used TSP high-volume sampler glass fiber filter, the Teflon® membrane filter used by the dichotomous sampler, and the cellulose fiber filter material (Whatman No. 1) used by the British Smoke Shade Sampler. The latter filter shows some inefficiency at the smallest particle sizes, while the glass fiber and nominal 2 μm porosity Teflon® filters are highly efficient for all particle sizes. The relationship of flowrate through the filter to the pressure drop across it is also a very important mechanical consideration since this determines the available operating flowrate range for a given size vacuum pump. Membrane filter samplers, because of the rapid increase in pressure drop as particles deposit, require lower flowrates than fiber filter samplers. This results in substantially less particulate matter being collected during a sampling interval and the use of a much more sensitive weighing device (balance).

3.3.2.1.1 TSP high-volume sampler. The high-volume (hi-vol) sampler is the current EPA reference method (U.S. Environmental Protection Agency, 1979c) for "total suspended particles" (TSP). It is intended to operate at flowrates from 1.1 to 1.7 m^3/min, drawing air through a 200 x 250 mm glass fiber filter. The mass of particles collected on the filter is determined from the difference between weights before and after exposure. The mass concentration is integrated over the sampling interval and is normally expressed in μg of mass collected per m^3 of air sampled (μg/m^3).

Glass fiber is the commonly used filter media for this sampler and is nearly 100 percent efficient for 0.3 μm particles (Liu et al., 1978). As noted by Friedlander (1977), this size particle is the most difficult to capture, since the collection of smaller and larger particles is assisted by diffusion and impaction, respectively. This filter material is not prone to rapid overloading as is a membrane substrate and permits sampling over 24-hr periods in ambient TSP concentrations in excess of 300 to 400 μg/m^3. Glass fiber filters do not provide a chemically inert surface and the surface impurities and basic pH may interfere with some measurements. The fibrous nature of the filter also makes surface measurements such as x-ray fluorescence impractical except for high atomic number elements such as lead.

The hi-vol is relatively simple to operate and reasonably inexpensive to purchase. The original method description in the Federal Register (U.S. Environmental Protection Agency, 1979c) was recognized to be an inadequate description of the procedure, and a much more detailed document was prepared by EPA (Smith and Nelson, 1973) to improve the quality of TSP data.

As shown in Figure A-3 (Appendix), the inlet is formed by the overhang of a gable roof which serves as a rainshield for the filter. The inlet effectiveness, as already discussed, does not produce a sharp particle size cutoff and is sensitive to wind speed. The collection efficiency of the hi-vol is also affected by sampler orientation, i.e., it is somewhat sensitive to wind direction, as described by Wedding et al. (1977). The average sampler flowrate is determined either by averaging single measurements before and after collection using an external flowmeter or by integration of a flow recorder trace. The effect of sampler flowrate

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on the sampling effectiveness for large particles as shown in Figure 3-8 is not substantial; however, use of a flow controller provides the most accurate sampler performance.

The absolute accuracy of ambient particulate measurements such as those made by the high volume sampler cannot be quantified with current state-of-the-art technology. Alternatively, estimates of components of the overall accuracy can be determined, including the collection effectiveness of the sampler inlet and filter media and the accuracy of the flow measurement system. Two commonly used flow measurement devices on high volume samplers are the rotameter and the orifice meter with a pressure recorder. The rotameter is used to measure the initial and final flowrates from which an average is calculated. The pressure recorder provides a continuous trace of the orifice pressure drop that can be integrated for a more accurate measurement. Smith et al. (1978) using high volume samplers with both types of devices noted that the pressure recorder produced smaller errors (2 to 4 percent) when compared with a reference flow device than the rotameters (6 to 11 percent).

The precision of the high volume sampler as determined from collocated sampler measurements under field conditions and expressed by the coefficient of variation (CV) have been reported by several investigators. McKee et al. (1971) determined the CV for a measurement by a single analyst to be 3.0 percent, while the same measure among multiple analysts in a collaborative test was 3.7 percent. Rogers et al. (1974) reported the precision of 4-6 hour TSP sampling to be 5.2 percent.

The design of the gable roof provides a settling chamber above the filter for larger particles blown in during periods when the sampler is not operational. McFarland and Rodes (1979) have quantified this deposition experimentally as a function of particle size and ambient wind speed. Interpreting these relationships, however, requires knowledge of the existing ambient size distribution of particle mass. For a typical distribution, the amount of mass added to a high-volume sampler filter during 5 days of exposure when it was not operational was predicted to be 6 to 8 percent. This effect has been measured in a field situation by Sides and Saiger (1976) and Lizarraga-Rocha (1976), who measured weight increases from 3 to 12 percent. Errors from this effect can be reduced by equipping the sampler with a mechanical device that keeps the filter covered during nonsampling periods. Alternatively, timely installation and retrieval of filters will also minimize the problem.

As shown by Coutant (1977), Spicer and Schumacher (1979) and Appel et al., 1979), artifact particulate matter can be formed by oxidation of acidic gases (e.g., SO_2, NO_2) or by retention of gaseous nitric acid on the surface of alkaline (e.g., glass fiber) filters and other filter types. The effect is a surface-limited reaction and, depending on the concentration of the acidic gas, should be especially significant early in the sampling period. The magnitude of the resulting error depends on such factors as the sampling period, filter composition and pH, and the relative humidity. The magnitude and the significance of artifact mass errors are variable and dependent on local conditions. Excluding the uncertainty

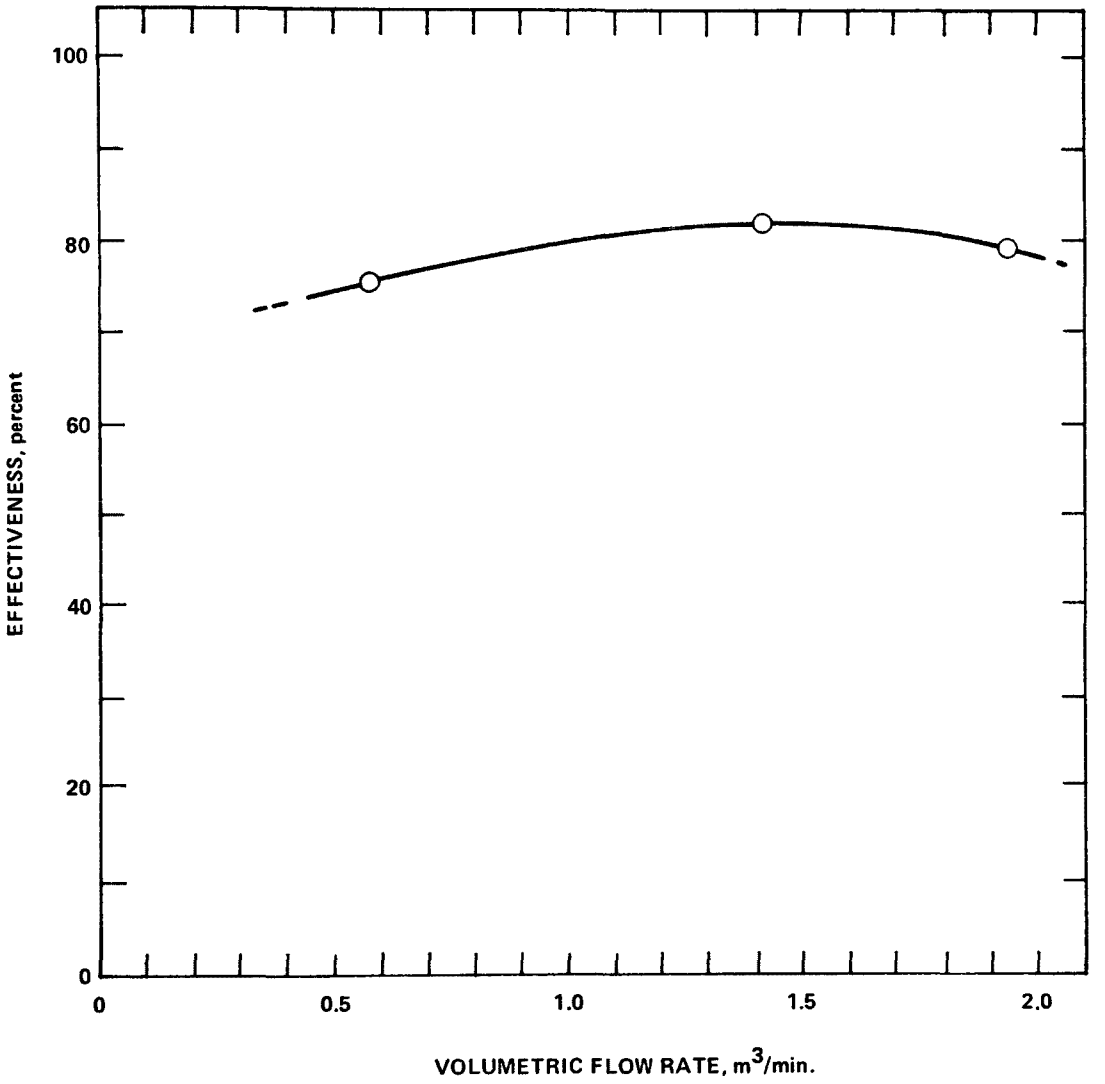

Figure 3-8. Effect of sampler flow rate on the performance of a Hi-Vol for 29 μm particles at a wind speed of 2 km/hr.

Source: McFarland and Rodes (1979).

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associated with the collection and retention of organic particulates with appreciable vapor pressure, artifact mass primarily reflects the sum of the sulfates and nitrates formed by filter surface reactions with sulfur dioxide and nitric acid gas, respectively. The ambient concentration of sulfur dioxide is primarily dependent on fossil fuel combustion, while the nitric acid concentration is dependent on atmospheric photochemistry and, possibly, reactions in suspended water droplets (Orel and Seinfeld, 1977). A laboratory study by Coutant (1977) reported artifact sulfate for 24 hr samples from 0.3 to 3 $\mu g/m^3$. Appel et al. (1978) observed up to 5 $\mu g/m^3$ artifact sulfate on alkaline glass fiber filters in 24 hr laboratory exposures, and up to 3.2 $\mu g/m^3$ artifact sulfate in atmospheric trials at two California sites. Stevens et al. (1978) similarly found 2.5 $\mu g/m^3$ average artifact sulfate sampling at 8 sites around St. Louis, Missouri; and Rodes and Evans (1977) noted 0.5 $\mu g/m^3$ artifact sulfate in West Los Angeles, California.

Artifact particulate nitrate values on glass fiber filters ranging from 1.9 to 26.4 $\mu g/m^3$ (mean 10.6 ± 6.9 $\mu g/m^3$, n = 13), were reported by Spicer and Schumacher (1979) in Upland, California. These values were obtained by comparison to nitrate concentrations measured simultaneously with quartz fiber filters. The likelihood of negative sampling artifacts on quartz fiber filters, as discussed below, make these artifact nitrate measurements upper limit values only. Appel et al. (1980) reported that artifact particulate nitrate on glass fiber filters is limited only by the gaseous nitric acid concentration. Such filters approximated total inorganic nitrate samplers, retaining both particulate nitrate and nitric acid even when the latter was present at very high atmospheric concentrations (e.g., 20 ppb). Nitric acid was found to represent from approximately 25 to 50 percent of the total inorganic nitrate at Pittsburgh, Pennsylvania., and Lennox and Claremont, California. Based on an estimate of the most probable 24 hr artifact sulfate error, 3 $\mu g/m^3$, and of the most probable artifact particulate nitrate, 8.2 $\mu g/m^3$ in the Los Angeles, California Basin and 3.8 $\mu g/m^3$ elsewhere, typical errors in mass due to sulfate plus nitrate artifacts are estimated at 11.2 $\mu g/m^3$ in the Los Angeles Basin and 6.8 $\mu g/m^3$ elsewhere.

Nitrate salts can be rapidly lost from inert filters (e.g., Teflon, quartz) by volatilization (Appel et al., 1980; Forrest et al., 1980), and by reactions with acidic materials (Harker et al., 1977; Forrest et al. 1979). Loss of atmospheric nitrate from glass fiber filters occurs slowly. For example Smith et al. (1978) observed a 25 percent decrease in nitrate over a three month period in storage at room temperature accompanied by a corresponding loss of ammonium ion. Colovos et al. (1977) noted loss of up to 1.5 $\mu g/m^3$ NH_4^+ after 30 days storage. Immediate analysis after collection would minimize the significance of such loss.

In general, the high volume sampler has been shown to be very reproducible (3 to 5 percent), if an orifice meter and flow recorder are used. The sampling effectiveness for larger particles is wind speed dependent and, based on the data in Figures 3-3 and 3-4, the effect of wind speed could be estimated to produce as much as a 10 percent day-to-day variability for the same ambient concentration for typical conditions. The effect of the sums of the reported

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positive and negative artifact related to the glass fiber filter could be expected to add 6-7 $\mu g/m^3$ to the collected mass.

3.3.2.1.2 Dichotomous sampler. The dichotomous sampler collects two particle size fractions, 0 to 2.5 μm and 2.5 to about 15 μm, the latter cutoff depending on the inlet. This bimodal collection effectively separates the fine particles from the coarse particles as described in Chapter 2 to assist in the identification of particle sources. Since the fine and coarse fractions collected in many locations tend to be acidic and basic, respectively, this separation also minimizes potential particle interaction after collection.

The particle separation principle used by this sampler was described by Hounam and Sherwood (1965) and Conner (1966). As shown in a simplified version in Figure A-4 (Appendix) the separation principle involves acceleration of the particles through a nozzle, after which 90 percent of the flow stream is drawn off at right angles. The small particles follow the right angle flow stream, while the larger particles, because of their inertia, continue toward the collection nozzle. A separate 37 mm Teflon® filter is used for each fraction. The sharpness of separation is shown in Figure 3-9 from data by Loo et al. (1976) for the design cutpoint at 2.5 μm. Inherent in this separation technique is a contamination of the coarse particle fraction with a small percentage of the fine particles in the total flow stream. This is not considered a substantial problem for mass measurements and a simple mathematical correction as described by Dzubay et al. (1977) can be applied.

Teflon® filters with porosities as large as 2.0 μm can be used in the sampler and have been shown to have essentially 100 percent collection efficiency for 0.3 μm particles (Liu et al. 1978). Because the sampler operates at a flowrate of 1 m^3/hr (16.7 ℓ/min) and collects sub milligrams quantities of particles, a microbalance with a 1 μg resolution is required for filter weighing. Removal of the stickier fine particles causes the collected coarse particles to have a greater tendency to fall off the filter if care is not exercised during filter handling and shipments (Shaw, 1979).

Dichotomous samplers are significantly more complicated to operate than single size fraction samples and hence are more prone to operator errors. As with the low flowrate cyclone samplers, the small mass collected on such filter requires careful weighing on a microbalance to provide reproducible results. The inlet currently available for this sampler is shown in Figure A-1 (Appendix). Testing has shown that this inlet is significantly wind speed sensitive, as shown in Figure 3-5. As the windspeed increases the D_{50} decreases, resulting in reduced collection of the larger particles.

Automated versions of this sampler can automatically change the sampler filters to provide unattended operation. Depending on atmospheric concentrations, short-term samples of as little as 4 hours are possible with the automatic samplers to provide diurnal pattern information. The mass collected during such short sample periods, however, is extremely small and the variability of the results could be expected to be very high. With an inlet sampling

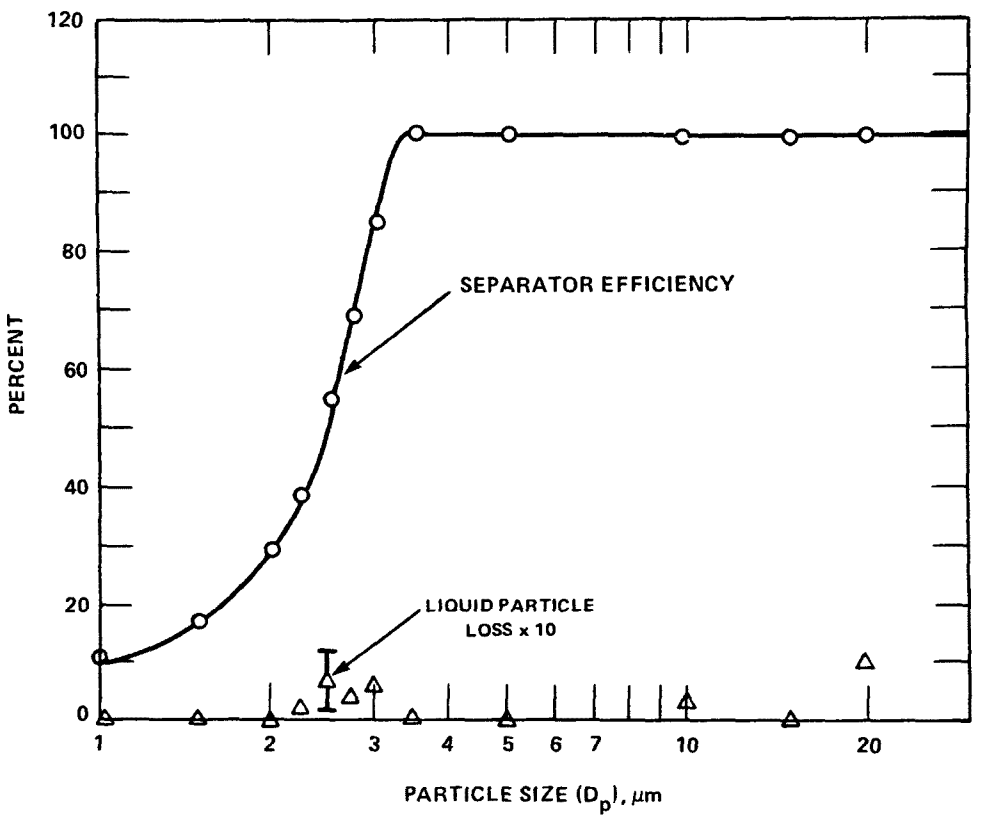

Figure 3-9. Separation efficiency and wall losses of the dichotomous sampler at 2.5 μm.

Source: Loo et al. (1976).

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effectiveness as described in Figure 3-5 the total mass collected would be 5-10 percent lower than the concentration during periods of average wind speed and typical ambient size distribution. The reproducibility is strongly dependent on the care taken during filter handling and weighing, but could be expected to be about ± 10 percent.

3.3.2.1.3 Cyclone Samplers. Ambient cyclone samplers are simple to operate and only moderately complex to build. Lippmann and Chan (1979) summarized the currently available cyclones for ambient particle sampling below 10 μm and noted that the separation effectiveness of cyclones can be designed to closely match respiratory deposition curves shown in Figure 3-1. The cyclone separation principle can be applied to larger particle cutpoints as demonstrated by Wedding (1980) for a 15 μm sampler inlet. The small physical size of some cyclones make them useful for personnel dosimetry sampling, if a suitably small pump and flow control system are employed. The Dorr-Oliver hydroclone, which is 10 cm in length and 10 mm inside diameter, matches the ACGIH curve (American Industrial Hygiene Association, 1970), and can be used for personnel sampling. This cyclone has also been used in ambient field studies including the Harvard 6-City Study (Lioy, et al., 1980).

A cyclone sampler used in the Community Health Environmental Surveillance Studies (CHESS) (Barnard, 1976) is shown in Figure A-4 (Appendix). This sampler as characterized in Figure 3-10, provides a relatively sharp separation with a D_{50} of 3.5 μm. The inlet of the sampler is the cyclone inlet, and a single 0 to 3.5 μm particle fraction is collected on the filter. The filter medium used in the CHESS network was glass fiber.

At an operational flowrate of 9.0 ℓ/min a typical fine fraction concentration of 30 $\mu g/m^3$ would result in the collection of only 390 μg of particulate matter on the filter. At this level Barnard (1976) determined the reproducibility of this sampler to be 13 percent. The effectiveness of the cyclone inlet for 3.5 μm and smaller particles should be nearly 100 percent. Use of the glass fiber filter would have similar artifact mass problems identified with the hi-vol sampler.

A discussion of the effect of sample flowrate on the performance of cyclones was given by Lippman (1970). Knight and Lichti (1969) compared the performance of the 10mm cyclone to that of horizontal elutriators and noted that the results were comparable if the appropriate flowrates were used. Caplan et al. (1977) noted that 5 different flowrates from 1.4 to 2.8 l/min have been recommended by researchers since 1962 for this cyclone to meet the ACGIH curve. They also noted that these small samplers are unaffected by (a) ambient air velocity, (b) dust loading, (c) mass loading, (d) orientation, or (e) aerosol charge. The reproducibility of this sampler has not been given in the literature, but the low sampler flowrate and proportionately small aerosol mass collected may result in values greater than ± 10 percent.

Collection of the larger particles excluded by a cyclone on a removable substrate is difficult, but alternative approaches such as that designed by John et al. (1978) and shown in Figure A-6 (Appendix) are available to provide a "total" sample dependent on the effectiveness of the inlet. The efficiency data for this cyclone as a function of sampler flowrate are shown

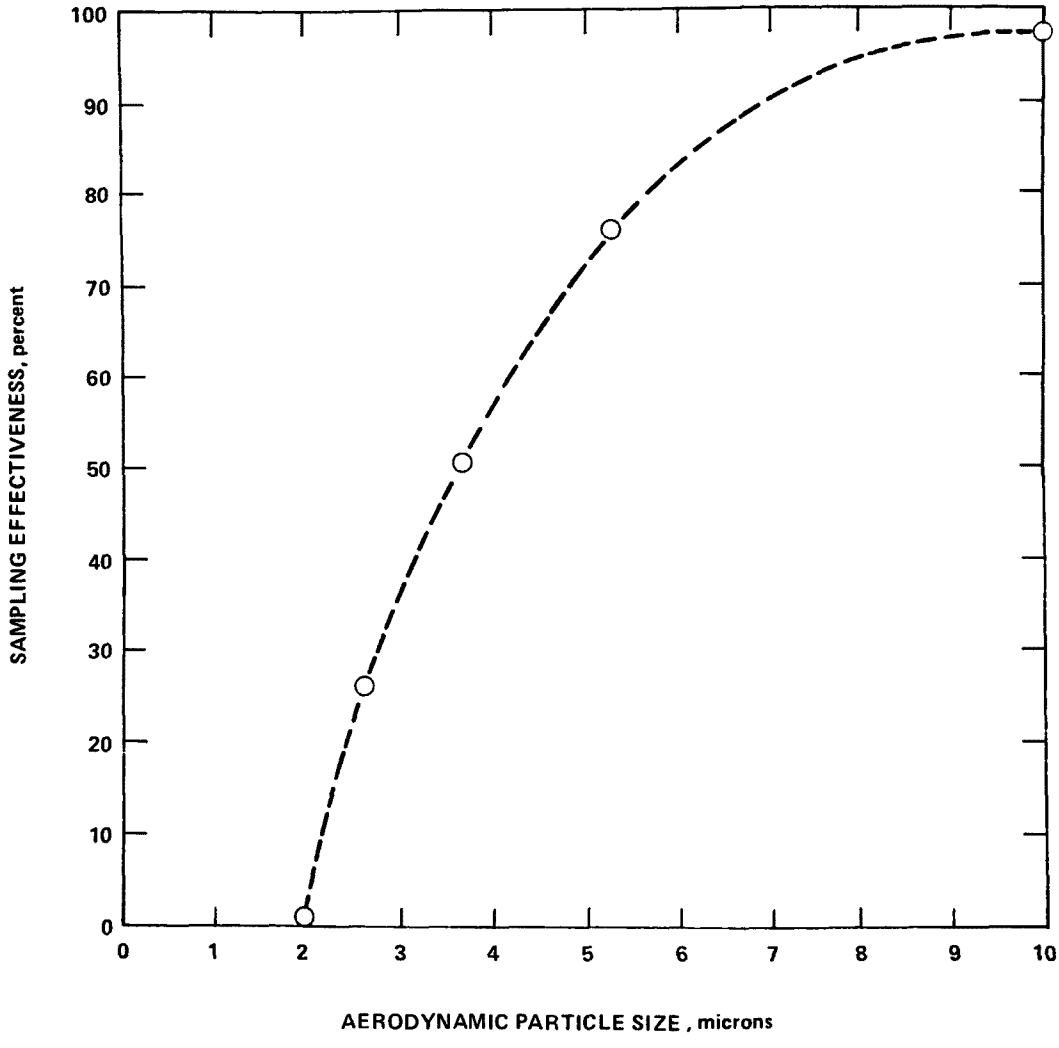

Figure 3-10. Sampling effectiveness for the 3.5-μm cutpoint CHESS cyclone sampler.

Source: Barnard (1976).

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in Figure 3-11 and indicate that sharp cutpoints with current state-of-the-art units are possible. A neutral pH Teflon® filter medium was recommended to minimize artifact mass formation. The inlet normally used for this sampler is the dichotomous sampler inlet shown in Figure A-1 (Appendix). This inlet was designed to operate at 16.7 ℓ/min. The wind speed influence on sampling effectiveness would be that shown in Figure 3-5. Reproducibility data for this sampler are not available but would be expected to be approximately 10 percent.

3.3.2.1.4 High-volume sampler with size selective inlet. To meet the monitoring requirements for Inhalable Particle (IP) as proposed by Miller et al. (1979), EPA commissioned the design of a size-selective inlet for existing TSP high-volume samplers to provide a single 0 to 15 μm particle size fraction. This inlet is mounted on a conventional high-volume sampler in place of the gable roof inlet. (See Figure A-7 (Appendix)) It has been tested by McFarland and Ortiz (1979) and has an inlet effectiveness as shown in Figure 3-12 and a sensitivity to wind speed as shown in Figure 3-13. Dry particle bounce and re-entrainment were also reported to be insignificant at the sampler flowrate of 1.1 m^3/min.

The glass fiber filter material is the same as that used for a TSP high-volume sampler, thereby presenting the same potential for artifact mass formation. This sampler, as with any size fractionating device, is somewhat sensitive to sampler flowrate for larger particles as shown in Figure 3-14. However, these data suggest that special flow controlling measures are not necessarily required to maintain consistent collection efficiencies over a range of sampler flowrates.

The inlet effectiveness data shown in Figure 3-12 would indicate reasonably accurate particle collection with minimal wind speed dependence. The influence of artifact mass on the total mass collected could be expected to add about 6-7 μg/m^3. The reproducibility should be similar to the 3-5 percent of the TSP hi-vol.

3.3.2.1.5 Elutriator Samplers. The British Medical Research Council (BMRC) (Orenstein, 1960) defined a respiratory system particle deposition curve as shown in Figure 3-1. As discussed by Hamilton and Walton (1961), this deposition curve is matched by a horizontal elutriator consisting of multiple parallel plates. A schematic diagram of this elutriator is shown in Figure A-8 (Appendix). This sampler has been used in Great Britain for ambient sampling and in the U.S. as an occupational exposure sampler during mining operations. Corn et al. (1967) successfully used a horizontal elutricator to selectively size ambient particles below 3 μm for optical examination on glass slides. Hamilton and Walton (1961) noted that reintrainment of coarse particles can be a problem in an elutriator if mechanical vibration exists. Because current ambient or wind tunnel test data on these samplers are not available, the reproducibility or accuracy cannot be estimated.

3.3.2.2 Impactor Samplers--Often referred to as cascade impactors when used in multiple stages, impactors provide a means of collecting an ambient particle sample which is divided into subfractions of specific particle sizes. This method involves acceleration of the

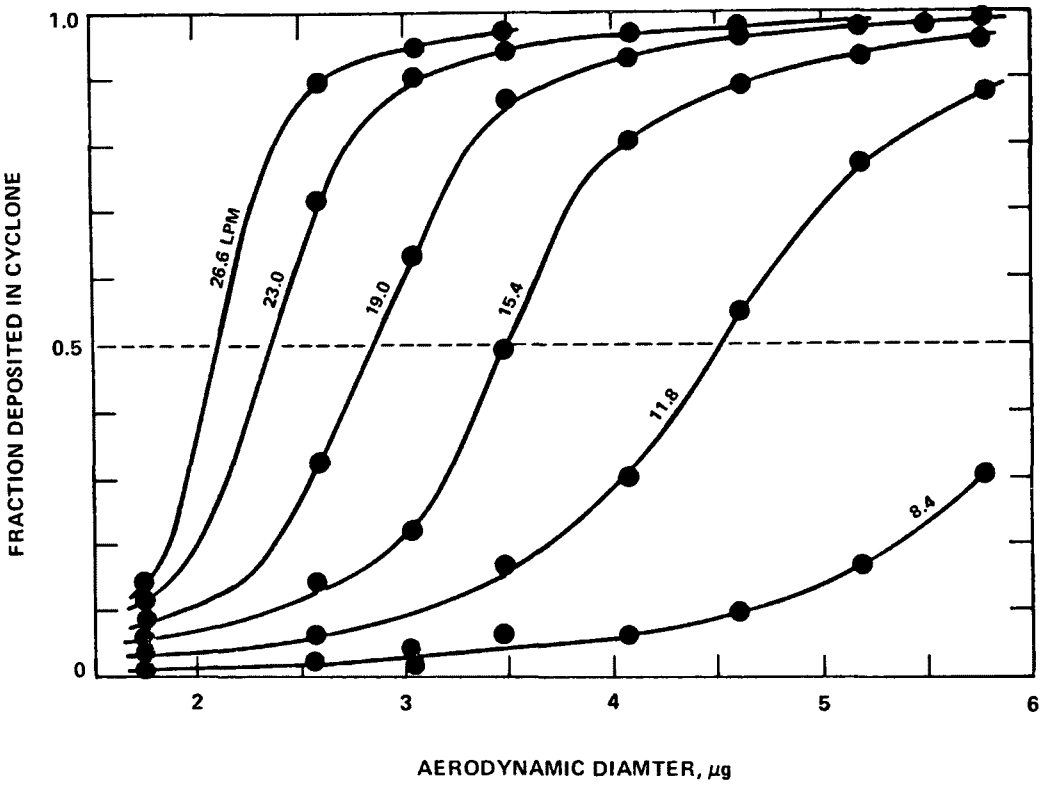

Figure 3-11. Fraction of methylene blue particle deposited in a cyclone as a function of the aerodynamic particle diameter. Curves are labeled with flow rate in liters/min.

Source: John et al. (1978).

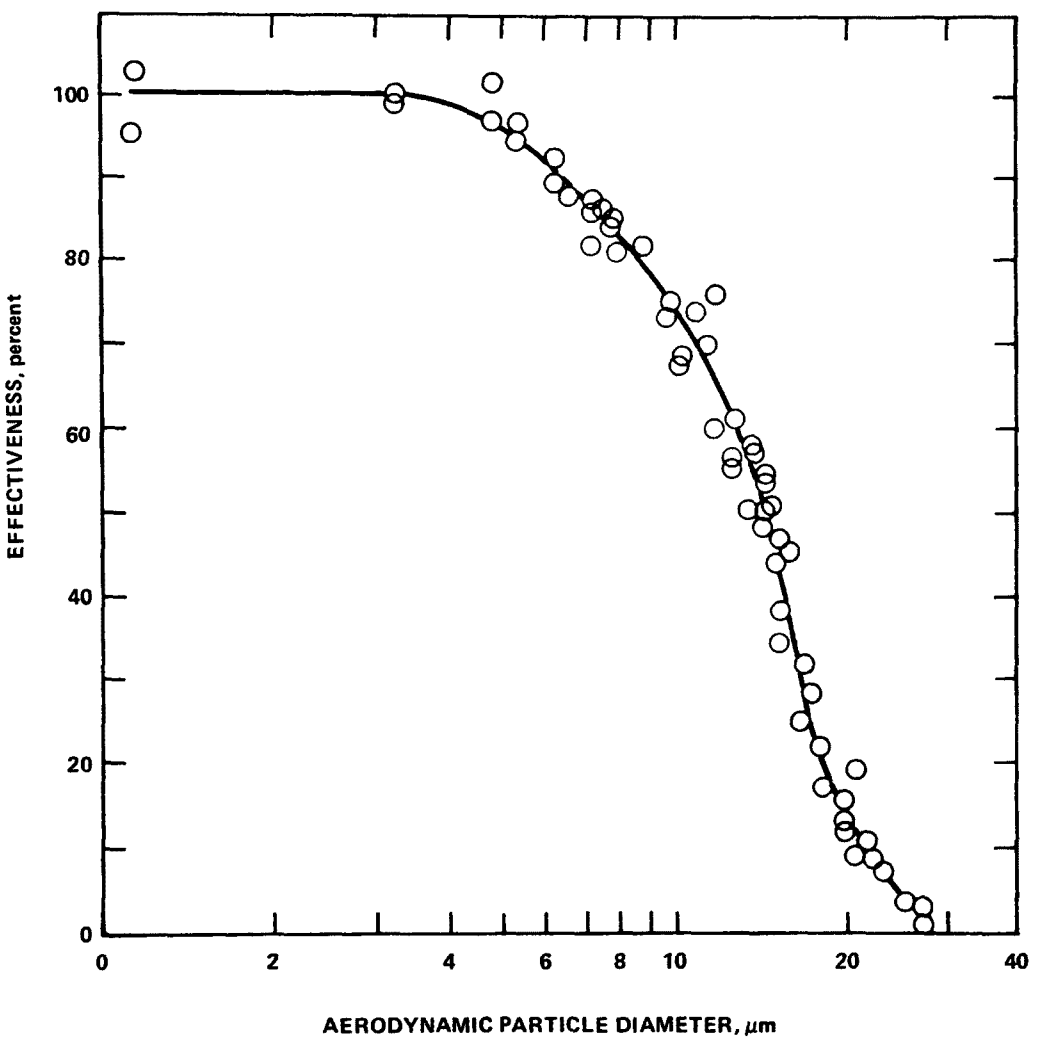

Figure 3-12. Sampling effectiveness for the size selective inlet Hi-Vol sampler for 2 km/hr.

Source: McFarland and Ortiz (1979).

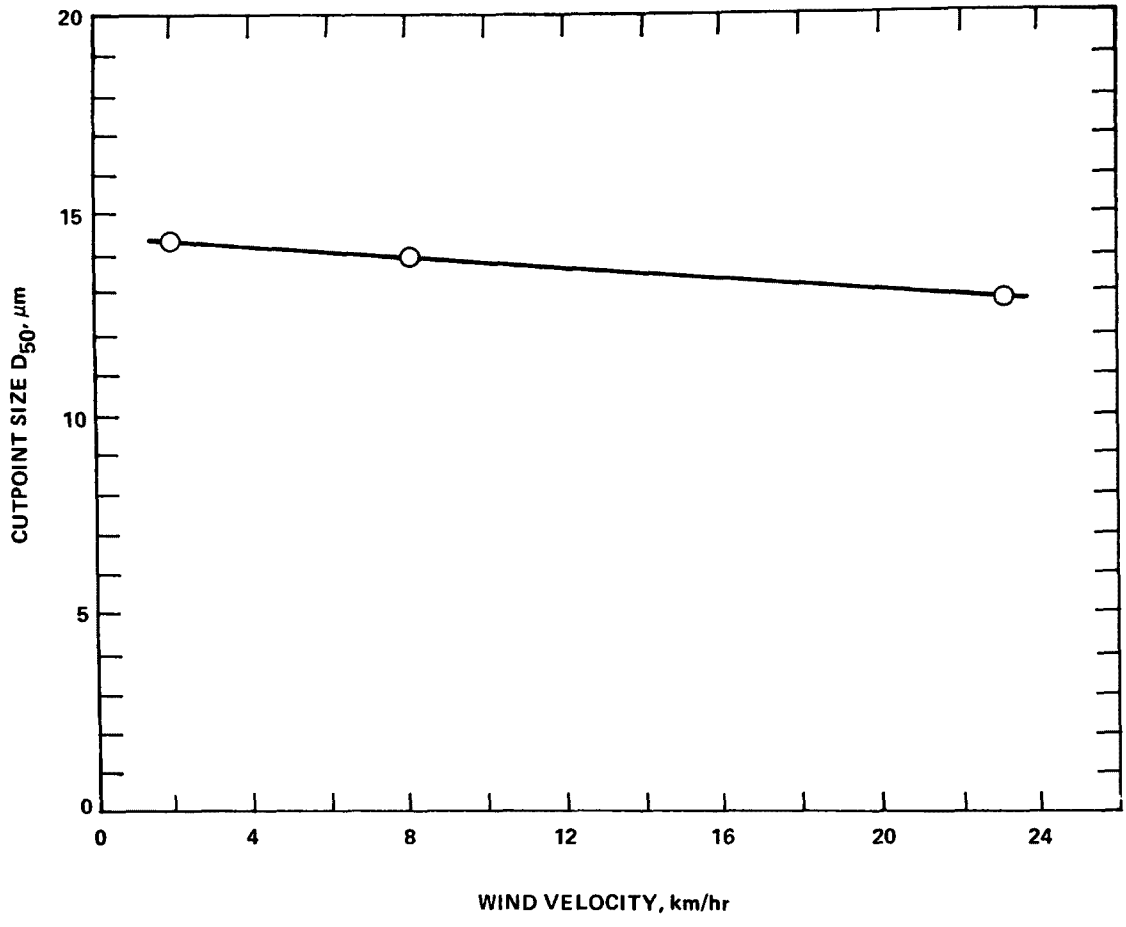

Figure 3-13. Effect of wind speed upon cutpoint size of the size selective inlet.

Source. McFarland and Ortiz (1979).

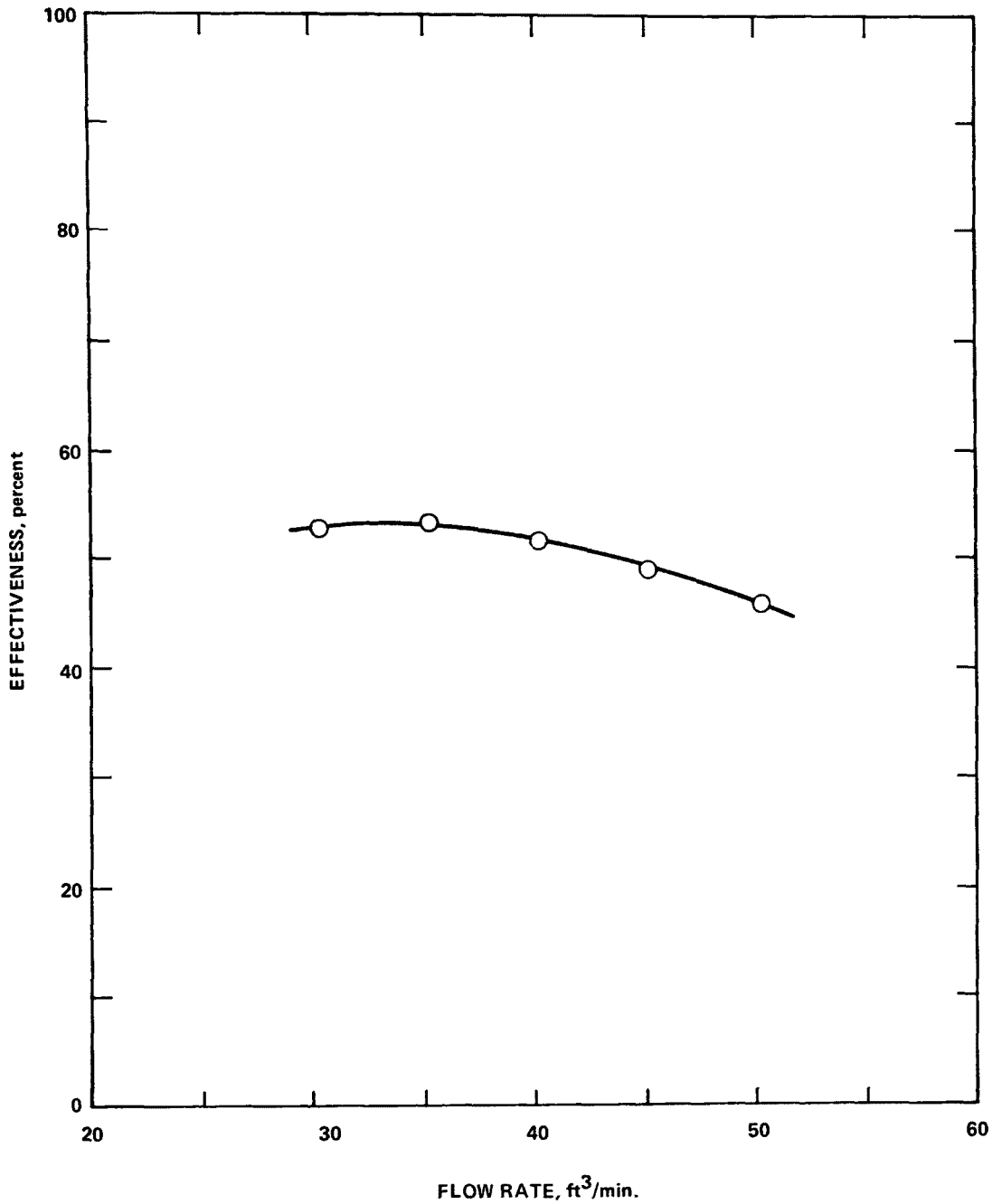

Figure 3-14. Effect of sampler flow rate on the sampling effectiveness of the size selective inlet Hi-Vol for a particle size of 14.1 μm and wind speed of 2 km/hr.

Source: McFarland and Ortiz (1979).

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ambient air stream by drawing it through one or more coverging nozzles or slots. As shown in Figure A-9 (Appendix) the jet of air is directed toward a collection surface, which is often coated with an adhesive or grease to enhance collection. Large, high-inertia particles are unable to turn with the air stream and consequently impact against the collection surface. Smaller particles follow the air stream and can be directed either to another stage of impaction or collected on a filter. Utilization of multiple stages, each with a different nozzle velocity, provides collection of particles in several size ranges.

Impactors use removable impaction surfaces for collecting particles. Impaction substrates are weighed before and after exposure and are typically metal foil plates or glass fiber filters. The selection and preparation of these substrates have a significant effect on the impactor performance. Improperly coated or overloaded surfaces can cause particle bounce to lower stages resulting in substantial cutpoint shifts (Dzubay et al., 1976). Marple and Willike (1976) showed the effect of various impactor substrates on the sharpness of the stage cutpoint. Glass fiber substrates can also cause particle bounce and are subject to the formation of artifact particles similar to high-volume sampler filters.

Cascade impactors typically have 2 to 10 stages, and commercial low volume version flowrates range from about 0.01 to 0.10 m^3/min. Lee and Goranson (1972) modified a commercially available 0.03 m^3/min low volume impactor and operated it at 0.14 m^3/min to obtain larger mass collections on each stage. Cascade impactors have also been designed to mount on a high-volume sampler and operate at much higher flowrates of approximately 0.6 to 1.1 m^3/min. A high volume sampler with a single impactor stage is shown in Figure A-10 (Appendix), was used in the Community Health Air Monitoring Program (CHAMP) program, and operated at 1.1 m^3/min.

The particle size cutpoints for each stage are dependent primarily on the sampler geometry and flowrate. The smallest particle size cutpoint routinely used is approximately 0.3 μm, although special low pressure impactors such as that described by Hering et al. (1978) are available with cutpoints as small as 0.05 μm. A high efficiency filter is typically used after the last impaction stage to collect the small particles not impacted previously. The masses collected on each stage plus the backup filter mass collection are often reported as shown in Figure 3-15 from data by Lee (1972). This cumulative distribution format permits determination of the Mass Median Diameter (MMD), at which point 50 percent of the mass is smaller than the indicated size. Utilization of straight line plotting techniques as shown in Figure 3-15 implies a lognormal mass distribution, which as noted by Natusch and Wallace (1976) can result in misinterpretation of the mass median diameter.

Cascade impactors are not normally operated in routine monitoring networks because of the manual labor requirements for sampling and analysis. Although impactor sampling systems are not extremely complex, careful operation is required to obtain reliable data, especially if coated collection surfaces are used. Analysis beyond mass to obtain size distributions of

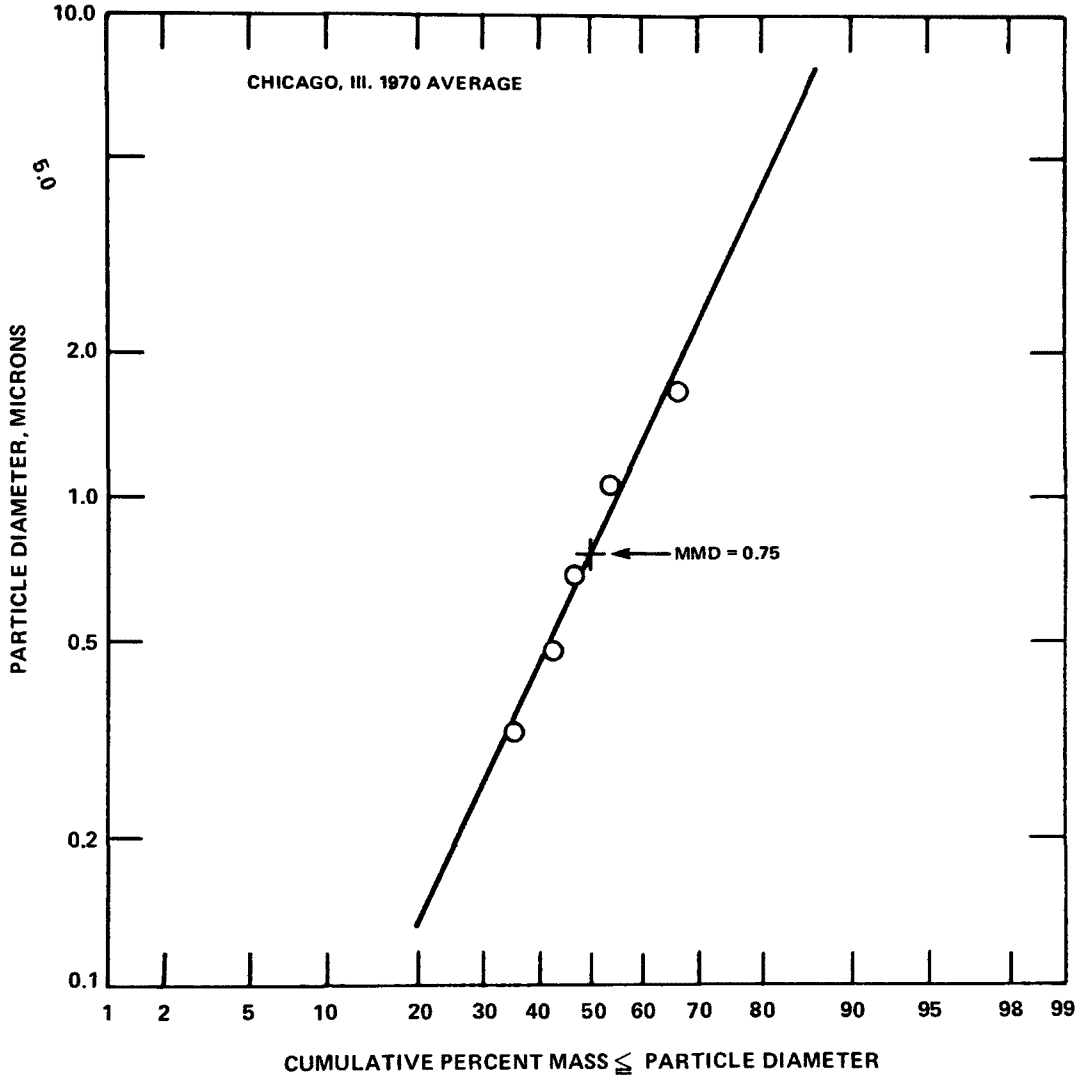

Figure 3-15. An example of a mass size distribution obtained using a cascade impactor.

Source: Lee (1972).

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species such as sulfates are possible, but require careful analytical techniques or compositing by stage with other samples to obtain an adequate quantity of material for analysis. Impactor stages which utilize grease coatings may prove undersireable for certain analyses because the grease may interfere with the method. Natusch and Wallace (1976) investigated the errors associated with impactor sampling and concluded that even under very unfavorable conditions the mass median diameter can be determined to well within 25 percent of the true value.

The inlet characteristics of most impactors have not been determined, resulting in uncertainty about the size range of particles sampled. McFarland (1980) has examined the inlet of the NASN low volume (0.14 m^3/min) cascade impactor and determined that particles larger than 10 μm were unlikely to reach the collection stages. Willeke and McFeters (1975) characterized the CHAMP high volume sampler inlet under static wind speed conditions as shown in Figure 3-16. If the characteristics of the impactor inlet are known, the total mass collected by the sampler can be used for comparison with other similar size specific measurements.

The particle separation efficiency of an impactor stage can be very sharp and mathematical models are available to permit stage sizing at selected cutpoints. The single impaction stage of the CHAMP high volume sampler designed to be 3.5 μm was characterized by Ranade and Van Osdell (1978) as shown in Figure 3-17 and demonstrated a close agreement with theory. Note, however, that solid particles above 5 μm deviate from the relationship, indicating possible particle bounce effects.

3.3.2.3 Dustfall Sampling--Since very large suspended particles have appreciable settling velocities, they are collected by deposition in a dustfall container and weighed as described by procedures such as that by American Society for Testing and Materials (ASTM) (1966). Although a cylindrical jar might be expected to collect the equivalent of the dust content of an air column of its own diameter extending to the top of the atmosphere, in fact the aerodynamic effects of the jar, the angle of approaching windflow, the mounting brackets for the jar, and adjacent structures tend to complicate the collection pattern. As noted by Nadel (1958), it is difficult to interpret the meaning of dustfall data and the significance of correlations with other measurements. There is no definitive study in the literature on the precision and accuracy of dustfall measurements or the effect of the height of the collector above the ground on measured dustfall.

3.3.3 Indirect Mass Measurements

A variety of techniques are available which report results in terms of pseudo-mass concentrations, using analytical techniques other than direct weighing. Many of these techniques collect the particles on a filter substrate, followed by an analysis which measures an integral property of the deposited particle other than the total mass. Examples include light reflectance, light transmittance, and beta ray attenuation. Other *in situ* measurements are also used which do not deposit the particles on a filter but measure a characteristic of the particles while still suspended such as light scattering. Most of these alternative methods are less

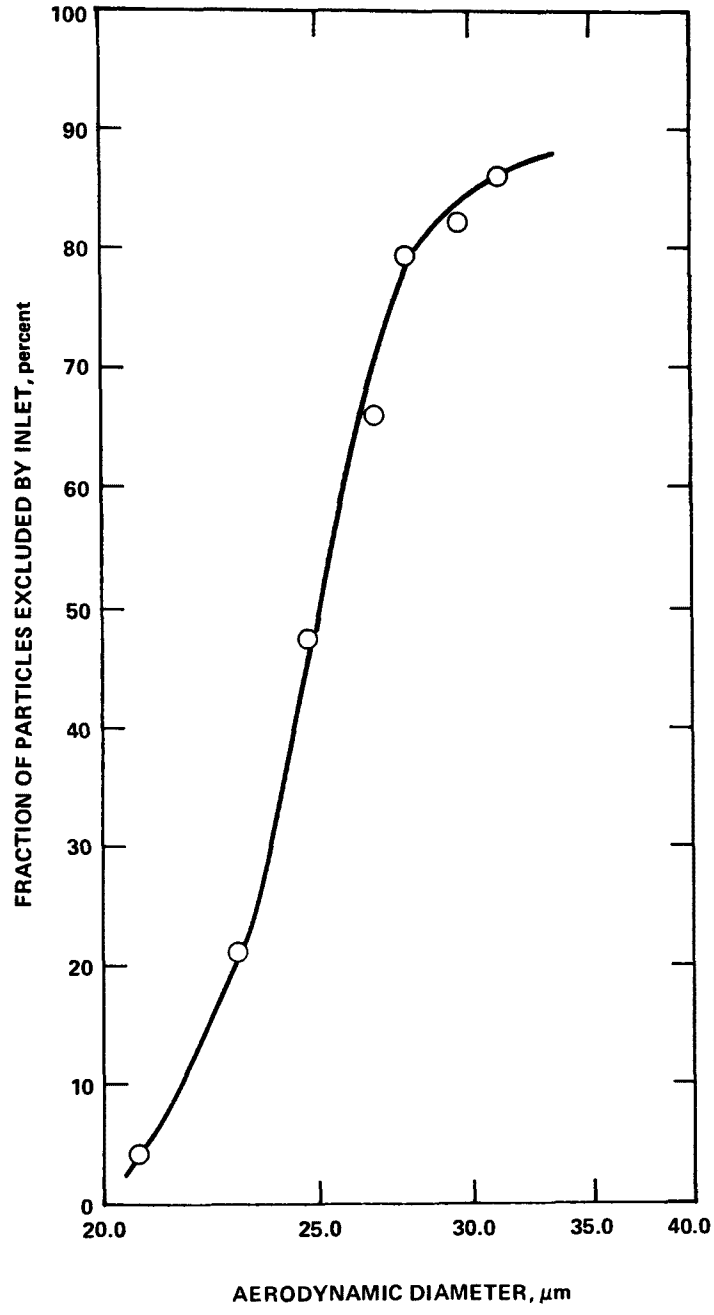

Figure 3-16. Fractional particle collection of the CHAMP fractionator inlet at a sampler flow rate of 1133 liters/min.

Source: Willeke and McFeters (1975).

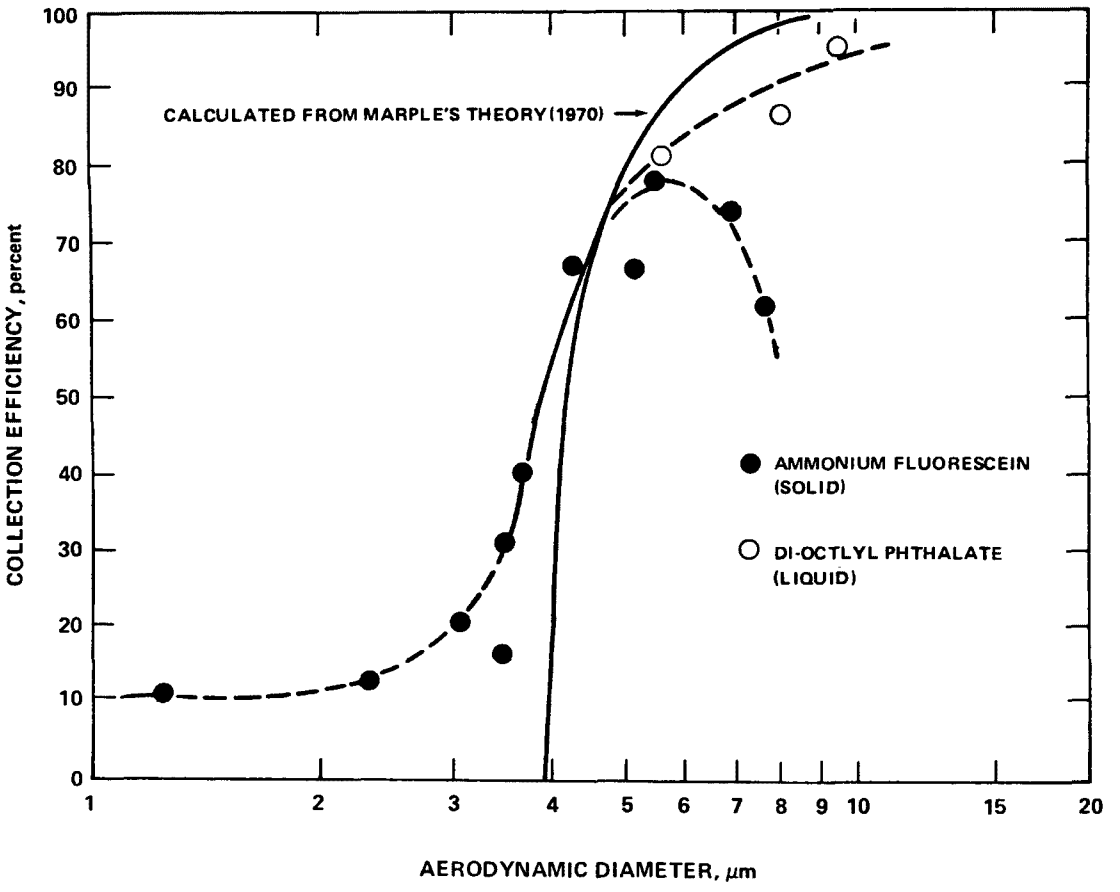

Figure 3-17. Efficiency of the single impaction stage of the CHAMP Hi-Vol sampler.

Source: Ranade and Van Osdell (1978).

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expensive per sample and provide more rapid collection and analysis of data than gravimetric analysis. However, the quality of the indirect methods is directly related to the quality of the relationship between the indirect measurements and mass. Some measurements are not generally useful because they depend heavily on site dependent particle characteristics such as color or density. In most cases a scientifically based physical model relating the measurements is not available, thereby providing no basis for regression analysis. A site-by-site best-fit regression must then be considered which provides questionable accuracy in predicting the true mass concentration.

3.3.3.1 Filtration and Impaction Samplers--Samplers in this category collect particles on a substrate and then utilize an alternative analytical technique as a surrogate to direct weighing.

3.3.3.1.1 British Smoke Shade sampler. The design of the currently used British Smoke Shade sampler is based in part upon early work by Hill (1936), who used transmitted light to assess the darkness of the stain resulting from particle collection on the filter paper. This sampler draws an air stream upward through an inverted funnel and 3 meters of nominal one-quarter inch diameter plastic tubing to an inverted filter holder containing a Whatman Number 1 cellulose fiber filter. A schematic diagram of a version of this sampler designed to sequentially collect samples for 8 days is shown in Figure A-11 (Appendix). A bubbler is often used downstream of the filter holder for subsequent SO_2 measurements. The sampler is operated at approximately 1.5 liters/min, which is verified by a dry test meter built into the sampler. The filter holder can be 25, 50, or 100 mm in diameter to collect a spot of the proper darkness range for subsequent measurements by reflectance. As noted earlier, the Whatman filter medium has been shown to be somewhat inefficient when sampling very small particles (Liu et al., 1978).

Many studies have been conducted since the early 1900's to establish relationships between the smoke shade reflectance and gravimetric measurements. A 1964 study supported by the Organization for Economic Cooperation and Development (OECD) established the currently used relationships between smoke shade reflectance measurements and gravimetrically determined particulate concentrations. These data were accepted by the World Health Organization (WHO, 1976) and compiled into a standard operating procedure for reporting smoke shade measurements in equivalent $\mu g/m^3$. These equivalent mass concentrations are not determined by weighing the smoke shade sampler filter but through comparison with a collocated gravimetric sampler. The gravimetric measurements which were made for OECD and compared to the Smoke Shade measurements were called "high volume sampler" readings, but were not the U.S. TSP high volume sampler. The OECD gravimetric "hi-vol" sampler as described by the British Standards Institution (1964) operates at approximately 60 liters/min compared to the 1.5 m^3/min of the U.S. hi-vol sampler. The OECD hi-vol was designed to be aerodynamically similar to the smoke shade unit but has not been characterized for aerosol collection effectiveness. Even if the aerosol collection capabilities were identical, this gravimetric sampler which uses very efficient cellulose membrane

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filters would collect more material than the smoke shade sampler because of the differences in filter efficiency. The selection of the filter holder diameter is also critical to the relationship since the darkness of the spot cannot be reliably used to predict mass if it is too light or too dark.

The aerosol collection properties of the smoke shade sampler have been examined by McFarland (1979). This examination produced the effectiveness plot shown in Figure 3-18, which shows that the D_{50} for particles reaching the filter is only about 4.5 μm. Most large particles are either rejected at the inlet or lost in the inlet line. Since the typical ambient size distribution contains only a small amount of mass between 2.5 and 4.5 μm, the size fraction reaching the filter for the British Smoke Shade sampler is nearly equivalent to the 0-2.5 μm fine fraction (Chapter 2) and the 0-3.5 μm respirable suspended particle (RSP) fraction defined by the American Conference of Governmental and Industrial Hygienists (ACGIH) (1968). Because the size range of particles collected by the smoke shade sampler is substantially less than that collected by the TSP high volume sampler, comparisons between the methods could be expected to be highly variable based on this incompatability alone. The variability is also influenced by factors such as the carbon content of the particles. Bailey and Clayton (1980) showed that smoke shade measurements correlated more closely with soot carbon content than to total mass. The reproducibility of collocated smoke shade sampler measurements was reported by the British Standards Institution (1964) as 6 percent.

The smoke shade sampler is relatively simple and inexpensive to use for routine monitoring. As noted by several investigators (e.g., Lodge, 1980), if a relationship could be developed between optical measurements and TSP samplers, it would be very site specific but still highly variable because of differences in the sources of collected particle size fractions and their carbon content with season. The accuracy of the smoke shade relationship to predict mass concentration for a given data set can be expected to be difficult to predict.

3.3.3.1.2 Tape sampler. A variation of the optical measurement of spot darkness is the use of a continuous filter tape and an automatic tape advancing system. A sampler using this approach, developed by Hemeon (1953) for the American Iron and Steel Institute (AISI), samples at a flowrate of approximately 7 liters/min using Whatman Number 4 filter paper and collects particles on a 25 mm filter spot. The spot darkness is read by either a transmittance or reflectance measurement. Transmittance measurement is the most popular measurement in the United States.

The sampler, often referred to as the AISI tape sampler, typically collects particles in selected time intervals of 1 to 4 hours, and then advances to an unexposed clean portion of the tape. Optical measurements are referenced to an unexposed filter area and can be made either external to the sampler after sample collection or with a continuous readout self-contained in the sampler.

Transmittance measurements are converted to optical density through a Beer's Law relationship and then to CoH (Coefficient of Haze) units per 1000 linear feet of air sampled.

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A CoH is defined as the quantity of particulate matter on the paper tape that produces a change in optical density of 0.01. The alternate RUDS (Reflectance Unit Dirt Shade) is equivalent to 0.1 CoH units per 1000 feet (ASTM, 1970).

As shown in Figure A-12 (Appendix), this sampler utilizes a funnel inlet and a small diameter transport tube nearly identical to the British Smoke Shade sampler. Although the two samplers operate at different flowrates, the particles reaching the filter tape could be expected to have a size range similar to that illustrated in Figure 3-18.

The utility of the sampler to estimate mass concentrations has been investigated by many researchers, usually in comparison with the TSP high-volume sampler. Since these two samplers do not collect similar particle size ranges, such comparisons could be expected to be variable unless only a small proportion of coarse particles are present. Regan et al. (1979) as well as others have shown with field data that the correlation improves substantially when the tape sampler data are compared with smaller particle fractions such as the 0-2.5 μm fine fraction. As was noted for the smoke shade sampler, the accuracy of a relationship between AISI readings and mass concentration for a given data set can be expected to be difficult to predict.

3.3.3.1.3 Beta-ray attenuation. Beta-ray attenuation is another technique for estimating the mass of particles collected on a filter without direct weighing. An exposed filter is placed between a beta-ray source such as ^{63}Ni, ^{14}C, or ^{147}Pm and a beta detector used to measure the amount of attenuation caused by the particle as compared to a clean filter. A set of gravimetrically prepared standards are used to relate the results to units of mass. This method is useful because it can be automated to handle a large number of samples (Goulding et al., 1978; Loo et al., 1978). Real time mass measurements are also feasible (Macias and Husar, 1976).

Investigators (Macias and Husar, 1976; Goulding et al., 1978) have studied the dependence of the beta ray absorption coefficient on elemental composition of the sample. Goulding et al. (1978) have found the dependence on composition to be very slight for the ranges of average compositions that occur in aerosol samples. In a recent interlaboratory comparison of aerosol sampling and measurement methods (Camp et al., 1978), it was demonstrated that laboratory beta gauge measurements of ambient aerosols collected by dichotomous samplers on Teflon® filters compared favorably in precision and accuracy with concurrent gravimetric analyses. Principal sources of error in the method are possible changes in the orientation filter substrate between the pre- and post-sampling measurements, and changes in attenuation because of absorption of water from the atmosphere by the filter material or the collected particulate (Lawrence Berkeley Laboratory, 1975). A definitive study to show the general utility of this technique has yet to be conducted.

3.3.3.1.4 Piezoelectric microbalance. The piezoelectric microbalance technique collects particles on an oscillating quartz crystal either by impaction or electrostatic precipitation. The frequency change of the crystal oscillation is proportional to the mass collected and the rate of change in frequency is proportional to the mass concentration (Woods, 1979).

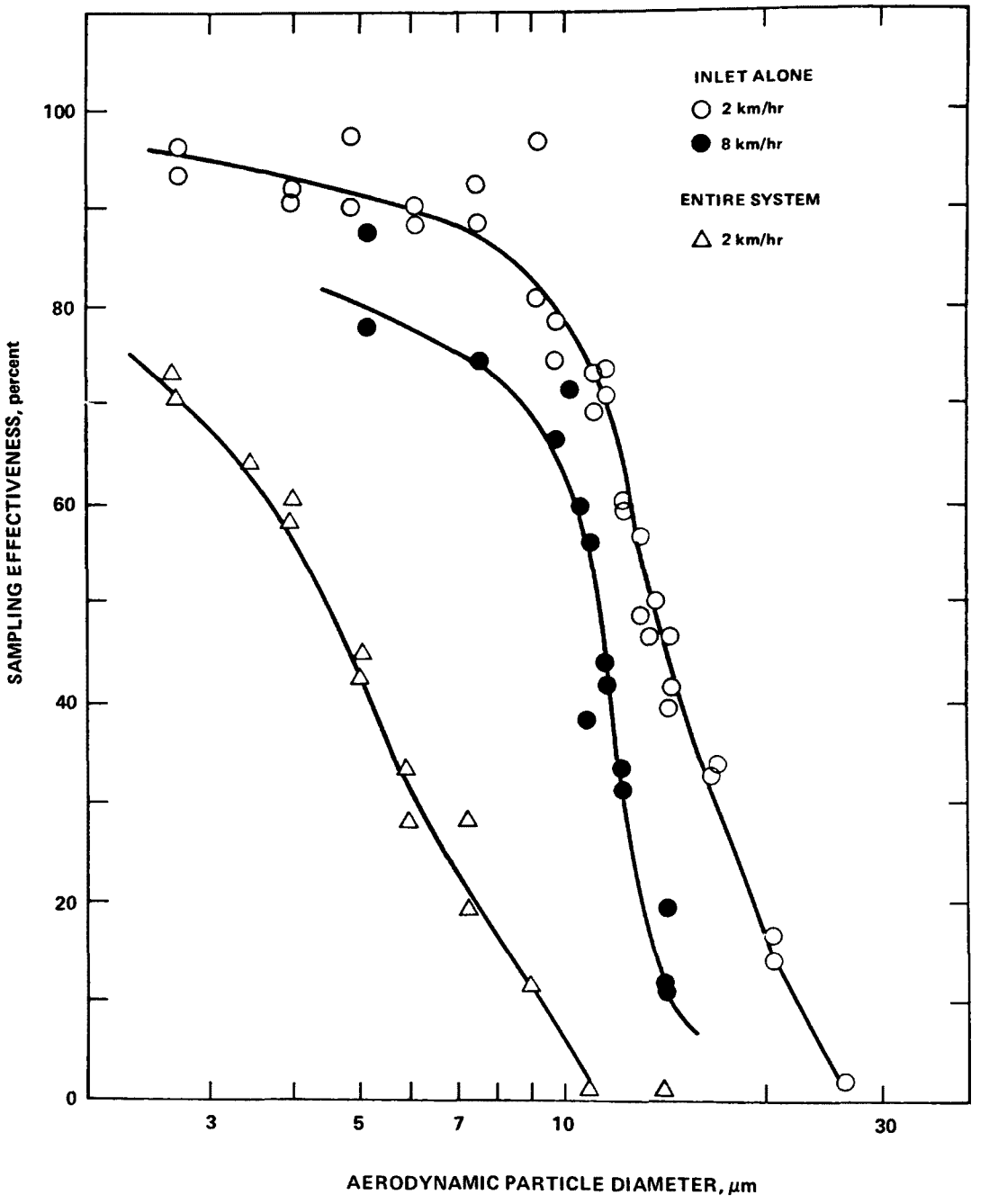

Figure 3-18. Sampling effectiveness of the inlet alone and through the entire flow system of the British Smoke Shade sampler.

Source: McFarland (1979).

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Advantages of the piezoelectric detection principal as noted by Lundgren et al. (1976) include extreme sensitivity and real time response. The technique can also be applied in a multiple stage impactor form using crystals as the collection plates. This approach provides rapid determination of particle size destributions.

Disadvantages of the microbalance principle include severe interference from large relative humidity changes and non-linearity of crystal response to large particle concentrations. As shown by the data of Lungren et al. (1976) in Figure 3-19, the effect of humidity is dependent on particle type and therefore nearly impossible to predict. Daley and Lundgren (1974) studied the potential errors in piezoelectric detection and noted that although not currently a routine monitoring method, it can be used sucessfully for short-term studies when realistic operating limits are observed.

3.3.3.2 In Situ Samplers--Instead of collecting particles on a filter before analysis, certain aerosol characteristics can be examined while the particles are still suspended in the air stream.

3.3.3.2.1 Integrating nephelometer. The integrating nephelometer measures the light scatter caused by varying particle concentrations in the air stream. These differences can be related to the scattering coefficient (b_{scat} with units of m^{-1}) and the particle size distribution present, but are normally expressed in terms of visual range in kilometers (Friedlander, 1977). The initial designs for this technique were made by Buttell and Brewer (1949) and subsequently improved by Ahlquist and Charlson (1967). Light scattering is at a maximum for particles in the 0.3 to 0.8 μm range, as shown in Figure 3-20, and hence the response of techniques based on this principle must be corrected for particle size effects. Light scattering is primarily caused by accumulation mode particles and only slightly affected by particles in the nucleation or coarse particle modes (Waggoner, 1973).

The nephelometer is simple to operate and can provide real time particle measurements. Comparisons between nephelometer and high-volume sampler mass concentrations, such as those by Charlson et al. (1968), showed that a reasonable correlation existed under the conditions tested. However, comparison of the nephelometer with any integrated sampling method which collects the coarse particle mode will at times provide erratic, site-dependent results.

3.3.3.2.2 Condensation nuclei counter. The condensation nuclei counter measures the total light scatter of submicron particles whose size has been increased by condensing vapor in a cloud chamber onto their surface. This device is of interest in examining the number of particles in the nuclei mode but is not useful for particle sizes above about 0.5 μm (Perera and Ahmed, 1978). It is often used in conjunction with prior size separation stages to obtain a particle size distribution for submicron size particles. The condensation nuclei counter is rarely used for routine monitoring.

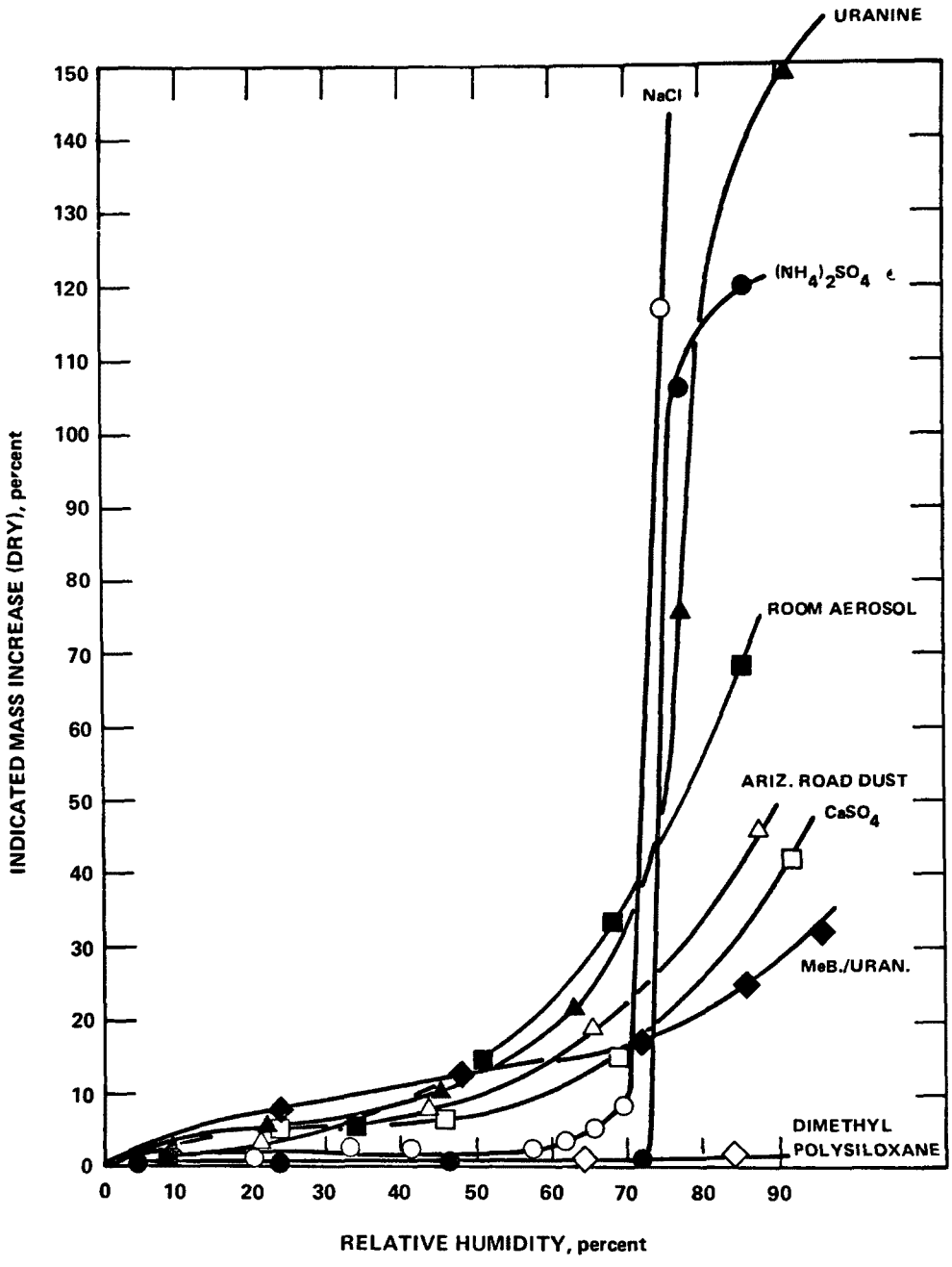

Figure 3-19. Response of a Piezoelectric Microbalance to relative humidity for various particle types.

Source: Lundgren et al. (1976).

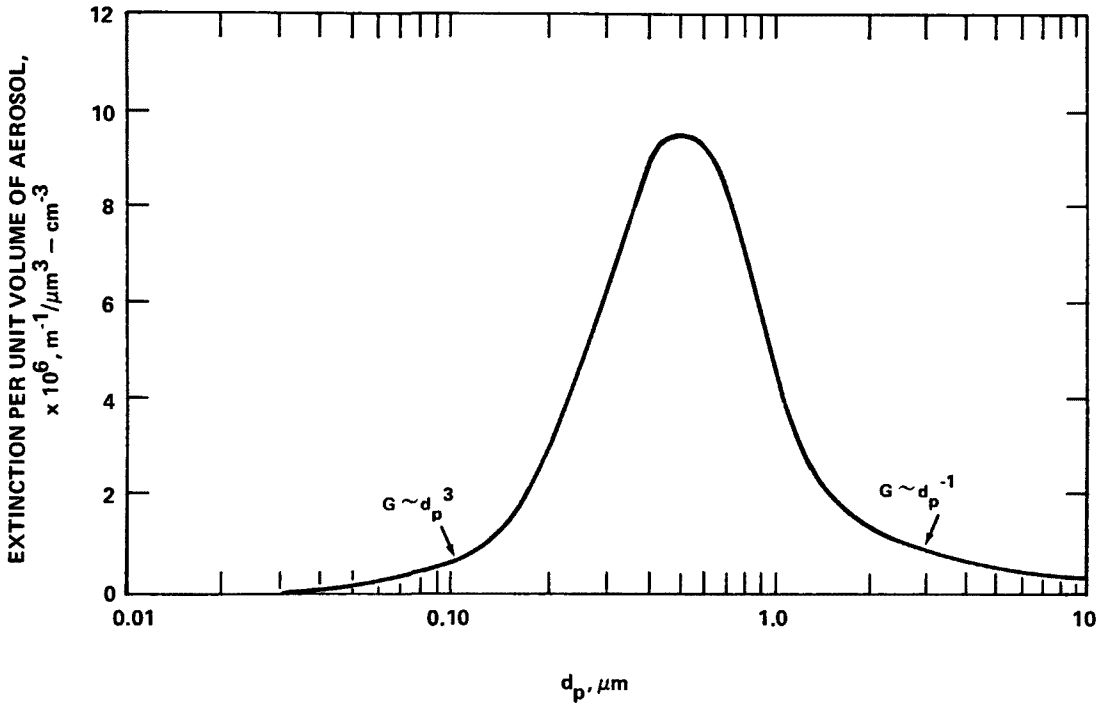

Figure 3-20. Light scattering expressed as extinction per unit volume of aerosol as a function of particle size integrated over all wavelengths for a refractive index of 1.5.

Source: Bolz and Tuve (1970).

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3.3.3.2.3 Electrical aerosol analyzer (EAA). The Electrical Aerosol Analyzer, as described by Whitby and Clark (1966), measures the electrical mobility of particles as related to their size. This device provides a detailed size distribution over the range of approximately 0.01 to 0.5 μm electrical diameter (Liu and Pui, 1975). The analyzer must be empirically calibrated to obtain the relationship to aerodynamically sized particles. The size range sampled does not include the entire 0-2.5 μm fine fraction, and comparision between the measurements must include extrapolations.

3.3.3.2.4 Diffusion battery. The diffusion battery, as described by Sinclair et al. (1979), is a set of parallel tubes or plates through which the air stream flows to produce selected differential particle removal by diffusion to the walls as a function of particle size. A condensation nuclei counter is used as the particle counter. This diffusion separation principle is useful in the range from about 0.01 to 0.3 μm.

3.3.3.2.5 Optical particle counters. Optical particle counters direct the flow stream through a small nozzle into a narrow collimated light beam such that the light scatter from single particles can be measured. This scatter produces a signal which is related to the size of a spherical particle which scatters an equal amount of light. These devices analyze a size spectrum of particle sizes from about 0.5 to 10 μm (Whitby and Willeke, 1979). Calibration with monodispersed particles is required. For sampling of particles larger than 10 μm, modification of commercially available devices are required. Mass concentrations for specific size ranges can be estimated by selecting an appropriate particle density. These devices can be operated routinely, but their utility to estimate mass concentrations is limited by the accuracy and consistency of the selected average particle density and index of refraction.

3.3.3.2.6 Long path optical measurement. Long path (typically >1 km) optical measurement devices for ambient air are available which examine one of several aspects of visibility over a defined distance. Transmissometers measure the attenuation of transmitted light resulting from scattering and absorption in the atmosphere. These devices are similar to their in-stack counterparts, requiring either a light source and receptor or light source, retro-reflector, and receptor at separate locations. Telephotometers measure the contrast caused by brightness differences between a distant object and its surroundings. These devices appear promising as visibility monitors (see Chapter 9), but they have not been demonstrated to estimate ambient mass concentration.

3.3.4 Particle Composition

Particles collected from ambient air contain a wide range of metallic elements and inorganic and organic compounds. Their identification and quantification usually involves the collection of the particles upon a substrate (e.g., glass fiber filters in a high volume sampler) with subsequent chemical analysis in a laboratory. Most methods for the analysis of the inorganic fraction of particulate matter have focused on elemental and ionic composition. Atomic absorption spectrometry has been the technique most used for the determination of

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metallic elements, although multielement analytical tools such as optical emission spectroscopy, X-ray flourescence spectroscopy, and neutron activation analysis have been successfully applied to the analysis of elements. Inorganic ionic species (e.g., NH_4^+, SO_4^{-2}, NO_3^-, etc.) have been analyzed for the most part with wet-chemical spectrophotometric techniques. The organic fraction of particulate matter contains aliphatic and aromatic hydrocarbons, acids, bases, and other organic compounds such as those containing nitrogen. Methods for analyzing organics generally involve solvent extraction, some form of chromatographic separation and detection based on some physical or chemical property of the specific compound.

Due to the complexity of the chemical composition of the particulate matter in the atmosphere and the wide variety of compounds likely to be present, it is not practical nor within the scope of this chapter to review all of the possible methods and techniques in use or likely to be used for their analysis and characterization. Only those methods and techniques pertinent to the primary objectives of this document are reviewed in detail. Primary emphasis is placed on methodology for measuring particulate sulfur compounds with lesser emphasis on metallic elements and other inorganic ionic species. Additional detailed information concerning the analysis of airborne particles can be obtained from a recent monograph edited by H. Malissa (1978).

3.3.4.1 Analysis of Sulfates--Analytical techniques for determining trace amounts of sulfate in clean, uncomplicated solution matrices are numerous (Forrest and Newman, 1973). However, application of these techniques to complex, atmospheric particles is not straightforward. Quantitative transfer from the collection medium and homogeneous dispersion in the analysis medium without contamination, chemical alteration, or co-transfer of analytical interferents is required.

A detailed critical review of the state of development of analytical methodologies for aerosol sulfur compounds has been compiled by Tanner et al. (1978). Tanner's review includes methods for total aerosol sulfur, for total water soluble sulfates and for quantitative differentiation of aerosol sulfur compounds of various oxidation states as well as a detailed definitive review of methods for speciation of aerosol sulfate. Much of the discussion in this section is taken from Tanner's review with emphasis on the more widely used methodology. Where information is available, a critical assessment of the methods capabilities is provided.

3.3.4.1.1 Total water soluble sulfates. A comprehensive review of wet chemical methods has been compiled by Hoffer and Kothny (1974) providing background information concerning methods for the determination of trace sulfate in aqueous extracts of particulate matter collected on filters. The principal methods for determination of sulfate that are applicable to aqueous extracts of airborne particles are reviewed here. Sulfate measurements made with these methods, particularly when applied to the analysis of samples collected with alkaline filter media, are vulnerable to error due to "artifact sulfate" formation caused by the absorption and subsequent oxidation of ambient SO_2 in the presence of the basic components of the filter

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media. With the use of common glass fiber filters under normal high-volume sampling conditions, this error has been estimated to range from 0.3 to >3 μg/m^3 depending on the ambient levels of SO_2 at the time of sampling (Coutant, 1977; Pierson et al., 1980). This potential error should be considered when assessing any data collected using any of the methods for water soluble sulfates which are discussed below.

Currently, the techniques most widely employed for soluble sulfate determinations are the $BaSO_4$ Turbidimetric, Methylthymol Blue, Thorin, and Ion Exchange Chromatographic procedures. Each of these techniques has inherent analytical precisions, accuracies, working range and other operational characteristics, which will be discussed in detail. Each technique has an analytical lower and upper detection limit for sulfate in the aqueous extract which are usually expressed in μg/ml. The detection limits of the technique for measuring sulfate in the air depends upon the sensitivity of the analysis technique and the size of the sample (volume of air, size of filter taken for extraction, etc.) and these values are expressed in μg/m^3. For example, if an analytical technique having a working range of 1 to 10 μg SO_4/ml is used to measure sulfate from a typical Hi Vol sample (20.3 cm x 25.4 cm filter, 1.4 m^3/min flow rate, 24-hr sample, 1.9 cm x 20.3 cm strip extracted in 50 ml), the detection limits for sulfate in air would be 0.3 to 2.9 μg SO_4/m^3. It should be noted that the upper detection limit can usually be extended to higher concentrations by dilution of the aqueous extract prior to analysis.

3.3.4.1.1.1 <u>$BaSO_4$ Turbidimetry</u>. Sulfate in the aqueous extract from a particulate sample is precipitated by addition of barium chloride. The resulting $BaSO_4$ turbidity is measured spectrophotometrically or nephelometrically and compared to a standard curve prepared by measuring the absorbance of standard solutions of sulfate. Numerous versions and modifications of methods based on this principle appear in the literature (Kolthoff et al., 1969; Technicon Corp., 1959; Taras et al., 1971; Appel et al., 1979a). Appel, et al. (1979a) described and evaluated a procedure applicable to the measurement of sulfate in aqueous extracts from 24-hr Hi Vol particulate samples. They reported an analytical working range from 10 to 70 μg SO_4/ml (2.9 to 20.6 μg SO_4/m^3 for a typical Hi Vol sample), an accuracy within 4 percent, and an average precision of 3.8 percent (coefficent of variation) of the working range. They also reported that extract background turbidity and color interfere with the procedure but are minimized by means of blanks and that sulfur compounds converted by air oxidation to sulfate interfere. The apparatus required for turbidimetric sulfate determination is relatively inexpensive and if proper care is taken, the procedure is capable of producing reliable data.

3.3.4.1.1.2 <u>Methylthymol Blue (MTB)</u>. A reagent containing equimolar amounts of barium ions and MTB, at a pH of 2.8, is added to the aqueous extract from a particulate sample. Sulfate in the solution is precipitated as $BaSO_4$ and the pH of the solution is raised to 12.4 by addition of NaOH. The barium combines with the anionic MTB and leaves an amount of free MTB equivalent to the sulfate. The MTB is measured spectrophotometrically at 460 nm and compared

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to a standard curve of absorbance vs. concentration. Lazarus et al. (1966) described an automated version of this method and reported that the reagent is oxidized in air when made alkaline, thus limiting the use of the method to a closed system.

An evaluation by Appel et al. (1979a) of automated MTB methods examined two procedures; one covering an analytical range of 0 to 100 μg SO_4/ml developed by Midwest Research Institute (MRI) for EPA and the other covering a range of 0-10 μg SO_4/ml developed by Colovos et al. (1976). The results for the MRI procedure indicated a working range of 17 to 90 μg SO_4/ml (5.0 to 26.5 μg SO_4/m^3 for a typical Hi Vol sample), an accuracy of 1.06 (mean observed/theoretical) with an average coefficient of variation of 2.8 percent for analyses of filter strips spiked with known amounts of sulfate. Similarly, the results for the Colovos (1976) procedure indicated a working range of 2 to 10 μg SO_4/ml (0.6 to 2.9 g SO_4/m^3 for a typical Hi Vol sample), an accuracy of 0.98 and a precision of 1.3 percent. The samples must be treated with an ion exchange resin to remove metal ions which may also react with MTB. No significant sources of interference were found in this evaluation. The automated versions of the MTB procedure are widely used and are capable of producing reliable results. Large sample loads can be analyzed in relatively short periods of time. However, the equipment is relatively expensive.

3.3.4.1.1.3 Thorin. Titrimetric methods for sulfate using barium ion and thorin indicator for visual or spectrophotometric detection of the endpoint are popular (Akiyama, 1957; ASTM, 1974; Bakas, 1956; Dubois, 1969; Fritz, 1955 and 1957; Menis, 1958; Rayner, 1966). These procedures provide for titration of aqueous sulfate with a solution of barium ion to precipitate barium sulfate ($BaSO_4$). When the sulfate is completely reacted, excess barium complexes with thorin to produce a pink color indicating the end-point of the titration. The samples must be treated with a cation exchange resin to remove metal ions which also complex with thorin.

A recent modification of this technique by Brosset and Ferm (1978) allows rapid determination of sulfate by employing an automatic pipetting system. Aqueous sulfate extract is treated with a solution containing an amount of barium in excess of the anticipated sulfate and $BaSO_4$ is precipitated. Then, a solution of thorin indicator is added which combines with the remaining barium to form a colored-complex. The absorbance of the solution is measured at 520 nm and compared to a standard curve obtained from sulfate standards. The absorbance of the solution is inversely proportional to the sulfate concentration. This procedure has been evaluated by Appel et al. (1977) who reported an effective working range of 3 to 13 μg SO_4/ml (0.8 to 3.8 μg SO_4/m^3 for a typical Hi Vol sample), an accuracy of 1.04 (mean observed/theoretical), and a precision of 5 to 9 percent (coefficient of variation). No significant source of interference is reported but the samples must have corrections for background turbidity and color. The Brosset modification employs an automatic pipet which is relatively expensive.

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3.3.4.1.1.4 Ion exchange chromatography. The principle of the ion exchange chromatographic technique is described under Section 3.2.2.3.6. Stevens et al. (1978) described the use of this technique for analysis of sulfate as well as other ions. Appel et al. (1979a) evaluated a procedure for sulfate analysis using a system manufactured by Dionex Corp. (1975). This procedure showed a working range of 7 to 130 μg SO_4/ml, an accuracy of 1.08 (mean observed/theoretical), and a precision of 6.2 percent (coefficient of variation). A small interference from nitrate ion was also reported. Apparatus for this procedure is relatively expensive and requires a skilled operator. Nevertheless, the procedure is considered to be reliable, specific, and other ionic species can be determined simultaneously.

3.3.4.1.2 Total aerosol sulfur. It is generally found that nearly 100 percent of aerosol sulfur mass is present in the form of sulfate (Forrest and Newman, 1973a). This was experimentally demonstrated by Stevens et al. (1978), who also showed that most of the data on airborne sulfur concentrations can be accurately described as total sulfur calculated as sulfate or total soluble sulfate. X-ray fluorescence is the primary and most practical technique for measuring total aerosol sulfur collected on filters. This technique is applicable to the analysis of numerous elements including sulfur, is nondistructive and can be automated to facilitate the analysis of large numbers of ambient aerosol samples. A particulate sample, collected on an appropriate filter, usually Teflon®, is irradiated with photons (x-rays, gamma rays, etc.), protons, or other charged particles, and the intensity of x-ray fluorescence induced is measured as a function of wavelength or energy to determine the amounts of the constituent elements present. Qualitative and quantitative analysis can be obtained when the system is properly calibrated. This calibration step is difficult, since few standards of known elemental composition are available in disks of known thickness in an appropriate matrix (Adams and Van Grieken, 1975) However, recent work by Dzubay et al. (1977) has shown that calibration standards can be prepared to an accuracy of ± 5 percent.

The most extensive set of aerosol sulfur data were reported by Stevens et al. (1978) and Loo et al. (1978) using a energy nondispersive X-ray fluorescence spectrometer designed by Goulding and Jaklevic (1973). Stevens et al. (1977) reported sulfur and 18 other elements from dichotomous samplers operated in New York City, New York; Philadelphia, Pennsylvania; Charleston, West Virginia; St. Louis, Missouri; Portland, Oregon; and Glendora, California. Loo et al. (1978) reported sulfur concentrations determined from samples collected over a 2-year period from a network of 10 automated dichotomous samplers operated in St. Louis, Missouri, during the Regional Air Pollution Study (RAPS). They reported a detection limit of 0.034 μg/cm^2 of filter, which corresponds to a concentration value of <0.1 μg/m^3 sulfur for a 2-hour sample collected at 50 liters/minute on a 37-mm filter and is adequately sensitive for a 1-hour time discrimination at ambient sulfur levels.

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The advantages of proton-induced XRF--lower bremsstrahlung background and focusing properties of the exitation beam may lead to its use when short-time resolution of ambient sulfur levels is desired (Johansson et al., 1975). However, substantially more energy must be put into a sample with charged particles than with photons to produce an X-ray, and in some cases, vaporization or decomposition of the sample may occur (Shaw and Willis, 1978). A related approach to nondestructive aerosol sulfur analysis based on cyclotron in-beam gamma-ray spectroscopy has been reported by Macias (1977). Gamma rays induced by proton or α-irradiation are detected by a Li drifted, Ge detector and used to determine S and other light elements such as Mg and C in aerosol samples. This technique is less sensitive for S than X-ray emission methods. It is clear that induced x-ray fluorescence methods will continue to be important tools in determining total sulfur in large numbers of ambient aerosol samples.

Other techniques have been applied to the determination of total sulfur in aerosol particles including electron spectroscopy for chemical analysis (ESCA) (Novakov, 1973; and Novakov et al., 1974), various applications of flame photometric detectors (FPD) (Crider et al, 1969; Kittleson et al., 1977; Huntzicker et al., 1976, 1977; Tanner et al., 1978, 1980), and an isotope tracer technique utilizing ^{110}Ag tracer (Forrest and Newman, 1977). ESCA is sensitive to surface composition of samples, which is an advantage for surface-oriented studies but not for ambient aerosol samples whose elemental composition is likely to be heterogeneous. A comparison of ESCA to wet chemical sulfate measurements by Appel et al. (1976) showed agreement only within a factor of two. Direct flame photometry has potential as a sensitive total aerosol sulfur analyzer, but its application is complicated because SO_2 must be removed and the FID response varies with the chemical form of the aerosol sulfate. Recent work by Huntzicker et al. (1978) and Tanner et al. (1980) has shown that direct flame photometry can not only provide a sensitive total aerosol analysis but when combined with thermal volatilization can provide semi-continuous measures of sulfuric acid (H_2SO_4), ammonium sulfates and metal sulfates.

3.3.4.1.3 Sulfuric Acid Determination. Most of the efforts to determine the species composition of sulfate in airborne particles have concentrated on development of a specific analytical method for H_2SO_4 in air. Despite the substantial efforts of several groups, the existence of free aerosol H_2SO_4 in the ambient atmosphere has been unequivocally established in only a few cases. Interference problems and difficulties in sample preservation have contributed markedly to the lack of valid H_2SO_4 measurements. The procedures discussed below have been applied primarily by research analysts, are vulnerable to error both in sampling and analysis, and are not generally applicable to routine monitoring.

Procedures for determining H_2SO_4 and other sulfate species include thermal volatilization and solvent extraction techniques, gas phase ammonia (NH_3) titration, infrared and visible spectrometry, flame photometry and electron microscopy. The determination of H_2SO_4 by its selective thermal volatilization from filters has been reported by several workers (Scaringelli

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and Rehme, 1969; Dubois et al., 1969a; Maddalone et al., 1975; Thomas et al, 1976; Leahy et al., 1975; Tanner and Cordova, 1978). This technique generally suffers from poor H_2SO_4 recoveries, poor reproducibility, and interferences from ammonium sulfate salts. The most successful approach to thermal volatilization of H_2SO_4 in ambient aerosol samples was reported by Mudgett et al. (1974). Aerosol samples are collected on Fluoropore® filters, the H_2SO_4 subsequently volatilized by passage of heated (~150°C), dry N_2 in the reverse direction through the filter and released H_2SO_4 determined with a flame photometric detector. Lamothe and Stevens (1976) reported that laboratory aerosol samples of as little as 0.25 μg H_2SO_4 may be determined with reasonable precision. However, serious difficulties were encountered in removing H_2SO_4 quantitatively in the presence of ammonium bisulfate (NH_4HSO_4). They observed that H_2SO_4 is totally removed at 180°C, but NH_4HSO_4 is also partially volatilized; at 140°C NH_4HSO_4 is not volatilized but H_2SO_4 is incompletely volatilized.

A solvent extraction procedure to selectively remove collected H_2SO_4 aerosol in the presence of other aerosol sulfates was first reported by Barton and McAdie (1971). They concluded that aerosol collection on Nuclepore® filters followed by extraction with 2-propanol for subsequent analysis by the chloranilate procedure was selective for airborne H_2SO_4. Subsequent work by Barton and McAdie (1973) reported reduction of interference by buffer control of the 2-propanol extract and also reported development of an automated instrument for the extraction procedure. Leahy et al. (1975) reported, however, that 2-propanol will also extract NH_4HSO_4 quantitatively and partially extract other bisulfates and that it should not be considered as a selective extractant for H_2SO_4. They demonstrated that benzaldehyde is a selective extractant for H_2SO_4 in the presence of bisulfates and sulfates. Subsequent radiochemical experiments (Tanner et al., 1977) with $H_2{}^{35}SO_4$ have established that H_2SO_4 may be reproducibly removed from a variety of filter media (Mitex®, Fluoropore®, H_3PO_4-treated quartz) with recoveries varying from 75 percent for 10 μg H_2SO_4 samples to 95 percent for 100 μg samples. The selectivity of the benzaldehyde extraction technique has been confirmed in a study by Barrett et al. (1977) employing laboratory aerosol H_2SO_4 samples as low as 5 μg in the presence of bisulfate and sulfate.

As discussed briefly in an earlier section, systems for the measurement of ambient levels of H_2SO_4 and other sulfate aerosols using flame photometry have been recently developed by Huntzicker et al. (1978) and Tanner et al. (1980). A heated denuder for SO_2 removal allows the direct measurement of total sulfate aerosol and selective thermal volatilization allows the descrimination of semi-continuous measurements of H_2SO_4 ammonium sulfates and metal sulfates. Conversion of the H_2SO_4 or the aerosol sulfates to ammonium sulfate [$(NH_4)_2SO_4$] by addition of NH_3 elimates the problem of FPD response variations with the chemical form of the aerosol sulfate.

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Since atmospheric sulfate can be associated with various cations, the compounds of sulfate can sometimes be inferred by measuring the cation. If the ions in a series of samples are measured and the ammonium (NH_4^+) content is highly correlated with the sulfate content, then it can be inferred that various NH_4^+ salts of H_2SO_4 are probably present. Brosset and Ferm (1978) and Stevens et al. (1978) describe a Gran titration procedure for hydrogen ion (H^+) and a procedure using ion selective electrode for NH_4^+ in aqueous extracts of aerosols collected on Teflon® filters. Stevens et al. (1978) applied such techniques to aerosols collected at Research Triangle Park, North Carolina during the summer of 1977 and 1978 and found a stoichiometric balance between sulfate ion (SO_4^{++}) and the sum of H^+ and NH_4^+ ion concentrations. The acidity was found to range from none [$(NH_4)_2SO_4$] to that of NH_4HSO_4.

Dzubay (1979) has developed and used a sensitive radio-labeling technique for measurements of acid sulfate aerosols. Several semiquantitative methods for estimating sulfate species have been investigated. These include gas phase ammonia titration techniques (Dzubay et al., 1974), methods based on infrared spectroscopy (Blanco et al., 1968, 1972; Cunningham et al., 1974; Cunningham and Johnson, 1976), and microscopy techniques (Heard and Wiffen, 1969; Lodge et al., 1960; Mamane and de Pena, 1978).

3.3.4.1.4 Filter sampling problems related to sulfate analysis. The measurement of aerosol sulfate species in particulate matter requires that the sulfate-containing particles from the air be quantitatively collected onto a filter surface which does not lead to chemical or physical transformations and which does not lead to spurious sulfate particle formation from SO_2 present in the gas stream. The particles must then be transferred to the analysis medium under the same constraints. Sampling for airborne sulfate is especially difficult since acidic sulfate species are reactive toward many common filter materials (e.g., "neutral" glass fiber filters and many plastic filters - Nuclepore®, Acropore®, Millipore®), the result of which is neutralization of the acid sulfate and alteration of the composition from that extant in ambient air. Many of the historical data on sulfate species are questionable due to insufficient consideration of the above sampling difficulties.

Several filter materials made of Teflon®, have been found to be inert and suitable for non-reactive collection of aerosols including acid sulfates. The most widely used are backed Teflon® membranes, Flouropore®, and Mitex®. A modified quartz filter material has been developed (Tanner et al., 1977) from which impurities are removed by preheating to 750°C, and reactive basic sites are removed by treatment with hot, concentrated phosphoric acid. After rinsing and drying, the quartz filters may be used for high volume, high efficiency particle collection without interfering with acid determinations of the collected particles at the fractional microequivalent level.

Two additional problems have been identified in filter sampling for airborne sulfate analysis. Sulfur dioxide may be converted to sulfate by adsorption on and catalytic oxidation by the filter material (Lee and Wagman, 1966) and/or by previously collected particulate matter (Coffer et al., 1974). In addition to the original discovery of artifact sulfate formation,

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more recent studies (Forrest and Newman, 1973a) seem to indicate that active catalytic sites on the filter material are the likely culprits. Experiments by Tanner et al. (1978) with high and low level SO_2-spiked ambient air passed through preloaded and clean H_3PO_4-treated quartz filters at high and low linear flow velocities failed to find any evidence of artifact sulfate formation for this filter material. This work was confirmed by the work of Pierson and co-workers (1976) from whose data it is clear that the low sodium content of the Pallflex GAO quartz is the probable reason for the negligibly low artifact sulfate formation.

A second problem results from potential neutralization of acidic sulfate particles by NH_3 in the gas stream traversing the filter. Neutralization by NH_3 and oxidation of SO_2 may both be reduced by "diffusion-denuding" the stream of these gases (without removing significant particles), but this is a cumbersome process, especially for high volume sampling.

The most effective method for reducing particle formation and transformation reactions on the filter is by collecting the minimum airborne particle sample that is compatible with available analytical methods. Minimum-quantity sampling also reduces collision-induced interaction of particles on the filter surface and thus real-life chemical inhomogenities in ambient particles are more likely to be unaffected by the sampling process. The only way to totally eliminate confounding interparticle interactions on filters is to determine the sulfate in situ without filter collection.

3.3.4.2 Ammonium and Gaseous Ammonia Determination--An important supplementary measurement aiding speciation of sulfate in airborne particles is the measurement of ammonium ion (NH_4^+) and ammonia (NH_3). Ammonium ion is found predominantly in the optical-scattering size range or below and is presumed to be secondary in origin, being formed in the neutralization of acidic sulfate particles. The high correlation of NH_4^+ content with soluble sulfate in both urban (Tanner et al., 1977a), and rural (Tanner et al., 1977) aerosol samples and the identification by x-ray diffraction of $(NH_4)_2SO_4$ in dried aqueous extracts of airborne particles would tend to confirm the above hypothesis (Brosset et al., 1975).

Ammonium ion in particulate matter is nearly universally determined by collection on filters, extraction into an appropriate leach solution, and determination by one of the two methods described below. The first is a concentration measurement by an ion-selective electrode sensitive to either NH_4^+ (Beckman electrode) or NH_3 (Orion or Markson electrodes). The limit of detection is determined by the equilibration time of the electrode, a representative value being 5 to 7 minutes for 20 ppb NH_4^+ concentration in water (Eagan and DuBois, 1974; Gilbert and Clay, 1973). This is marginally sensitive for high-volume samples of rural ambient air where NH_4^+ may be as low as 0.3 $\mu g/m^3$. A later development, the air gap electrode, (Ruzicka and Hansen, 1974; and Bisgaard and Reyman, 1974) eliminates the problems of electrode contamination by sensing of the NH_3-water equilibrium across an air gap between the analyte solution and the electrode surface. This system has not been applied to a significant extent by other laboratories.

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The second commonly used method for NH_4^+ traces in aqueous solution is the indophenol colorimetric method based on the color-producing reaction of phenol and hypochlorite in the presence of NH_3. Modifications most analytically useful for determination of NH_4^+ in aqueous leaches were reported by Bolleter et al. (1961) and by Tetlow and Wilson (1964). An automated procedure has been proposed by Keay and Menage (1970). The method is capable of a lower detection limit of 0.05 μg/ml (as nitrogen), requires only a few minutes of analysis time, and has a minimum sample volume of 2 ml.

Methods for determination of free atmospheric NH_3 can be divided into direct methods and methods in which NH_3 is first immobilized on acid-treated filters, leached, and determined as NH_4^+ by one of the methods described above. Ammonia has been analyzed directly by quantitative conversion to nitric oxide (NO) over a hot catalyst and determination by chemiluminescence of NO (Hodgeson et al., 1971. and Baumgardner et al., 1979). This method is marginally sensitive enough for ambient levels of NH_3 (limit of detection = ~ 1 $\mu g/m^3$) and must be carefully zeroed in the NH_3 scrubber mode to eliminate interference from atmospheric oxides of nitrogen (NO_x). Filter pack methods using either $KHSO_4$ (Eggleton and Atkins, 1972) or oxalic acid impregnants have been used to collect ambient levels of NH_3, but they are fraught with blank and contamination problems and may not collect ambient levels of 0.5-5 ppb NH_3 with reproducible efficiency under commonly observed temperature and relative humidity conditions.

It has also been proposed to determine gaseous NH_3 at or below ambient levels by gas phase reaction with HCl vapor with the resultant ammonium chloride (NH_4Cl) aerosol particles measured by a condensation nuclei counter (CNC) (General Electric Ordinance Systems, 1972). Unfortunately, there are several difficulties which severely limit the usefulness of this technique. The concentration of HCl and the relative humidity must be carefully controlled to attain proportionality between number of particles and NH_3 concentration. In addition, it is necessary to provide an ionization source (a corona discharge or a UV light source) in the air stream just prior to HCl vapor addition in order to even approximate precise, proportional CNC response. However, this method has potential for extremely high sensitivity and real time operation. McClenny and Bennett (1980) have developed a semi-real time detection technique for ambient NH_3 based on integrative collection on Teflon® beads followed by thermal desorption and detection by either chemiluminescence or photoacoustics. Ferm (1979) and Braman and Shelley (1980) have reported collection of NH_3 on diffusion tubes. Ferm used oxyalic acid as a coating which is rinsed from the tube at the end of a 24 hour run and analyzed for NH_4^+ by ion selective electrode techniques. Braman and Shelley used a tungsten oxide coating for 20 min samples and release the NH_3 into a chemiluminescence analyzer by thermal desorption. Hoell, et al. (1980) have determined vertical concentration profiles by interpretation of infrared solar spectra obtained with a heterodyne radiometer. Abbos and Tanner (1980) have reported work on the continuous determination of gaseous NH_3 using flourescence devolatilization. These recent advances in the development on new techniques for measuring NH_3 will be very helpful in determining the role of NH_3 in the conversion of H_2SO_4 to less harmful materials.

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3.3.4.3 Analysis of Nitrates--The analyses of nitrate have been performed routinely for many years and a large number of chemical methods have been reported. In typical monitoring for nitrate in air, a portion of a particulate filter is subjected to aqueous extraction and the water-soluble nitrate is analyzed by one of the methods discussed below.

3.3.4.3.1 Measurement techniques for nitrates. The oldest procedures for analyzing nitrate used brucine (Intersociety Committee of Methods of Ambient Air Sampling and Analysis, 1977) or phenol disulfonic acid (Intersociety Committee of Methods of Ambient Air Sampling and Analysis, 1977a). Numerous other analyses methods for nitrates have been reported, including the nitration of chromotrophic acid (West and Ramachandron, 1966) and courmarin analogs (Laby and Morton, 1966; Skujins, 1964) the quenching of the flourescence after nitration of flourescein (Axelrod et al. 1970), reduction with Devarda alloy to ammonia (Kieselbach, 1944; Richardson, 1938), and the use of ion-selective electrodes (DiMartini, 1970; Driscoll et al., 1972; Gordiewskii et al., 1972). Microscopic techniques also allow analysis of individual nitrate particles (Bigg et al., 1974).

One of the most extensively used techniques to analyze nitrates in atmospheric particulate extracts involves reduction of the nitrate to nitrite by zinc (Chow and Johnstone, 1962), cadmium (Morris and Riley, 1963; Strickland and Parsons, 1972; Wood et al., 1967), or hydrazine (Mullin and Riley, 1955). Measurement of the nitrite produced is accomplished by a sensitive diazotization-coupling reaction (Saltzman, 1954). Automated versions of this technique provide much better results because critical reduction parameters such as temperature, surface contact area, and reaction time can be precisely controlled (Technicon, 1973). Another technique which has been extensively used to analyze nitrate in atmospheric particulate matter extracts involves the nitration of xylenols and separation of the nitro-derivative by extraction or distillation. A comparison of a 2,4-xylenol procedure (Intersociety Committee of Methods of Ambient Air Sampling and Analysis, 1977b) with the automated copper-cadium reduction and diazotization method in samples collected near high density vehicular traffic, demonstrated a negative interference in the former up to a factor of 3 (Appel et al. 1977a).

Small et al. (1975) report an application of ion exchange chromatography to the measurement of a wide variety of cations and anions including the nitrate and nitrite ion. The novel feature of this method is the use of a second ion exchange "stripper" column (after a conventional separating column) which effectively eliminates or neutralizes the eluting ions. Since chromatographically separated species of interest leaves the stripper column in a background of deionized water, concentration determinations may be made by a simple and sensitive conductometric technique. Mulik et al. (1976) report the application of this technique to measurement of watersoluble nitrate on Hi Vol filters. The separator column, containing a strong basic resin, separates anions in a background of carbonate eluant. The stripper column, containing a strong acid resin, converts the sample ion and the carbonate eluant to nitric and carbonic acid, respectively. Since carbonic acid has low conductivity, the nitrate ion alone is effectively measured in a conductivity detector. Under the experimental conditions,

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sensitivity of 0.1 μg/ml was reported. The relative standard deviation was 1 percent (95 percent confidence level) for ten replicate injections at the 5 μg/ml level. At this concentration level, no interferences were found from fluoride, chloride, nitrite, sulfite, sulfate, silicate, or carbonate. Positive interferences were found for bromide and phosphate but the authors suggest techniques for eliminating these.

In other work, Glover and Hoffsommer (1974) and Ross et al. (1975) report a technique for assay of aqueous nitrate and nitrite extractions by conversion to nitrobenzene. Both techniques involve the nitration of benzene in the presence of H_2SO_4 to form nitrobenzene, a relatively stable compound, followed by gas chromatographic analysis. Careful calibration is required in both procedures, since a significant fraction of the nitrobenzene formed may be lost to the acid layer. Ross et al. recommend a calibration procedure whereby a standard is subject to the same procedures as the unknown, while Glover and Hoffsommer use internal calibration with added nitrotoluene. The lower detection limits reported by Ross et al. (1975) are in the range of 10^{-12}g nitrobenzene in a 1 μl sample. Conversion efficiences for KNO_3, KNO_2 and HNO_3 were reported as 90.3 ± 7.9, 100.4 ± 4.2 and 99.9 ± 5.2 percent, respectivley. Glover and Hoffsommer report similar recovery rates for KNO_3 and KNO_2.

3.3.4.3.2 Filter sampling problems related to nitrate analysis. Serious difficulties associated with the routine analysis of nitrates in particulate matter collected using glass fiber filters have been reported. In a study of nitrate in auto exhaust, Pierson et al. (1975) report that glass fiber filters collected about twice the amount of nitrate when compared to quartz fiber filters. Nitrate also was found on glass fiber filters which were inserted downstream of either quartz or glass fiber primary filters, providing additional evidence of artifact formation from gaseous constituents. Spicer (1976) reported that glass fiber filters completely removed gaseous nitric acid (HNO_3) when in low concentration in gas streams, while Teflon® and quartz filters showed no corresponding effect. O'Brien et al. (1974) describe very unusual results of particle size distribution determinations of photochemical aerosol collected in the Los Angeles basin using a cascade impactor where all particle size fractions were collected on glass fiber filters. The authors speculated that conversion of gaseous nitrate precursors on the filter masked the true nitrate size distribution. Okita et al. (1976) report that untreated glass fiber filters collect nitric acid vapor with a highly variable collection efficiency (0-56 percent), suggesting erratic nitrate artifact formation in urban atmospheres containing HNO_3.

In an intensive laboratory investigation of interferences in atmospheric particulate nitrate sampling, Spicer et al. (1978) concluded that all five types of glass filters investigated exhibited serious artifact formation due to collection of gaseous HNO_3 and, to a small extent, NO_2 as nitrate. Cellulose acetate and nylon filters were also reported to exhibit severe interferences from HNO_3. Negligible interferences were reported for polycarbonate and Teflon® filters. Interferences from NO_2 on quartz fiber filters varied with the filter type, with ADL Microquartz showing the least effect. Artifact nitrate formed on the Gelman AE

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filter was calculated to be less than 2 $\mu g/m^3$ during a standard 24-hour Hi Vol measurement. This estimate was derived from drawing air samples of about 1 m^3 containing 4,512 $\mu g/m^3$ (2.4 ppm) NO_2 through the filters. The relative humidity was 30 ± 10 percent.

Spicer and Schumacher (1977) also reported the results of a comparison of nitrate concentrations in samples collected on various filter types in Upland, California during October and November, 1976. During the experiment, meteorological conditions varied from warm, hazy weather to hot, dry, very clean desert wind conditions. Nitrate analyses were performed by ion exchange chromatography. All filter types used had comparable particle collection efficiencies according to the manufacturer's specifications. The ratio of nitrate collected on glass fiber filters to that collected simultaneously with identical Hi Vol samplers on a quartz filters ranged from 2.8 to 49.

Harker et al. (1977) have reported laboratory observations of loss of particulate nitrate from collecting filters through chemical reaction with H_2SO_4 aerosol, formed from the photochemical oxidation of SO_2. Most recently, Appel and co-workers (1979, 1980) have conducted several studies bearing on both positive artifact formation and loss of nitrate from a variety of filter media. They concluded that gaseous HNO_3 is the principal source of artifact nitrate formation, NO_2 collection only became substantial at high ozone levels. Ambient particulate nitrate values (at San José and Los Alamitos, California) differed by up to a factor of 2.4 depending upon filter medium and sampling rate, in contrast to the much larger sampling errors reported by Spicer and Schumacher, 1977. Flouropore (Teflon®) filters in low volume samplers were subject to small error although, under laboratory conditions, passage of NH_3- and HNO_3-free air through the filter could result in the loss of up to 50 percent of the particulate nitrate. They also reported that at low HNO_3 levels, nitrate on glass filters, indicated (within 3 percent) total nitrate, i.e., particulate matter plus HNO_3 rather than particulate nitrate alone. They concluded that the degree of error associated with glass fiber filter media could be expected to vary with location, time of year and day, paralleling changes in HNO_3 levels.

These results point to the conclusion that most of the existing data on urban ambient nitrate concentrations must be considered to be of doubtful validity. It is, furthermore, doubtful that any of these data can be corrected even if mechanisms for artifact formation are clarified in the future since HNO_3, which presently appears to play a significant role in positive artifact formation, is not routinely monitored. It is, however, possible that data from certain monitoring sites may be validated in special cases where it can be shown that the species responsible for the artifact processes were all sufficiently low during the monitoring period of interest.

3.3.4.4 Analysis of Trace Elements--Although over the years quite a variety of techniques have been applied to the analysis for elements, presently the most commonly used techniques utilize spectroscopic detection of some type. By definition, these techniques respond only to the presence of the elements in the particulate matter and do not provide information

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concerning the chemical compounds present. By and large techniques for trace elements have not provided information concerning the oxidation state of the elements, although Braman et al. (1977) have reported attempts at such for arsenic.

3.3.4.4.1 Atomic absorption spectrometry. Atomic absorption spectrometry (Morrison, 1965) has been widely employed for the quantitative analysis of a large number of elements in particles. In principle, a beam of light which is characteristic of an electronic transition for the element of interest is made to traverse a region of space with a constant intensity and impinge on a detector. The element of interest is atomized in a portion of the beam of light. The amount of light absorbed by the atoms of interest in the sample can be related to the amount of that element present. Any element can be determined if a lamp is available to produce the characteristic light.

A variety of techniques can be used for atomizing and introducing the element into the appropriate region of space. Typically, a flame or a heated rod atomizer is used. Flame techniques are most commonly used for atmospheric particulate matter. An extract of the particulate matter is prepared and aspirated into the flame which decomposes any substances there and produces a sufficiently large population of groundstate atoms for absorption. An example of this kind of application is the EPA reference method for lead (U.S. Environmental Protection Agency, 1979d). Alternatively if the concentration of the element of interest is too low for flame application or if an extremely limited amount of sample is available, an electrically heated atomizer can be used to volatilize atoms into the light beam. In this application, solutions can be utilized or a small portion of soiled filter without any other preparation may be examined directly. In the latter case the filter substrate must be oxidizable and there may be question concerning the representativeness of the sample.

Atomic absorption spectrometry is generally highly specific for the analysis of those elements for which this technique is applicable. The instrumentation can be inexpensive relative to other instrumental techniques for the analysis of trace elements and is generally available as standard equipment in most analytical laboratories. However, it can do an analysis of only one element at a time. Additional elements must be determined serially. This can be a severe disadvantage when a number of elements need to be determined on the same sample both from the standpoint of the resources required to obtain the information and the limitations of the volume of extract available to perform the analysis. Useful though it is, significant interference problems can be important in atomic absorption measurements. Spectral interferences from other elements absorbing at the same wavelength can be a problem but can usually be avoided by judicious choice of wavelengths. However, interference effects on the element of interest caused by other substances present in the material introduced into the spectrometer, refered to as matrix effects, can be much more difficult to resolve. These effects can differ significantly, ranging from the effect of viscosity on the amount of material which can be atomized, to effects due to the presence of refractory compounds containing the element of interest, which may not be completely decomposed at the flame or

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atomizer temperature. Matrix effects can adversely affect the concentration of atoms in the beam and result in significant errors in the measurement of an element. The literature is replete with discussions of these difficulties and provides both general and specific techniques for overcoming them. One of the more convenient ways to keep abreast of developments in this area is through the use of a continually updated bibliography with convenient indexing such as that provided by "Atomic Spectroscopy." (Slavin, S., ed.) Bibliographies for this publication are routinely updated and appear each January and July.

3.3.4.4.2 Optical emission spectrometry. Optical Emission Spectrometry is a technique which can determine the amounts of numerous elements simultaneously. The advantage of this technique in situations of limited sample availability or limited time and resources with which to do a measurement are obvious. Conventional arc or spark excited optical emission spectrometry has been used extensively on atmospheric particulate (Scott et al., 1976). In most applications of this technique an extract of the particulate matter is excited by a spark or arc discharge. This decomposes any substances present and excites the atoms to other than their ground electronic states. In the de-excitation to the ground state light at a characteristic wavelength is emitted. The intensity of the light emitted is an indication of the quantity of the element present. Most conventional optical emission spectrometers are capable of simultaneously analyzing 20 to 30 elements.

The conventional arc or spark excited optical emission spectrometers were never very popular partly because of detection limits that were higher than desirable. The development of optical emission spectrometers based on plasma excitation (Boumans and DeBoer, 1975) has resulted in significant improvements. Although there are several kinds of plasma excitation, the commercial availability of optical emission spectrometers with inductively coupled argon plasma excitation has proven most advantageous. In this technique an extract of particle matter is aspirated into an inductively coupled argon plasma whose very high temperature decomposes the materials and excites the atoms. The light emitted when these excited species fall back to the ground state is collected and monitored just as before. However, this approach has numerous advantages not available with the older excitation techniques. The technique is capable of using the same acid extract used in atomic absorption; is more free of matrix affects than atomic absorption; requires, for a single multielement determination on a given sample, about the same amount of time and solution as a single element determination on atomic absorption; has usually a much longer linear range than atomic absorption; and has detection limits equal to or smaller than flame atomic absorption (Fassel, 1978). If an acid extract of atmospheric particulate matter is to be analyzed, inductively coupled argon plasma optical emission spectrometry is usually the technique of current choice.

3.3.4.4.3 Spark source mass spectrometry. Spark source mass spectrometers are relatively uncommon, very expensive, high resolution magnetic sectoring mass spectrometors which usually utilize photographic emulsion detection and very high resolution densitometry for quantitative

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analysis. The material to be analyzed is incorporated into two small, usually graphite, electrodes which are placed in the spectrometer with a well controlled gap between them. The passage of a spark across the electrodes vaporizes the electrodes and ionizes the material in it. The ions are subsequently led into the mass analyzer portion of the spectrometer (Ahern, 1972).

The electrodes used in the spark source mass spectrometer can be fabricated from either particulate matter itself that has been separated from a filter or an extract of the particulate matter. The technique is not suitable for the generation of large data bases because only a few samples can be analyzed on any given day. The time required to prepare the instrument and to obtain a set of spectra necessary for quantitation is substantial. Double ionization of elements is common and so are ionized oligomers of carbon. Therefore high resolution detection and complex interpretation are the rule rather than the exception. The advantage of Spark Source mass spectrometry is that it can simultaneously estimate the quantity of all nonvolatile elements in the periodic table and do so with roughly equal sensitivity.

3.3.4.4.4 Neutron activation analysis. Neutron activation analysis (Morrison, 1965) implies a variety of distinct procedures all of which produce unstable atomic nuclei which then emit high energy radiation or particles. The intensity of a specific kind and energy emission is monitored as an indicator of the element and its quantity.

The technique most commonly applied to atmospheric particulate has been instrumental thermal neutron activation analysis. With this approach, a nuclear reactor is used to produce neutrons which bombard the samples and produce the unstable nuclei. The emitted gamma radiation is detected by a GeLi detector whose output is processed to produce the gamma ray spectrum of the irradiated particulate matter. The method has small detection limits, can simultaneously determine up to about 25 elements in a given sample, and particulate matter can be analyzed directly as received on a very small portion of the filter surface. The technique has been successfully applied with the glass fiber used in hi-vol samplers (Lambert et al., 1979). The time required for analysis is small and a large number of samples can be analyzed during a given period of time. However, data are usually not available for 2 to 3 weeks after the sample is irradiated because there is a significant delay period between the irradiation and the collection of gamma ray spectrum for certain long lived isotopes. Some important elements (e.g., S and Pb) are not practically measured using this method. These limitations and the need for very complex, highly specialized and expensive equipment are the main disadvantages of the neutron activation technique.

3.3.4.4.5 X-ray fluorescence spectrometry. X-ray fluorescence spectrometry is a multielement, nondestructive technique which can simultaneously determine numerous trace elements in particulate matter directly on the filter media. It involves the excitation of tightly bound electrons in the atoms by an X-ray generator and observation of the X-ray emissions which occur as the deexcitation of the excited electrons proceed (Dzubay, 1977).

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X-ray Flourescence spectrometers utilize either energy dispersive or wavelength dispersive detection. Spectrometers utilizing energy dispersive detection collect simultaneously, all emitted quanta with a SiLi detector and through subsequent processing, can analyze about 30 elements. Spectrometers utilizing wavelength dispersive detection monitor use carefully preselected wavelengths that are characteristic of the deexcitation emissions of the elements of interest. With wavelength dispersive detection about 20 elements can be determined simultaneously on a single sample and interelement effects are minimal due to the high resolution capability of the instrumentation. With energy dispersive detection all wavelengths are simultaneously collected and interelement corrections must be handled in the data reduction process.

Good detection limits and the ability to handle a sizable number of samples nondestructively with minimal sample preparation are clear advantages of the X-ray flourescence technique. In order to analyze the sample directly however, it must be of uniform surface texture and it is best if the particulate layer is very thin. This obviously places some limitations on the kind of sample which can be analyzed without preparation. Even in the most ideal samples, concern with special corrections must exist (Gould et. al. 1976). The techniques has been applied extensively to analysis of filters from dichotomous samplers (Dzubay and Stevens, 1975).

3.3.4.4.6 Electrochemical Methods. Electrochemical methods have been used to a limited extent to determine a small number of elements in airborne particulates. These methods include potentiometry with ion selective electrodes, polarography, and anodic stripping voltammetry (Morrison, 1965). Electrochemical techniques have few advantages for airborne particulate analysis aside from their low initial capital equipment cost compared to other techniques. While useable (Ryan and Siemer, 1976) there appears to be fairly little activity in the application of such techniques at present.

3.3.4.4.7 Chemical methods--Many classical wet chemical procedures were employed in the past for trace element analysis of airborne particulate. In general, a colorforming reagent was involved. The amount of the given element present is determined by the extent of color development. Perhaps the best known of these procedures is based on the use of dithiocarbazone (dithizone) as the colorimetric reagent for lead (Snell, 1978). Wet chemical procedures are labor intensive and slow compared with spectral techniques. Sample preparation and interferences are also usually a problem. These procedures are not extensively used at present.

3.3.4.5 Analysis of Organics--Numerous papers have appeared dealing with the characterization of organic compounds in airborne particles. The following discussion was taken primarily from the monograph edited by H. Malissa (1978) and describes the principle methods used in this field and some typical examples mentioned in the literature.

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Organic compounds significantly contribute to the total particulate matter in urban aerosols. Sum concentrations up to 43 percent have been reported (Hidy, 1975). Characterization of organics in urban aerosols generally involves trace separation and identification by gas and liquid chromotagraphy, with detection methods having sensitivity in the nanogram range. The sample amount needed to allow analysis of substances in parts per million concentrations is in the milligram range (Cautreels and Van Cauwenberghe, 1976; Ketseridis, et al., 1976). Usually, high-volume samplers with glass-fiber filters are used to provide the needed sample amount.

One of the earlier simple and extensively used methods for estimating the organic content of particulate matter was called "benzene soluble organics". To obtain this estimate, filters were simply refluxed with benzene for several hours. The benzene was vaporized and the weight of the residue was measured and reported. Benzene soluble organic data were recorded in the National Aerometric Data Bank for several years. But, since these measurements were not readily interpretable, this method has not been used on a national scale by any single laboratory for roughly a decade. Extraction efficiencies of 25 different solvents and 24 binary mixtures were investigated by Grosjean, (1975). Grosjean determined that extraction with benzene or other nonpolar solvents usually leads to serious underestimation of aerosol organics, especially of the polar secondary (photochemical) products like carbonyl compounds, organic nitrates, or carboxylic acids. The use of binary mixtures for extraction or successive extractions using a nonpolar and a polar solvent were strongly recommended. This leads to a higher organic carbon extraction efficiency (in comparison to benzene as solvent) than with both single polar and nonpolar solvents. Ninety-five to one hundred percent of the aerosol organic carbon is extracted and measured with this method.

In the area of compound specific analysis a large amount of work and an earlier concern has been with polycyclic aromatic hydrocarbons (PAH). Numerous measurements have been proposed to analyze quantitatively for many of the polycyclic aromatics. Chromatography (Golden and Sawiki, 1975) was utilized in much of the earlier work and more recently frozen solution fluorimetry (Bacon et al., 1978) and matrix isolation spectroscopy (Wehry et al., 1979) have been explored. High-pressure liquid chromatography (HPLC) is a promising technique for separation of high molecular weight PAH. The development of bonded octadecylsilyl (ODS) columns of micro particle size allowed (Fox and Staley, 1976) the near baseline separation of the carcinogenic benzo[a]pyrene (BaP) and its noncarcinogenic isomer benzo[e]pyrene. A significant increase in sensitivity over other methods was achieved by use of flourescence spectroscopy for on-line detection. Perhaps the most extensive data base has been concerned only with BaP (Swanson et al., 1978) utilizing a thin layer chromatographic technique with fluorescence detection. Gas chromatographic (GC) separation of organic extracts of airborne particles requires the application of preseparation steps, such as thin layer chromatography (Zoccolillo, et al., 1972) or liquid-liquid extraction (Cautreels and Van Cauwenberghe, 1976,

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Ketseridis et al., 1976). Primary extraction is generally carried out by means of single solvents such as benzene, cyclohexane, or others. A typical procedure including solvent extraction for preseparation is described by Ketseridis et al.(1976)

The application of gas chromatography coupled with mass spectrometry for the analysis of benzene-extractable compounds in airborne particles is described in detail by Cautreels and Van Cauwenberghe (1976). This work led to the identification of more than 100 compounds in urban aerosols. The benzene-extractable compounds (5.8 percent of total particles) were separated into neutral, acidic, and basic substances. The acidic fraction was converted to the methylated derivatives for GC analysis. In the neutral fraction, 22 saturated aliphatic hydrocarbons, 36 polynuclear hydrocarbons, and 13 polar oxygenated substances were identified. In the acidic fraction, 19 fatty acids and 19 aromatic carboxylic acids were identified; in the basis fraction, 15 peaks of nitrogen-containing analogues of the PAH were identified.

Interest in the organic content of atmospheric particulate ranges from particulate carbon (Rosen and Novakov, 1978) to any other possible organic substance. A variety of techniques have been brought to bear on this problem (Fox and Jeffries, 1979), however, it is clear that this area of endeavor is in its infancy, is large, exceedingly complex, and will need a great deal of developmental effort.

3.3.5 Particle Morphology Measurements

Visual examination of particles collected on a filter or impaction substrate can provide extremely useful information concerning the sources and transport of airborne particles. A reticle-equipped light microscope can be used to examine particles larger than about 0.5 μm. Use of transmission and scanning electron microscopes can improve the resolution for particles as small as 0.001 μm. The effective ranges of microscopes and their utility are described by McCrone (1973) and shown in Figure A-12 (Appendix). Particle size distributions by number can be generated using statistically valid counting procedures. By applying an average density an estimate of the size distribution by mass can be made.

Microscopic identification and analysis requires a high degree of skill and experience plus extensive quality assurance to provide meaningful information. The selection of sampling substrates, allowable particle loadings, and sample handling are critical factors in utilizing these methods. In addition, particle interactions and structure changes on the collection surface must be minimized if accurate size distributions and characterizations are to be obtained. In a study of ambient particles collected on hi-vol filters, Bradway et al. (1976) examined the ability of multiple microcopists to characterize particles in specific categories. Significant problems were noted in mis-identification and mis-assignment which made it difficult to intercompare results. Multiple microscopists and blind replicates were recommended as standard procedures for optical characterization studies.

3.3.6 Intercomparison of PM Measurements

The intercomparison of particle sampling methods is not straightforward because of the complex nature of particulate matter. As noted earlier in this chapter direct mass measurement methods can differ dramatically in the particle size ranges collected and the sensitivity

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of the sampler to external factors such as wind speed. Indirect mass measurement methods also examine only specific portions of the particle size spectrum and additionally measure selected integral properties of particle rather than mass.

Intercomparison of direct mass measurement methods can be made by examining components of the sampling systems, such as the sampling effectiveness of the inlet or substage for various particle sizes. Because of the difficulty in simulating the character of real suspended particles, however, the final intercomparison test must be performed at selected field locations. The choice of the number and types of locations is important, since the local particle sources can have a substantial impact or the sampler performance, especially if coarse particles dominate the size distribution.

The most recent and comprehensive intercomparison of direct mass measurement particle samplers was reported by Camp et al. (1978). Eleven different types of samplers were compared for mass and other analyses including sulfates, nitrates, and elemental composition. The most salient observation of the study was the difficulty of intercomparison of the samplers because of differences in inlet or substage particle size cutpoints. Since there is no reference sampler, all measurements of the same size fraction were averaged as a comparison measurement. Some samplers were present in duplicate permitting reproducibility measurements. The coefficient of variation for the automated dichotomas samplers was determined to be 11 percent for the coarse fraction and 3 percent for the fine fraction. The same values for a manual dichotomous sampler were 18 percent and 7 percent, respectively. The hi-vol impactor used in the CHAMP network gave values of 15 percent and 5 percent, respectively. The results from this study should be considered "best case" since the sampler operations were monitored continuously by highly skilled individuals. In some cases, the operators were the developers of the sampling method. It could be expected that routine field sampling by less qualified personnel could produce larger variabilities. The reproducibility of certain chemical analyses were reported to be better than the mass measurements, such as elemental sulfur which averaged ±3 percent for all size fractions. Overall the study showed that comparable results could be obtained by different particle samplers if appropriate quality assurance steps were taken and identical size fractions were compared.

Miller and DeKoning (1974) compared the TSP hi-vol with several commercially avialable cascade impactors. Their results indicated that none of the impactors gave comparable results to the hi-vol, but did correlate reasonably well. The agreement among cascade impactors for mass median diameter (MMD) was very poor, often differing by more than a factor of two.

Attempting to intercompare indirect mass measurements or direct mass with indirect mass measurements should only be attempted to determine correlation or to test a physical model relating the measurements. The literature contains many intercomparison studies attempting to relate the TSP hi-vol with surrogate techniques such as: (a) the British Smoke Shade Sampler (Commins and Waller, 1967) (Lee et al., 1972), (b) the integrating nephelometer (Charlson et al., 1968) (Kretzschman, 1975), and (c) the AISI Tape Sampler (Lee et al., 1972) (Ingram and

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Golden, 1973). Comparisons are also available between other direct and indirect mass measurements such as the dichotomous sampler with the AISI tape sampler (Regan et al, 1979). In most cases a simple repression was fitted between measurements rather than attempting to establish a physical basis for the companion for testing with empirical data. The general objective of most of these comparison was an attempt to use the data base from an indirect sampling method to predict the mass concentrations that would have been measured by a direct mass method. Mulholland et al. (1980) compared the estimated mass concentrations calculated from Electrical Aerosol Analyzer (EAA) measurements versus direct gravimetric analyses. It was noted that for spherical particles the errors are in the ± 20 to 30 percent range and for non-spherical particles the errors as high as ± 60 percent. Therefore, great care should be exercised in attempting to predict gravimetric mass concentration from indirect particle measurements. There is currently no indirect technique that has gained general acceptance as a surrogate for direct mass concentration measurements.

3.3.7 Summary - Measurement Techniques for Particulate Matter

Particulate matter suspended in ambient air contains a range of particle sizes and shapes. By separating particles according to aerodynamic size, variations in particle shape and settling velocity can be accounted for. Samplers can be designed to collect specific size fractions or match specific particle deposition patterns through carefully designed inlets and substage fractionators. Mass concentration measurements using gravimetric analysis is the most common measure of particulate matter. High volume samplers, dichotomous samplers, cascade impactors, and cyclone samplers are the most common examples of this type of measurement. Carefully collected size distributions of ambient particle mass have shown that most particle samplers underestimate the concentration of particles in the air because of external factors such as windspeed or because their particle transport systems are not effective for the larger particle sizes.

Mass concentrations can be estimated using methodologies that measure an integral property of particles such as optical reflectance. Empirical relationships between mass concentrations and the integral measurement have been developed and used to predict mass concentration. Without a valid physical model relating the measurements plus empirical data to demonstrate the model, these techniques have a limited ability to estimate mass concentrations. Examples of commonly used samplers include the AISI tape sampler, the integrating nephelometer, and beta attenuation analysis.

Sampling accuracy can be estimated through key sampling components, such as flow rate and inlet sampling effectiveness. These component measurements provide a means of intercomparing methods, even though a reference measurement technique is not available. Recent interest in larger particle sampler cutpoints (e.g., 15 μm) have resulted in wind tunnel test

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procedures for particle samplers which determine sampling effectiveness under controlled conditions. Such measurements have added significantly to the ability to estimate particle sampling accuracy.

Recent evaluations show that the hi-vol sampler collects a smaller particle size range than that stated in Air Quality Criteria for Particulate Matter (U.S. Department of Health Education and Welfare, 1969). The sampling effectiveness of the hi-vol inlet also is wind speed sensitive for larger (>10 μm) particles. Wind speed could be estimated to produce no more than a 10 percent day-to-day variability for the same ambient concentration for typical conditions. The hi-vol is one of the most reproducible particle samplers currently in use, with a typical coefficient of variation of 3-5 percent. A significant problem associated with the glass fiber filter used on the hi-vol is the formation of artifact mass caused by the presence of acid gases in the air. These artifacts can add 6-7 $\mu g/m^3$ to a 24-hour sample.

The dichotomous sampler was designed to collect two discreet ambient particle fractions: the fine (0-2 μm) and coarse (2-15 μm) modes. This sampler uses Teflon® filters to minimize artifact mass formation and is available in versions for manual or automatic field operation. The original inlet used with this sampler is very wind speed dependent, but newer versions are much improved. The dichotomous sampler collects submilligram quantities of particles because of low sampling flowrate and requires microbalance analyses, but is capable of reproducibilities of ± 10 percent or better.

Cyclone samplers with cutpoints at 2.5 μm have been used for years to measure the fine particle fraction. A recent development by Wedding (1980) has coupled the cyclone to a sampler inlet to give a 15 μm cutpoint. Cyclones can be designed to cover a range of sampling flowrates and are available in a variety of physical sizes. A 10mm version is available for personnel dosimeter sampling. Cyclone sampling systems could be expected to have coefficients of variations similar to that of the dichotomous sampler.

The Size Selective Inlet (SSI) for the hi-vol provides a means of comparing total suspended particles (TSP) with particles less than 15 μm. This sampler is identical to the TSP hi-vol except for the inlet and is expected to have the same basic characteristics.

Cascade impactors have been used extensively to obtain mass distribution by particle size. Because care must be exercised to prevent errors, such as those caused by particle bounce between stages, these samplers are normally not operated as routine monitors. A comparison study by Miller and DeKoning (1974) of impactors showed inconsistencies on the mass median diameter and on total mass collections compared with the hi-vol.

Samplers which predict mass concentrations using analytical techniques other than direct weight have been used extensively. One of the earliest was the British Smoke Shade sampler which measures the reflectance of particles collected on a filter and uses empirical

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relationships to predict mass concentration. These relationships have been shown by Baily and Clayton (1980) to be more sensitive to carbon concentrations than mass, and hence, are are very difficult to interpret. Another optical technique, the AISI Tape Sampler, uses transmittance instead of reflectance to predict mass. Regan et. al. (1979) showed that this sampler correlates favorably with gravimetric measurements limited to the smaller particle sizes. Similar investigations comparing other indirect measurement samplers such as the integrating nephelometer (Charlson et al., 1968) and the Electrical Aerosol Analyzer (EAA) (Mulholland, et al., 1980) have also shown difficulties in reliably predicting gravimetric mass measurements.

Optical particle morphology techniques are very useful for identifying the character and sources of collected particles. Bradway et al. (1976), however, noted that these techniques are dependent on the skill of the microscopist and stressed the need for careful quality assurance procedures.

An extensive list of analytical techniques is available to analyze particles collected on a suitable substrate. Many of the analytical techniques, such as those for elemental sulfur, have been demonstrated (Camp et al., 1978) to be more precise than the analyses for gravimetric mass concentration. Methods are available to provide reliable analyses for sulfates, nitrates, organic fractions, and elemental composition (e.g., sulfur, lead, silicon). Not all analyses can be performed on all particle samples because of factors such as incompatible substrates and inadequate sample size. Misinterpretation of analytical results can occur when samples have not been appropriately segregated by particle size and when artifact mass is formed on the substrate rather than collected in a particle form.

Sampling technology is available to meet specific requirements such as providing sharp cutpoints, cutpoints which match particle deposition models, separate collection of fine and coarse particles, automated sample collection capability, collection of at least milligram quantities of particles, minimal interaction of the substrate with the collected particles, ability to produce particle size distribution data, low purchase cost, and simple operating procedures. Not all of these sampling requirements may be needed for a measurement study. Currently, there is no single sampler which meets all requirements, but samplers are available which can meet most typical requirements if the overall accuracy and reproducibility of the method is acceptable to meet the study objectives.

3.4 MEASUREMENT TECHNIQUES FOR ACIDIC DEPOSITION

3.4.1 Introduction

Studies designed to monitor precipitation first appeared in the literature around the turn of the century. Numerous small scale networks were organized in the US and Europe during the 1920-1950s. Wilson (1926) and Collison and Mensching (1932) reported the earliest US precipitation chemistry studies at local sites. The physical size of the networks changed during the

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1950s from single or dual site studies to large scale national/international studies. During the 1950s, Barrett and Brodin (1955) organized a European monitoring network and Junge (1958) established the first continental U.S. network. The World Meteorological Organization (WMO) reported (1971) the formation of an international network to monitor global trends and changes in the chemical composition of acid precipitation. In addition to the existing WMO network, various local, regional and national acid precipitation studies currently operate in the industrialized nations.

The first scientific groups to become concerned with the causes and effects of acid precipitation were the ecologists and biologists. These two groups were responsible for the majority of the acid precipitation studies conducted prior to 1970. During the period 1974-1976, acid precipitation became multi-disciplined. International scientists from each and every scientific field focused their attention on the potential affects of acid precipitation. Symposiums, committees and groups were organized to examine every facet of past and existing studies (Dochinger and Seliga, 1976; Kronebach 1975; Likens et al, 1972; Likens, 1976). Network siting, sampling procedures and analysis schemes were critically reviewed. Special committees were formed to develop techniques to statistically describe the quality of the precipitation chemistry data being reported by the various international laboratories. During this period, concern regarding the effects of particulate deposition on vegetation increased. As a result, improved wet/dry collection devices were designed to give a better understanding of total acid deposition problems.

Numerous new studies have resulted from this increased emphasis on acid deposition, to include the proposal and initial development of a long-termed continental US monitoring network (Galloway and Cowling, 1978). Comprehensive reviews of past and current studies are provided by Niemann et al. (1979), Kennedy (1978), and the Chemist-Meteorologist Workshop Report (1974).

3.4.2 U.S. Precipitation Studies

Past U.S. precipitation chemistry studies can best be described as being "ad hoc" in nature (Chemist-Meteorologist Workshop, 1974). New studies were randomly developed without adequate consideration to either past or current proposals. General characteristics that can be used to describe past U.S. studies include:

(1) Overall study objectives varied among projects.

(2) Pre-1970 studies were short-termed, lasting only 1-2 years.

(3) Sites were randomly selected at locations of convenience. Siting with respect to program objectives or standard siting criteria were rarely considered.

(4) Sampling/storage procedures and the extent of sample chemical analysis varied among studies.

Each of these deviations in study design/protocol obviously affects the existing data and preclude any simplistic consolidation or correlation of past study results. Of these variations, the differences in sampling/storage procedures are the most difficult to resolve.

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By-and-large, when considering all the earlier studies, sampler collection efficiencies, sample representativeness, and sample integrity at the time of chemical analysis (i.e., does the sample reflect what was collected in the field or have chemical changes occurred?) can only be speculated.

Since 1900, techniques used to collect/store precipitation samples have undergone significant changes. The most significant change in wet-only or bulk precipitation sampling deals with the collector itself. In earlier reports, monthly bulk samples were manually collected in glass devices. Plastic devices became the collection medium during 1950-1960. Galloway and Likens (1976) note that plastic collectors are preferred today for inorganic species whereas glass collectors are currently used for organic sampling. Automated wet/dry samplers are replacing the manual wet-only and bulk collection techniques. The height of the collection device above ground level has varied throughout the years. Earlier studies placed collectors at ground level while current studies commonly place the collector 1-3 meters above ground level. Other study-dependent sampling variations observed in wet-only and bulk sampling procedures include: filtering versus non-filtering of the sample before chemical analysis; the use of biocides to preserve the sample and retard biological growth; and the storage techniques used after sample collection and before chemical analysis. Although the degree each of these sampling/storage differences affect the sample remains unanswered, it is generally agreed that the study data will be related to the study sampling techniques employed.

When reviewing past data, the analyst must determine if and to what extent these common variations bias the resulting data. For example, the effects of sample evaporation, splash contamination, loss of initial and usually most concentrated rainfall and contamination from insects, leaves, etc., have been commonly reported. How the authors addressed these problems differ. Some deleted the questionable data, others did not, and still others stated that these effects would be averaged out over the length of the study.

The data analyst must also know whether the samples were filtered before analysis. Past study data indicates that the inclusion of particulate "wash-out" material in bulk and wet-only samples as well as dry deposition in bulk samples changes the overall chemistry of the sample. Several studies routinely filtered the sample before analysis. This filtration of particulate matter, depending on technique and actual time when filtering occurred, could possibly change the resulting sample chemical composition and related analytical data. Whether glass or plastic collection devices were used could also affect the data. Galloway and Likens (1976) note the leaching of inorganic species into/out of glass collection devices and the loss of organic species with plastic devices. Other authors (Kadlecek and Mohnen, 1976; Norwegian Institute for Air Research, 1971) report similar findings. Metal ion losses in dilute samples have been repeatedly reported. To minimize this potential metal loss, various authors acidified a representative aliquot of the sample immediately following collection; again, others did not. Sample

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storage techniques also vary among studies. Larger networks usually kept the sample in a cool, dark place. Some smaller networks either froze the sample or refrigerated the sample at 4°C. Galloway and Likens (1976) indicate that significant changes do not occur when samplers are stored at 4°C. Unfortunately, this storage technique is cost prohibitive for large national/international networks. How long a sample is stored before chemical analysis may also affect the sample integrity. A review of the literature reveals that the reported length of time from sample collection to sample analysis has varied by as much as sixty days. Some authors used chemical biocides to retard green algae growth in samples collected in warmer climates as the presence of algae changes the sample chemical composition. Obviously, the sample storage technique affects the sample integrity at the time of chemical analysis.

Although procedures for the collection of dry deposition are not as well documented, similar sampling variations are expected depending on technique, i.e., dust-fall buckets, ambient air monitors or automated dry-only collection devices. Siting of the dry deposition collector is crucial; in particular, the height of the collector above ground level. Dry deposition samples, 0-1 meter above ground level, have been reported to be heavily influenced by contributions from the local terrain as well as bird and vegetation contamination.

Data from special studies is also available for summation. Behrmann (1975), Pickerell et al. (1979), Anderson (1978), Cooper et al. (1976) and Gatz et al. (1971) report special one-of-a-kind samplers to monitor the change in the chemical composition of precipitation events at single sites. Special sampling procedures have been developed for the collection of snow (Galloway and Likens, 1976; Hagen et al., 1973), fog (Waller, 1963; Rose, 1966), individual raindrops and canopy throughfall (McColl and Bush, 1978). Understanding these special sampling techniques is essential before this data is compiled or summarized.

The data analyst must also consider the various collection periods reported in past studies. Over the years, bulk samples have been typically collected on a monthly basis. However, wet deposition collection periods have ranged from event sampling to monthly sampling. Although clearly defined in terms of showers and thunderstorms, the definition of the beginning/ending of an event during a large frontal system varies from author to author. Monthly sampling is common in larger networks designed to monitor the change in chemical trends over time. Daily or more frequent sampling is typically reported at individual sites with the objective to determine exact chemical loadings at specific sites. Weekly sampling is currently recommended by Galloway and Cowling (1978) as the maximum allowable sampling frequency to obtain useable wet deposition results. Dry deposition is commonly collected on a 1 to 2 month basis as recommended by Galloway and Cowling.

Each of the sampling/storage variations addressed above can affect the sample integrity and resulting data. In addition, site meteorology and collector efficiency also affect the sample. Summers and Whelpdale (1976) stress the existing need to document both scavenging and collection mechanisms involved with acid precipitation. Initial reviews of the most commonly used collectors have been conducted and are provided by Niemann (1979) and Galloway and Likens

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(1976). Additional comprehensive collector evaluations, to include dry deposition collector efficiencies and species collected, along with a re-evaluation of the meteorological mechanisms involved in the acid precipitation processes are needed. Before any past data summarization can be developed, a careful analysis of the sampling/storage procedures and collection mechanisms must be performed.

3.4.3 Analytical Techniques

3.4.3.1 Introduction--Analytical methodologies currently employed to analyze precipitation samples are, for the most part, state-of-the-art freshwater or natural water analytical techniques. Typical procedures are presented in Methods of Air Sampling and Analysis (1977), Standard Methods for the Examination of Water and Waste Water (1971) and U.S. Environmental Protection Agency's "Methods for Chemical Analysis of Water and Waste" (1979). Theoretical detection limits and the quality of the data in terms of precision/accuracy for each technique are specified in the literature. Rainwater, however, is a dilute solution of chemical species, and represents extremely pure freshwater or natural water. Chemical analyses on rain water yield results at or below the published analytical detection limits (Miller and Highsmith, 1976). Added precautions must be taken to minimize field/laboratory contamination (Likens, 1972) which is analytically indistinguishable and sometimes larger than the natural rain water specie contributions. To preclude changes in the sample chemical composition, analyses should occur within 24 hours after sample collection. Although operator and instrumentation dependent, laboratory analyses should meet or exceed the analytical precisions and accuracies presented in Table 3-6. Operator and instrumentation biases must be minimized through supporting quality assurance programs. External as well as internal quality control procedures must co-exist to adequately describe the quality of the analytical data. Prior to 1975, no mechanism existed to externally evaluate the quality of the precipitation chemistry data being reported by the international precipitation laboratories. WMO instituted such an international quality assurance program in 1975. Potential errors in past data have subsequently been noted by Ridder (1978), Galloway et. al., (1979), Tyree et al. (1979), and Tyree (1980).

3.4.3.2 Analysis of Acid Deposition Samples

3.4.3.2.1 Sample Preparation. Wet deposition samples are allowed to equillibrate to room temperature before chemical analyses. Sample pH/conductivity are initially measured. Filtering/centrifuging of the sample may follow. A representative portion of the sample may then be acidified (HNO_3) to preserve the metal ion concentrations. Between analyses, samples are either stored in a dark, cool place or at 4°C. Dry deposition samples are dissolved with a known quantity of distilled water (typically 50 ml). Analytical procedures for these dissolved dry deposition samples are identical to the wet deposition analytical procedures described below.

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TABLE 3-6. RECOMMENDED PHYSICAL/CHEMICAL PARAMETERS FOR ANALYSIS

Parameter	Unit of Report	Expected Range	Suggested Precision	Suggested Accuracy
Volume (field)	inches	0.00-10.00	±.02"	±.02"
pH (field + lab)	pH	2.00-9.00	±.01pH	±.01pH
Conductivity (field + lab)	μS/cm	0.1-200.0	±5%	±5%
SO_4	mgS/l	0.1-10.0	±2%	±2%
NO_3	mgN/l	0.1-10.0	±2%	±2%
Cl	mgCl/l	0.1-10.0	±2%	±2%
NH_4	mgN/l	0.05-10.0	±3%	±2%
K	mgK/l	0.01-5.00	±2%	±2%
Ca	mgCa/l	0.01-5.00	±2%	±2%
Na	mgNa/l	0.01-10.00	±5%	±3%
Mg	mgMg/l	0.01-2.00	±2%	±2%
Acidity	μeq/l	1.0-500.0	±10%	±5%

3.4.3.2.2 Volume. Direct volume measurements, accuracy ± 3%, are made on the wet deposition sample with Class A graduated cylinders. Care must be taken to insure that the sample is not contaminated by the labware used in this procedure. Indirect volume techniques include weighing the collection container before and after the sampling period or measuring the collection in a standard rain gauge (cylinder, tipping bucket or weighing). Standard rain gauge accuracies are ± 0.02 in or better depending on the manufacturer. The weighing rain gauge is preferred since it offers minimal evaporation loss and a higher degree of reliability over the tipping bucket rain gauge during intense storms.

3.4.3.2.3 pH. pH is the measurement of the hydrogen ion activity, i.e., pH = -log $[H^+]$, commonly referred to as the free acid content of the solution. The pH of a typical United States wet deposition sample ranges between 4.0 - 5.0 pH units. Samples collected in more arid regions may range as high as pH 8.0 whereas samples collected in the northeastern United States typically range from pH 3.5 to pH 4.5. Precipitation pH measurements were not reported prior to 1962. Instead methyl orange indicator solution [endpoint pH = 4.4, Skoag and West (1965)]

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was added to assess the sample acidity. Cogbill and Likens (1974) and Granat (1972) have indirectly calculated and reported the pHs of prior-1962 precipitation samples. Currently, pH is electrometrically determined with a standard pH meter in conjunction with either glass/reference calomel electrodes or a combination electrode at 25°C. Three certified buffer solutions are used to calibrate the pH meter/electrode system in the pH range 3.50-7.50. Direct pH measurements are made on a representative aliquot of the sample. pH measurements are dependent on operator techniques and the condition of the electrode(s). Galloway et al. (1979), Ridder (1978) and Tyree et al. (1979) have noted potential sources of errors in pH measurements. With proper care and quality equipment, pH results with a precision of ± 0.02 pH units and accuracy of ± 0.05 pH units should be obtainable (Standard Methods, 1971).

3.4.3.2.4 Conductivity. The specific conductance of a wet deposition sample indicates the capability for that sample to carry an electrical current. Conductivity is related to the total concentration of dissolved ions, is directly determined on the sample with a standard Wheatstone bridge in conjunction with a calibrated conductivity cell at 25°C. Wet deposition sample conductivities normally range from ca. 10-200 μS/cm. Daily calibration of the conductivity meter and cell with freshly prepared standard KCl solution is required for accurate measurements. Operator techniques, the condition of the conductivity cell, and the quality of the standard KCl solutions determine the quality of data reported. Under careful supervision, conductivity measurements with precision/accuracy of 5 percent are obtainable (Standard Methods, 1971).

3.4.3.2.5 Acidity. An acidity measurement indicates the capacity of the wet deposition sample to donate protons from both strong and weak acids. Numerous techniques have been reported to measure sample acidity. Each technique can yield a slightly different result (Tyree, 1980). Acidity values from - 200 μeg/liter to + 200 μeg/liter are routinely reported. The precision and accuracy of any acidity measurement is dependent on the analytical technique employed and the ability of the operator to standardize and titrate minute quantities of highly diluted strong base. Tyree (1980) notes that the operator is the key to good acidity measurements. The presence of carbon dioxide, aluminum, iron, ammonium and the method endpoint pH influence the results.

3.4.3.2.5.1 pH. See Section 3.4.3.2.3. Depending on the actual sample pH, acidity based on a pH measurement yields either the strong acid proton component (sample pH <4.5) or the strong acid component plus some undetermined contribution from the weak acid component (sample pH >4.5). Acidity based on pH alone is not considered conclusive.

3.4.3.2.5.2 Titrimetric. Various titrimetric endpoint procedures are available.

Phenolphthalein Endpoint. The rainwater sample is titrated with standardized 0.01-0.001 strong base (NaOH) to the phenolphthalein endpoint (8.0-9.6 pH units per Skoag and West, 1965). Precision and accuracy (± 5 percent) are dependent on the ability of the operator to standardize and deliver minute quantities of dilute base and the repeatability of the endpoint color. (Standard Methods, 1971).

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WMO. A prescribed quantity of strong acid (H_2SO_4) is added to the sample, lowering the sample pH to less than 4.0 and thus removing the CO_2. The sample is titrated against standardized base until the sample pH, monitored via a pH meter, reads pH 5.6. Precision (± 0.02 pH units) and accuracy (± 0.05 pH units) are dependent on the quality of the pH meter and standardized base, the condition of the electrodes and operator technique.

American Public Health Association. Strong acid is added to lower the sample pH below 4.0. Hydrogen peroxide is then added. The sample is boiled to eliminate CO_2, cooled to room temperature and titrated electrometrically with strong base to pH 8.3 (EPA method endpoint = 8.2). The U.S. Environmental Protection Agency (1979) reports a standard deviation of 1-2 mg $CaCO_3$/liter and bias of ca. ± 20 percent for sample measurements in the 10-120 mg $CaCO_3$/liter range.

Likens (1972). Nitrogen is bubbled through the sample to eliminate any CO_2 interference. Samples are titrated to pH 9.00 with standard base. The accuracy of the pH meter is reported to be ± 0.03 pH units (1972). Hendry and Brezonik (1980), following this technique, titrated samples to pH 7.00 endpoint.

Coulometric/Potentiometric. The sample is titrated with cathodic generated hydroxyl ion (OH^-), i.e., (-) reference electrode/test solution/glass electrode (+) as outlined by Liberti, et al. (1972) and Askne et al. (1973). Gran plots (1952) are interpreted to determine the strong and weak acid contributions. Liberti et al. (1972) report a ± 5 percent standard derivation and 0.1 mg/liter H_2SO_4 sensitivity when analyzing strong acids. The Norwegian Institute for Air Research (NAIR) (1971) reported a 2-5 μeg acidity/liter standard deviation in rainwater samples having 10^{-4}-10^{-5} acidity concentrations. Askne et al. (1973) observed "exact agreement" in strong acid analyses, but only "reasonable-to-good agreement" with samples containing various concentrations of strong and weak acids. Tyree et al. (1979) and Krupa et al. (1976) also observed difficulties in determining strong/weak acid contributions in rainwater samples using this technique.

3.4.3.2.5.3 Ion Balance. Granat (1972) and Cogbill and Likens (1974) have reported a technique to calculate sample pHs based on the total ionic strength. In this technique, the charge difference in favor of the anion concentration is related to the sample hydronium ion concentration. Possession of accurate analytical data for the individual principle ions is essential. The overall precision and accuracy of this technique is no better than the summation of precisions/accuracies of the analytical methods used to determine the individual ionic species. Tyree et al. (1979) states that this technique could possibly be used to determine the strong acid contribution in samples with observed pH 5.6 or below.

3.4.3.2.6 Sulfate ($SO_4^=$). Analytical procedure for sulfate analysis are described in Section 3.3.4.1.1. Typical wet deposition samples contain 0.1-5.0 mg $SO_4^=$/liter.

3.4.3.2.7 Ammonium (NH_4^+). Ammonium concentration of 0.1-1.0 mg N/liter are normally observed in wet deposition samples. Two techniques (ion selective electrode and indophenol colorimetry) are discussed in Section 3.3.4.2. Manual Nesslerization techniques (Standard

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Methods, 1971) are commonly used. The Nessler reagent is thoroughly mixed with the sample (ca. 30 minutes). The characteristic yellow color is photometrically determined (425 mμ with 1 cm cell path). Analyses of samples containing 0.2 mg N/liter typically produce results with ± 0.12 mg N/liter standard deviation and ± 18 percent bias (U.S. Environmental Protection Agency, 1979).

3.4.3.2.8 Nitrate (NO_3^-). The rainwater sample nitrate concentration quantitatively (normal range 0.1-5.0 mg N/liter) is reduced to nitrate by the addition of hydrazine sulfate (Kamphake et al., 1967) or by passing the sample through a copper-cadmium column (Fiore et al., 1962). The addition of sulfanilamide and N-(1-naptha)-ethylene diamine dihydrochloride yields a highly colored azo dye measureable colorimetrically at 520 nm. Automated techniques (U.S. Environmental Protection Agency, 1979c) minimize operator error and increases the sample throughout. A second analysis without the nitrate reduction step is required to correct for sample nitrite concentration. Precision/accuracy of ± 5 percent are expected with samples above 1 mg N per liter. Butler et al. (1978) and Tyree et al. (1979) report comparable sensitivity, precision and accuracy using an automated IC technique (see Section 3.3.4.2.2.4).

3.4.3.2.9 Chloride (Cl^-). Various manual and automated procedures are used to determine chloride in rainwater in the concentration range 0.1-10.0 mg Cl^-/liter with precision ca. ± 0.2 mg Cl/liter. The WMO method adds mercuric nitrate and diphenylcarbazone-bromophenol blue to the sample forming mercuric chloride. The excess mercury complexes with the indicator to form a blue-violet dye measured photometrically at 525 nm. Zall et al. (1956) displace the thiocyonate ion (SCN^-) in $Hg(SCN)_2$ and form $HgCl_2$. In the presence of excess iron, the highly colored dye [Fe $(SCN)^{+}_{+}$] is formed and can be photometrically measured at 460 μm. The automated ferricyanide procedure (EPA) is preferred over the manual methods since operator/standard solution errors are minimized. Automated IC techniques (Butler et al., 1978; Tyree et al., 1979 and Section 3.3.4.1.1.4) yield comparable results.

3.4.3.2.10 Fluoride (F^-). Fluoride in wet deposition (range 0.01-0.1 mg F/liter) is generally determined by the ion selective electrode technique. The condition of the fluoride ion selective electrode is critical. Analysis of synthetic samples containing 0.85 mg F/liter yielded results with a 3.6 percent relative standard deviation and 0.7 percent relative error (Standard Methods, 1971). Automated IC techniques (Butler et al., 1978; Tyree et al., 1979 and Section 3.3.4.1.1.4) yields similar results.

3.4.3.2.11 Trace Metals. Techniques used to determine trace metal concentration in rainwater are described in Section 3.3.4.3. Observed metal concentration ranges generally approximate the lower detection limit for flame atomic absorption metal analysis.

3.4.4 Interlaboratory Comparisons

WMO (1975) instituted an international interlaboratory program to describe the quality of the wet deposition chemistry data being reported by the various WMO laboratories. Participation in this program is on a voluntary basis. The results of three comparisons on synthetic rainwater samples (WMO, 1976; Thompson, 1978; WMO, 1980) have been previously reported. The

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United States Department of Energy (DOE) sponsored a similar round robin (MAP3S, 1979) on both simulated and composited rainwater samples. Tyree et al. (1979, 1980)) discuss the WMO and DOE results.

Three physical analyses (pH, conductivity, and acidity) are most frequently reported and compared. pH and conductivity laboratory results have been extracted from the three WMO reports and are provided in Table 3-7. WMO did not summarize the acidity measurement results in the first and second analysis sessions. The synthetic samples used in the first two sessions contained only weak acids. The laboratory results indicated that the WMO laboratories, as a whole, could not perform acidity measurements on samples containing only weak acids. Four new samples were used in the third WMO analysis session. Three of the third analysis session samples (samples 71, 72, 73) contained both weak and strong acids. Sample type 74 contained only strong sulfuric acid. The results of the acidity measurements reported in the third analysis session have also been extracted. Table 3-8 lists the between laboratory percent coefficient of variation by session for those chemical analyses routinely performed by the WMO participants, where

$$\% \text{ C. V.} = \left\{ \frac{\sqrt{\dfrac{\Sigma(d_i-\bar{d})^2}{N-1}}}{\bar{x}} \right\} \times 100\%$$

Improvement in the analysis for a given constituent by the WMO laboratories, as a whole, is indicated by decreasing % C. V. from session 1 to session 3. In general, the WMO laboratories as a whole, showed improvement from session 1 to session 3.

WMO and DOE intercomparision results highlight the difficulties encountered when analyzing dilute precipitation samples. When comparing data from various studies, the data analyst must include the appropriate biases resulting from the laboratory's sampling/storage techniques as well as the ability of that laboratory to perform chemical analyses on the sample.

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TABLE 3-7. RESULTS OF WMO INTERCOMPARISONS ON SYNTHETIC PRECIPITATION SAMPLES

	pH (pH Units)							Conductivity (μS/cm)							Acidity (μeq/l)					
Session	Sample type	$\bar{x}$	σ_x	N	High x	Low x	Session	Sample type	$\bar{x}$	σ_x	N	High x	Low x	Session	Sample type	$\bar{x}$	σ_x	N	High x	Low x
1976	A	5.45	.74	17	6.40	3.65	1976	A	6.9	4.3	17	22.0	3.9	1976	NOT REPORTED BY WMO					
	B	5.53	.76	18	7.22	3.85		B	17.3	4.9	18	28.0	20.0							
	C	5.53	.52	17	6.20	4.10		C	56.3	4.8	17	62.0	44.0							
	D	5.56	.41	18	6.10	4.20		D	109.3	8.1	18	119.0	84.0							
1978	A	5.66	.49	25	6.54	4.61	1978	A	6.7	3.0	25	19.0	3.9	1978	NOT REPORTED BY WMO					
	B	5.77	.51	25	7.07	4.65		B	17.9	8.8	25	57.0	9.0							
	C	5.60	.44	25	6.58	4.54		C	52.4	12.0	25	67.5	19.1							
	D	5.65	.39	25	6.64	4.79		D	103.6	23.9	25	132.0	37.9							
1980	71	4.21	.16	26	4.55	3.80	1980	71	29.1	4.0	25	37.3	18.3	1980	71	70.0	36.7	22	206.0	18.9
	72	4.02	.11	26	4.17	3.72		72	80.4	9.1	25	95.6	57.3		72	106.3	43.6	22	260.0	29.2
	73	5.58	.19	26	6.02	5.17		73	195.9	21.6	25	224.0	132.0		73	25.3	63.7	18	202.0	-37.0
	*74	3.91	.16	24	4.30	3.60		*74	64.4	8.0	23	81.5	48.0		*74	10.9	16.1	22	68.0	4.7

*Sample contains only H_2SO_4

$\bar{x}$ = sample mean = $\frac{\Sigma x_i}{i}$

σ_x = standard deviation = $\sqrt{\frac{\Sigma(x_i-\bar{x})^2}{N-1}}$

N = number of laboratories.

*

TABLE 3-8. COEFFICIENTS OF VARIATION OF WMO INTERCOMPARISONS ON SYNTHETIC PRECIPITATION SAMPLES

Constituent	Between laboratory percent coefficient of variation (% C.V.) % C.V. by session 1976	1978	1980
pH	10	8	3.4
Conductivity	15	22	12
SO_4	13	24	34
NH_4	38	32	33
NO_3	79	64	74
Cl	58	24	25
Ca	27	25	25
K	32	30	22
Ma	21	8	99
Na	29	27	19

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APPENDIX 3A

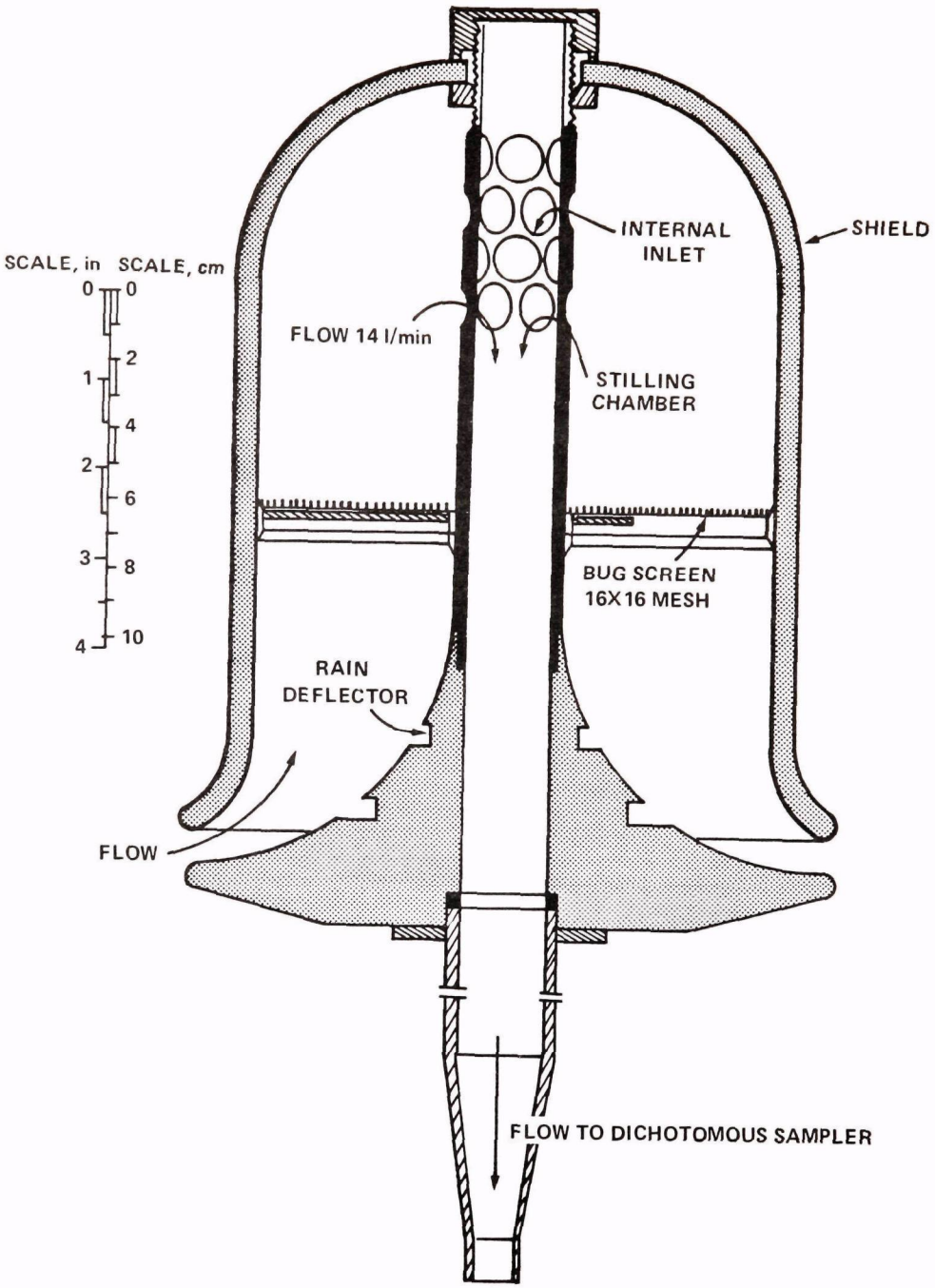


Figure 3A-1. Early inlet for the dichotomous sampler.

Source: Stevens and Dzubay (1978).

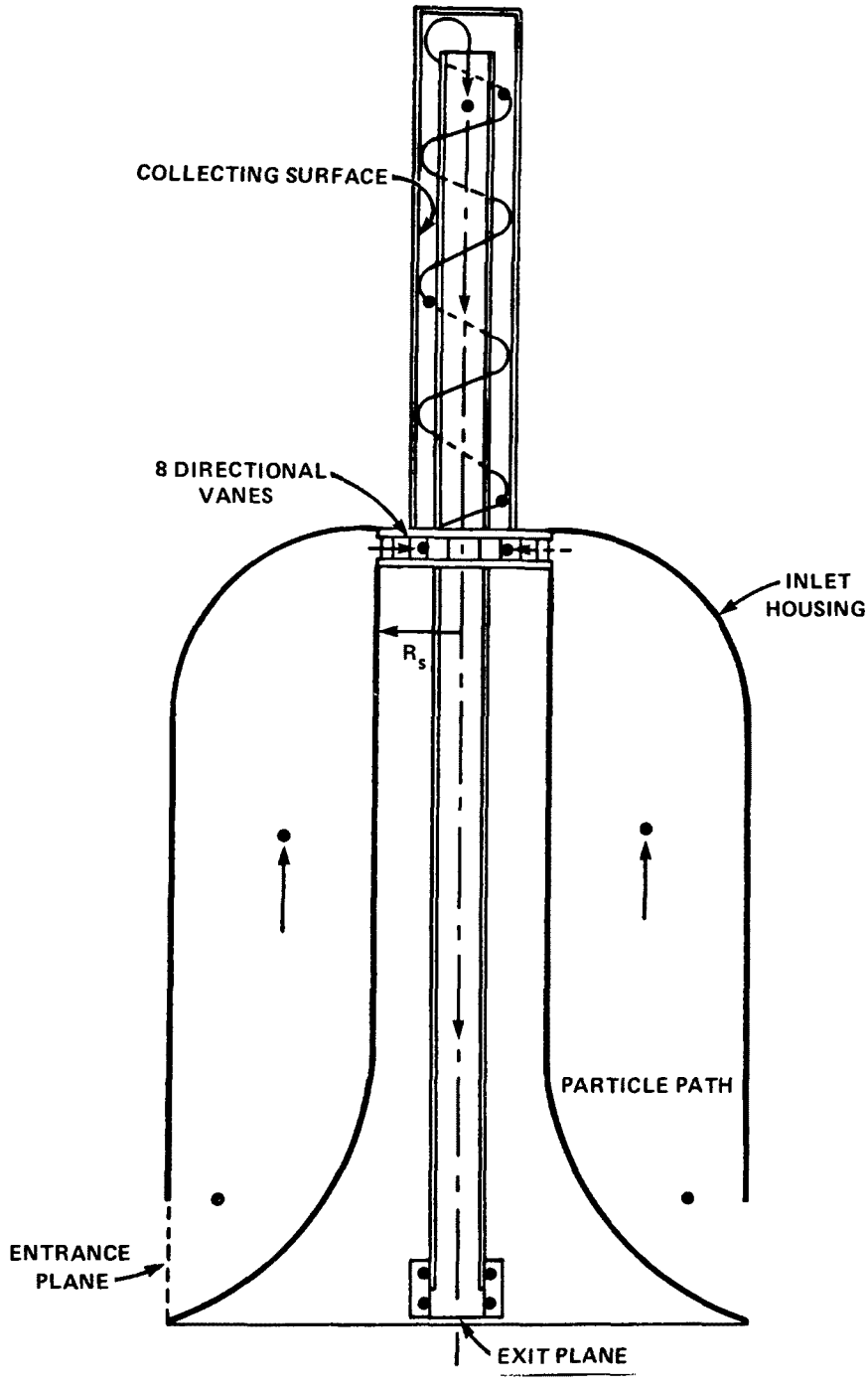


Figure 3A-2. Wedding IPM inlet, section view, not to scale.

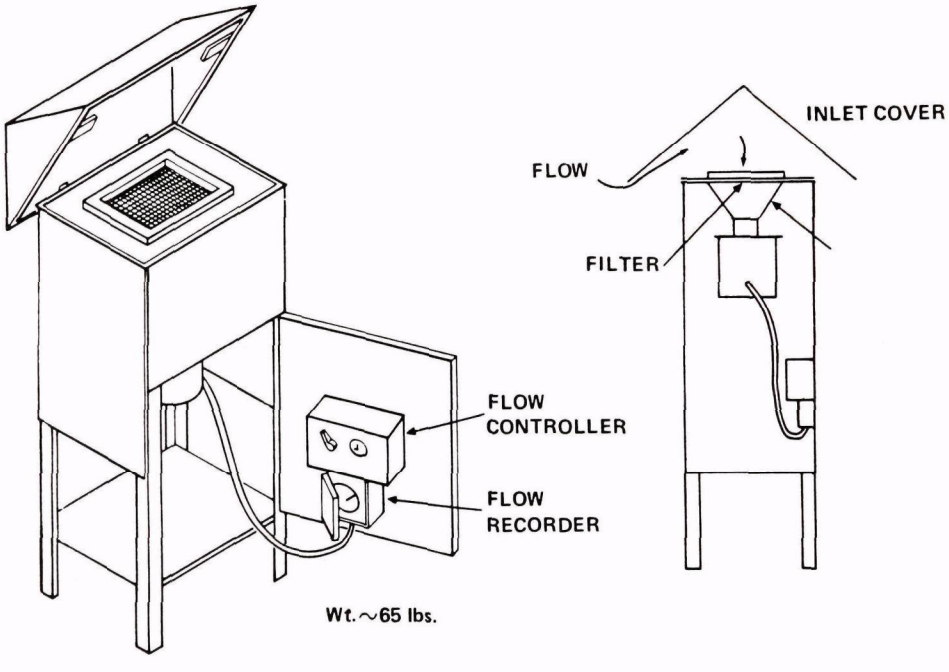


Figure 3A-3. TSP Hi-Vol.

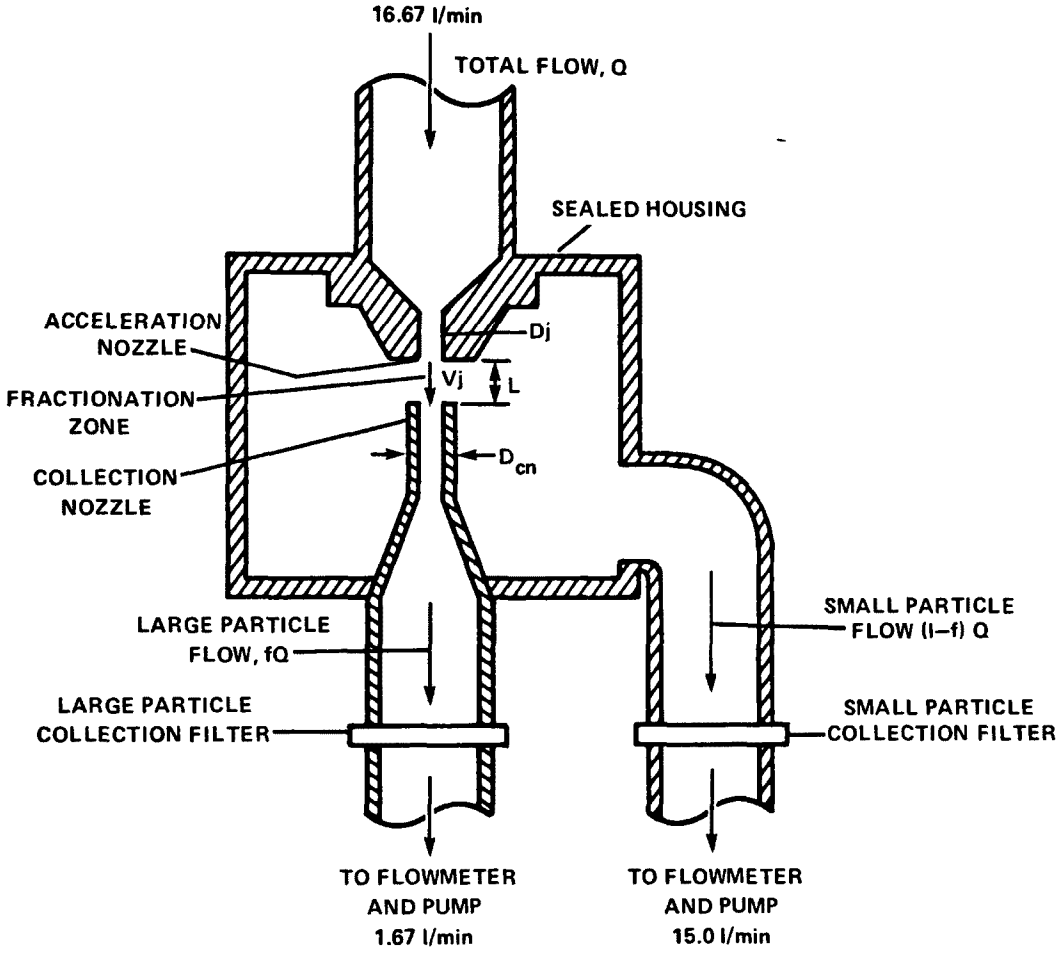


Figure 3A-4. Dichotomous sampler separator.

Source: Loo et al. (1979)

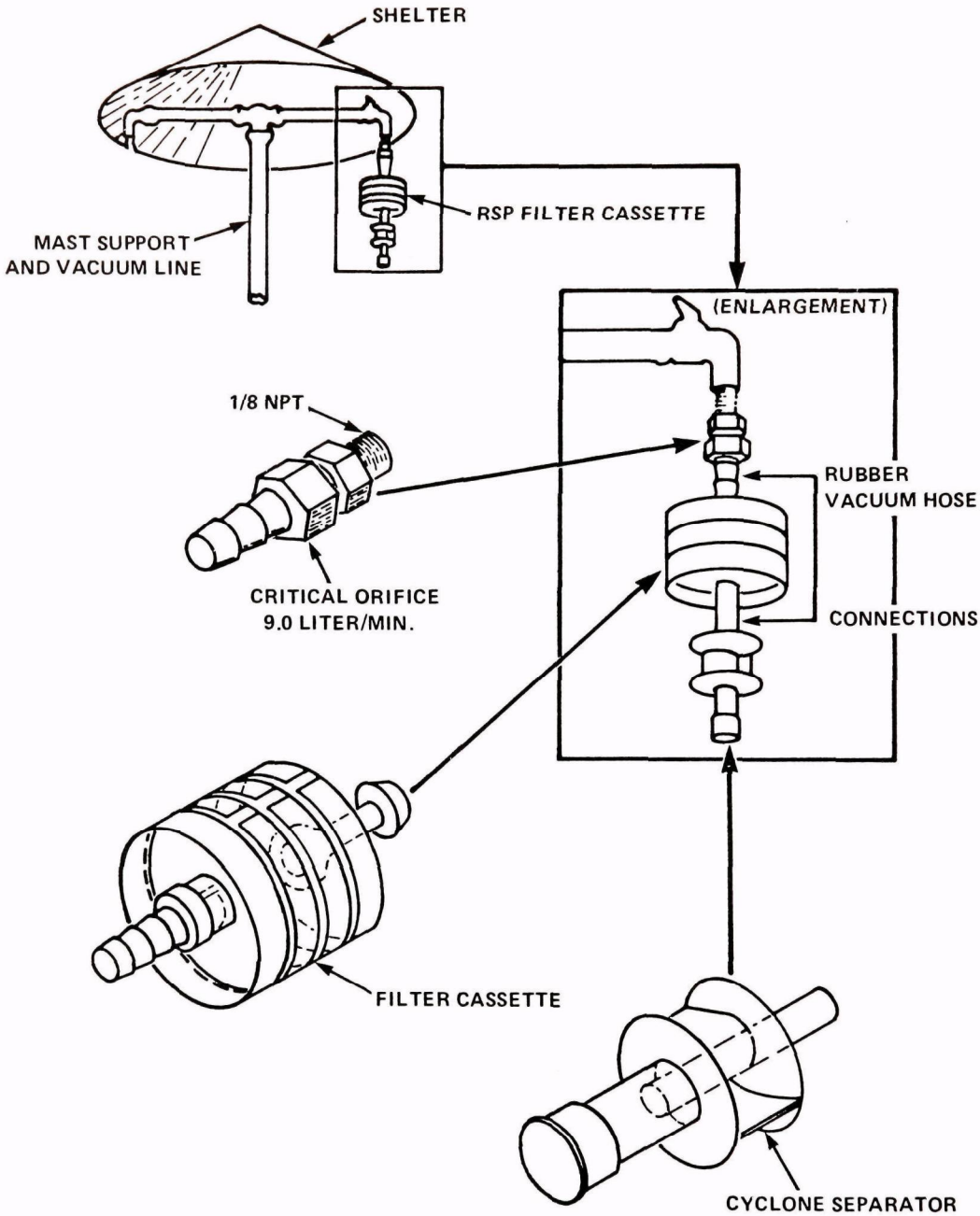


Figure 3A-5. Chess cyclone sampler and shelter assembly.

Source: Barnard (1976).

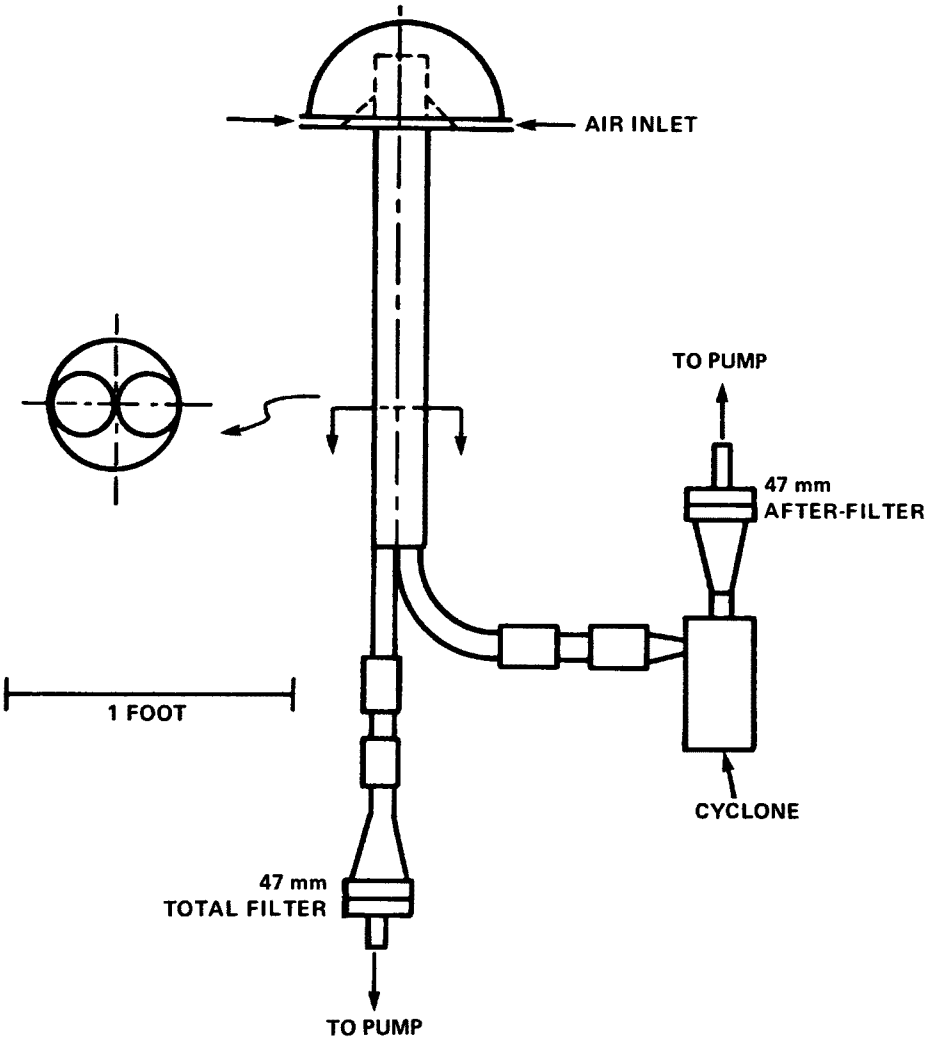


Figure 3A-6. Assembly for sampling with a total filter and cyclone in parallel.

Source: John et al. (1978)

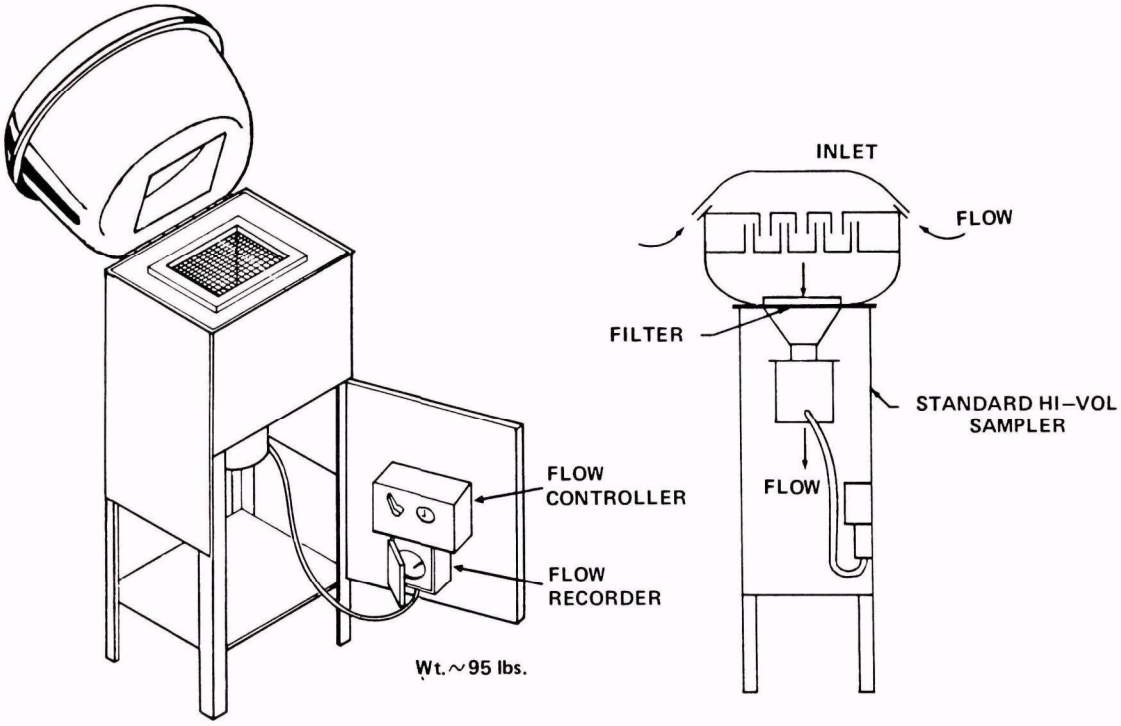


Figure 3A-7. Size-Selective Inlet (SSI) hi-vol.

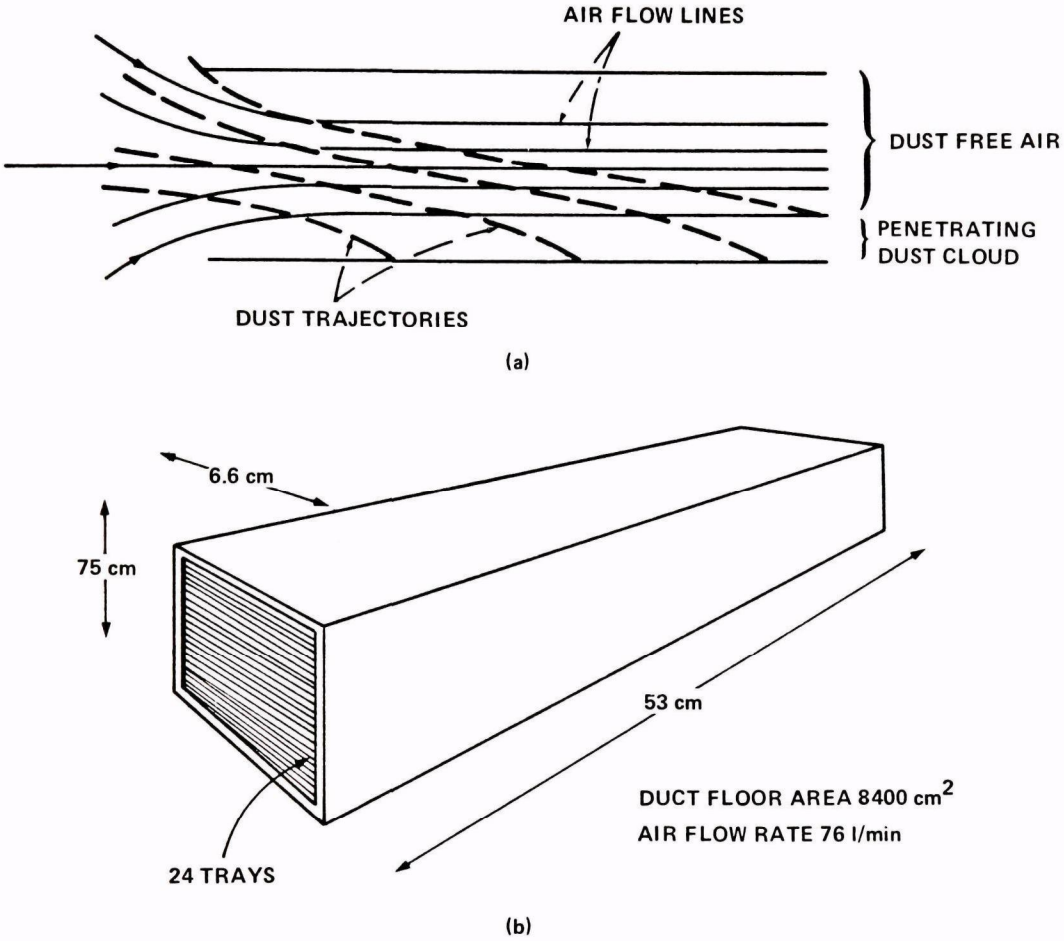


Figure 3A-8. The horizontal elutriator designed to match the BMRC deposition curve.

Source: Hamilton and Walton (1961).

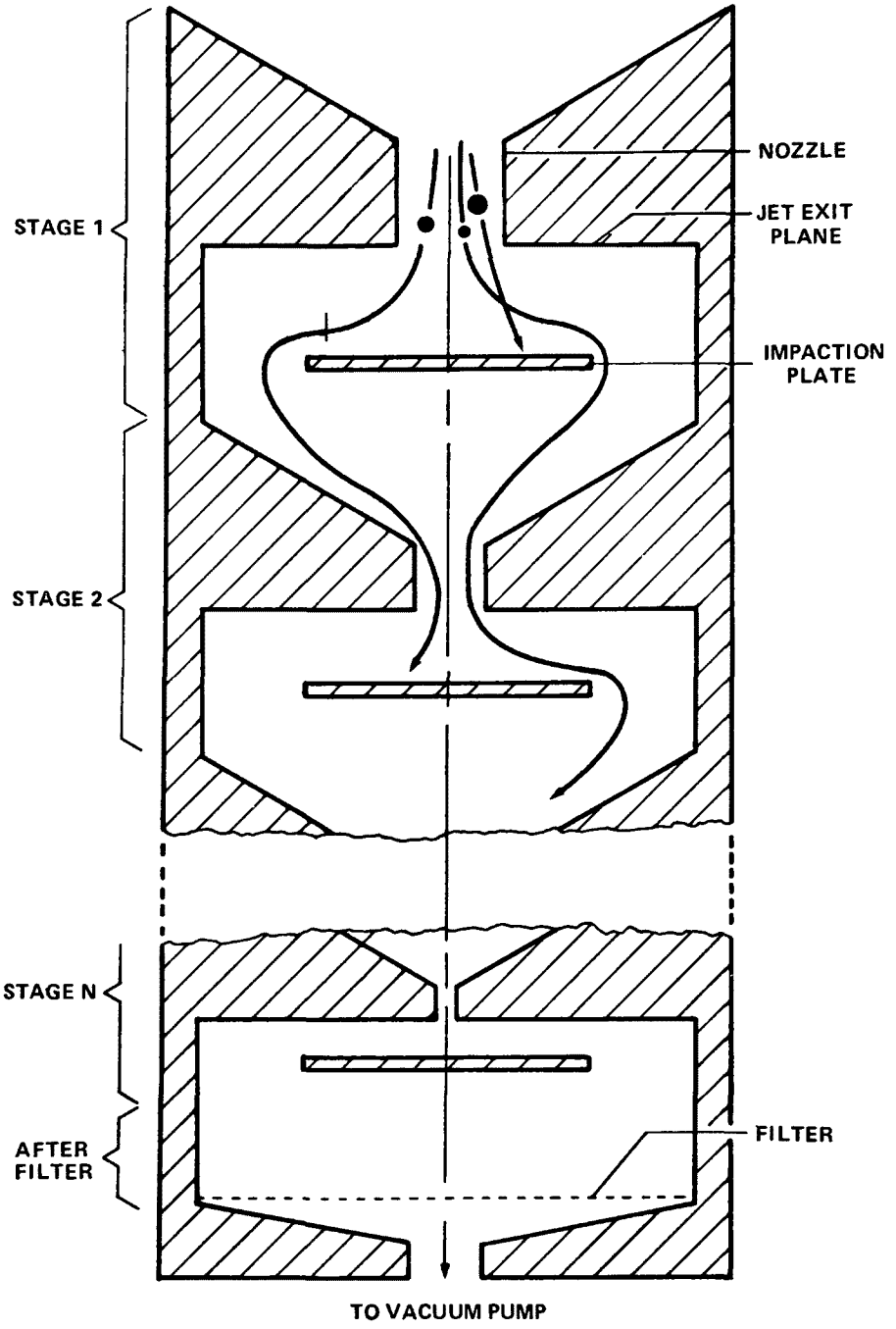


Figure 3A-9. Schematic diagram of a cascade impactor.

Source: Marple and Willeke (1979).

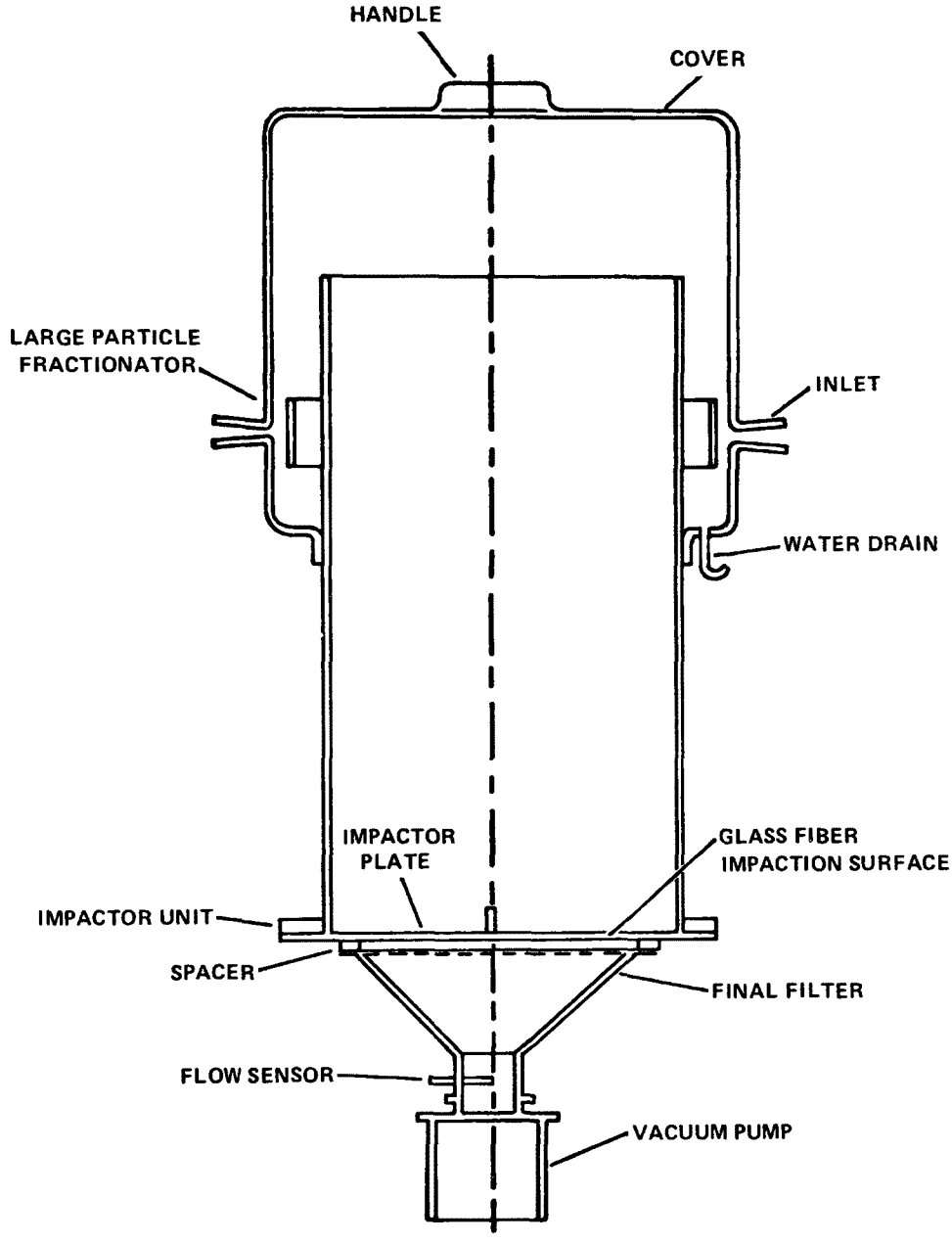
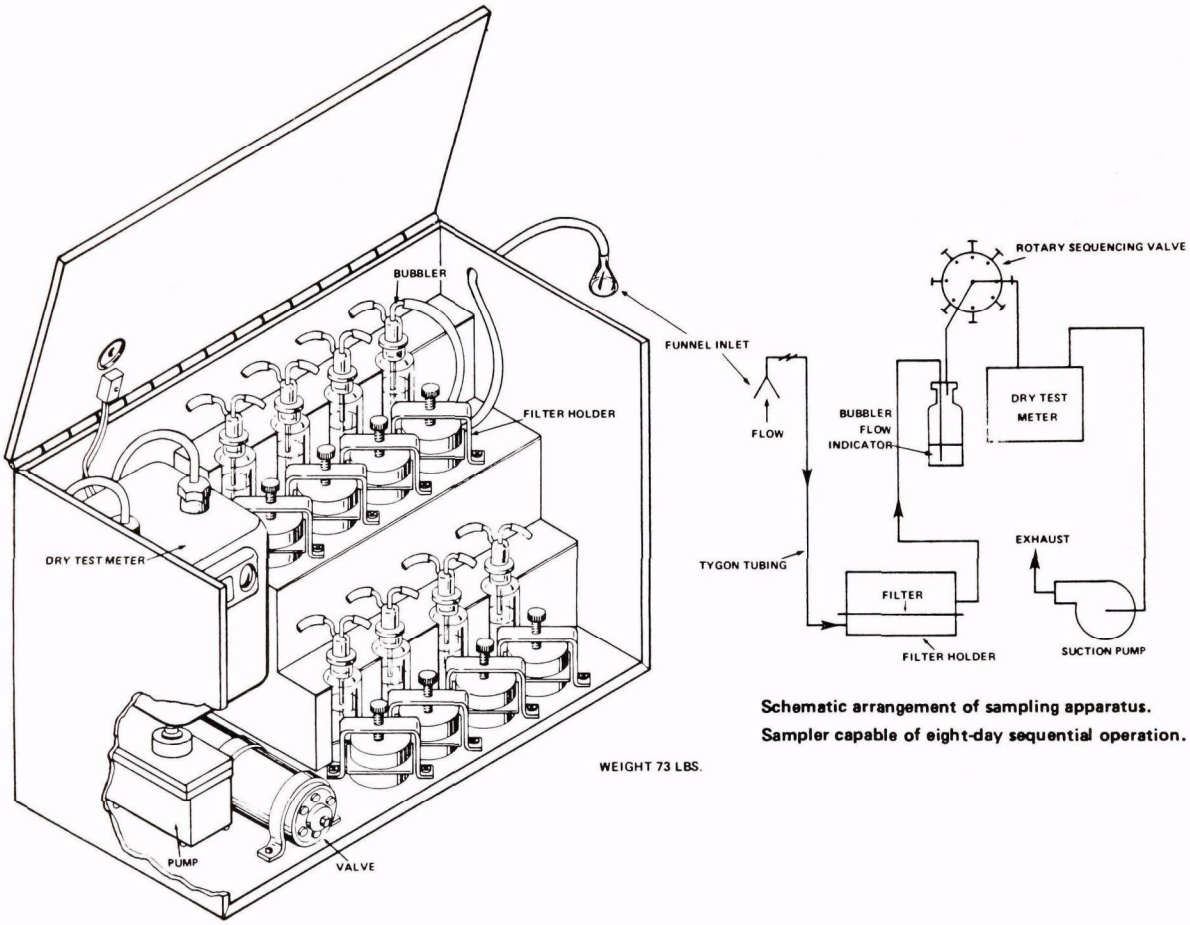


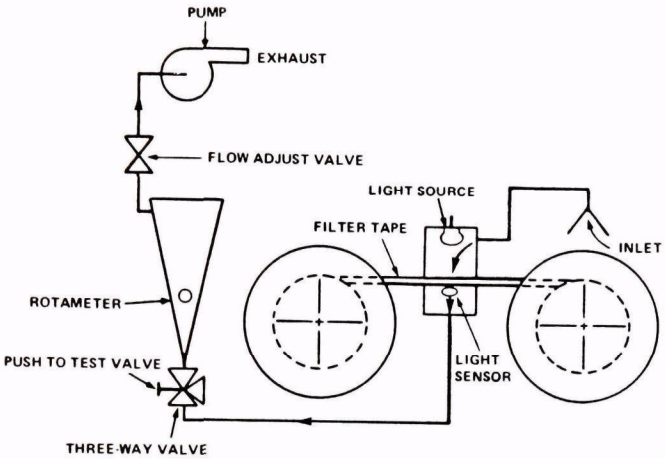
Figure 3A-10. Cross section schematic of the CHAMP aerosol sampler.

Source: Ranade and Osdell (1978).



Schematic arrangement of sampling apparatus. Sampler capable of eight-day sequential operation.

Figure 3A-11. British smoke shade sampler.



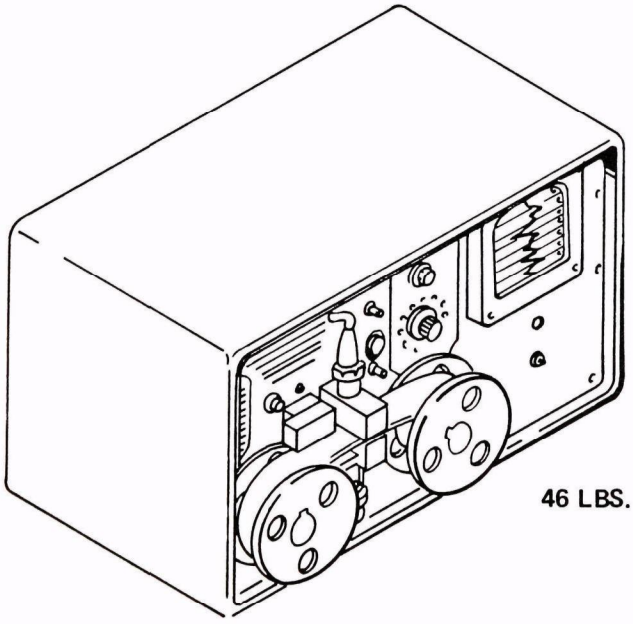


Figure 3A-12. AISI tape sampler.

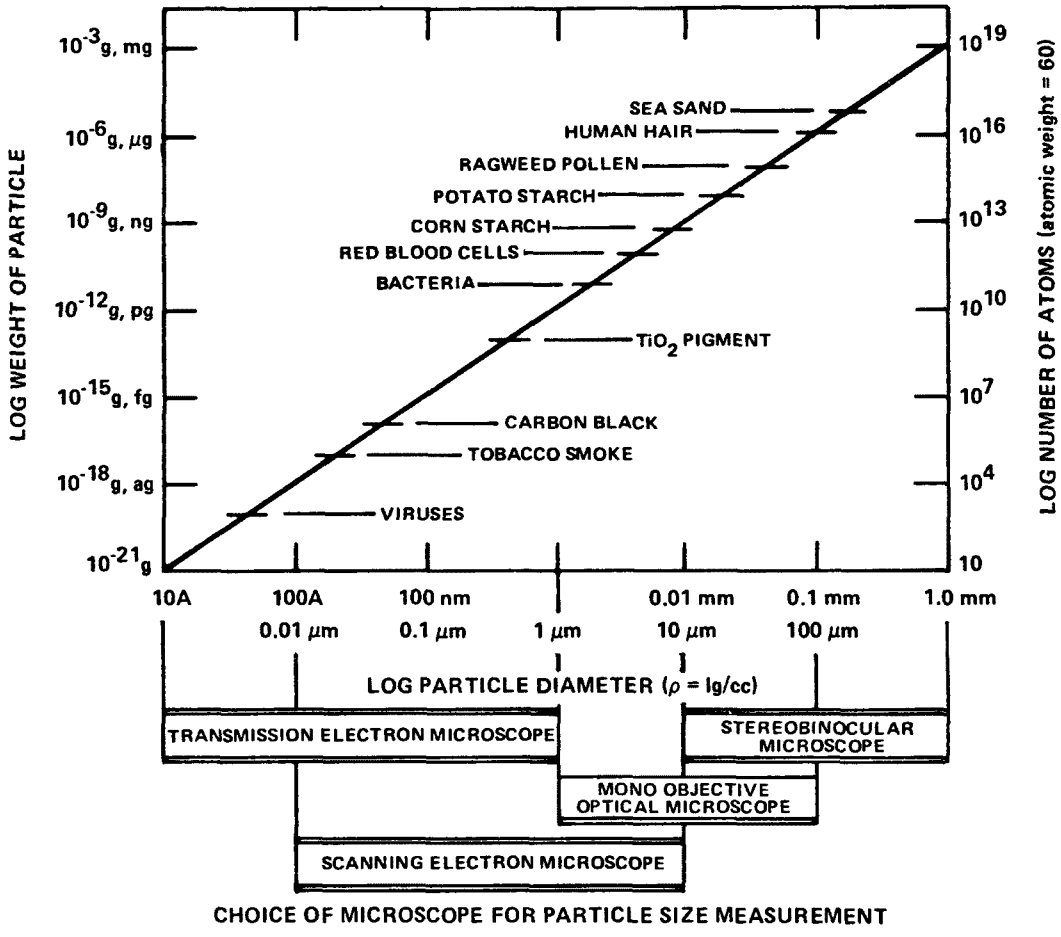


Figure 3A-13. Relationship between particle size, diameter and number of atoms for the light and electron microscope range.

Source: McCrone (1973).

FILTER: Gelman Type A, glass fiber

ΔP, cm Hg	1	1.5	3	10
V, cm/sec	11.2	16.9	32.7	108
D_p, μm		PENETRATION		
0.035	<0.0001	<0.0001	<0.0001	0.0008
0.10	<0.0001	<0.0001	<0.0001	0.00054
0.30	<0.0001	<0.0001	<0.0001	<0.00007
1.0	<0.0001	<0.0001	<0.0001	<0.0002

FILTER: Ghia S2 37PJ 02, teflon membrane, 2.0 μm pore

ΔP, cm Hg	1	3	10
V, cm/sec	23.4	64.1	187
D_p, μm		PENETRATION	
0.035	<0.0002	0.0011	0.0005
0.10	<0.00006	0.00008	<0.00024
0.30	<0.00007	<0.00007	<0.00022
1.0	<0.00007	<0.00009	<0.00008

FILTER: Whatman No. 1, cellulose fiber

ΔP, cm Hg	1	3	10	30
V, cm/sec	6.1	17.4	47.6	102
D_p, μm		PENETRATION		
0.035	0.56	0.52	0.34	0.058
0.10	0.46	0.43	0.13	0.0071
0.30	0.16	0.044	0.0049	0.00051
1.0	0.019	0.034	0.0044	0.00042

Table A-1. Fractional penetration by particle size and face velocity for three selected filter types Lin et al. (1978).

SOURCES AND EMISSIONS

4.1 INTRODUCTION

This chapter presents a characterization of sources and emissions of particulate matter and sulfur oxides. It highlights the magnitude and characteristics of both natural and manmade emissions. Emissions from natural sources are those not caused by man. Volcanoes and the biosphere are prime examples of natural emissions sources. Manmade sources include stationary point sources (utility power plants, industrial facilities, etc.), fugitive sources (both industrial and non-industrial; roadway dust, for example), and transportation sources (vehicle exhausts). All of these emissions categories are discussed further in this chapter.

Chapter 4 is closely linked with Chapter 5 and 6. These three chapters, taken as a whole, present the known material concerning the relationship between emissions and ambient air concentrations. Chapter 4 summarizes sources and emissions of particulate matter and sulfur oxides, while Chapter 5 summarizes measured ambient pollutant concentrations and characteristics. Chapter 6 presents what is known about the complex processes altering and dispersing the emitted substances as they move through the atmosphere. Chapter 4 also relates directly to other chapters in this document, particularly those discussing pollutant effects on visibility, acidic deposition, and health.

One issue worthy of mention at this point concerns the relationship between emission intensity and possible effects on humans. The proximity of emissions to humans can often be more important than relative intensity. For example, mass emissions from residential fuel combustion (home heating) and transportation sources are minor on a national level. However, they are emitted in highly populated areas, close to ground level, thereby elevating their possible effects on human health and welfare. Dust from unpaved roads, on the other hand, appears significant in comparison. But these emissions usually occur in rural areas, and tend to settle out quickly, lessening any possible consequences. Conversely, some natural source emissions can be fairly intense (volcanic ash or sulfur from marshlands, for example). But in general they tend to be distributed fairly evenly nationwide. For reasons such as these, certain manmade emission sources, particularly stationary point sources, have been given a greater share of the attention in this chapter.

A number of other issues raised in this chapter have, for good reason, been discussed only briefly or not at all. First, predictions of future emissions trends have not been presented due to the complexities of supporting assumptions. Other documents where adequate discussion of assumptions was possible are referenced. Data on the particle size distribution and chemical composition of particulate emissions are incomplete or inadequate in many cases. Some available data have been summarized, but discussion has been kept brief. Also, discussion of the effects of control devices on emission particle size distributions has been limited. Other documents where these effects are thoroughly discussed have been referenced.

4.2 SUMMARY

Particulate matter and sulfur oxides are emitted into the atmosphere from a number of sources, both natural and manmade. Natural source emissions include terrestrial dust, sea spray, biogenic emanations, volcanic emissions, and emissions from wildfires. The predominant manmade sources are stationary point sources, industrial and non-industrial fugitive sources, and transportation sources. Annual U.S. emissions from natural sources are estimated at 84 x 10^6 metric tons of particulate matter and 5 x 10^6 metric tons of sulfur (the equivalent of 10 x 10^6 metric tons of sulfur dioxide). Manmade sources emit roughly 125 - 385 x 10^6 metric tons of particulate matter per year and 27 x 10^6 metric tons of sulfur oxides per year in the U.S. Because of the assumptions and approximations inherent in emissions calculations, the numbers quoted above should not be considered more than estimates. Section 4.3 further discusses the problem involved with emissions estimates.

The characteristics of particulate matter emissions vary according to source type and a number of other factors. Particulate emissions from natural sources tend to be rather coarse. (For the purposes of this chapter, coarse refers to particles with a diameter greater than 2.5 micrometers.) Particulate matter generated by non-industrial fugitive sources--unpaved roads and wind erosion of cropland, for example--is quite significant on a mass basis. However, only about 50 and 20 percent are less than 10 and 1 micrometers (μm), respectively. Most of the particulate matter emitted by stationary sources and transportation sources, on the other hand, is relatively fine, or less than 2.5 μm in diameter. Adding control devices further concentrates particulate emissions in the finer ranges since most control devices are more efficient at removing larger particles. Therefore, the estimated 10.5 x 10^6 metric tons of particulate matter generated in 1978 by stationary point sources probably consists largely of finer particulates, since that estimate was arrived at assuming the application of control devices. In addition, the finer particles emitted by stationary point sources tend to include more toxic elements than do emissions from natural or manmade fugitive sources.

Virtually all of the manmade sulfur oxide emissions result from stationary point sources. Over 90 percent of these manmade sulfur oxide emissions are in the form of sulfur dioxide (SO_2). The balance consists of sulfates in various forms. Most natural sulfur is emitted as reduced sulfur compounds. But these compounds are probably oxidized in the atmosphere to sulfur dioxide and sulfates.

4.3 DATA SOURCES AND ACCURACY

The most important information presented in this chapter concerns emission quantities and characteristics. Though this information was gathered from the best and most recent literature available, problems are still apparent. Specifically, estimates of emission quantities vary, as do those of emission characteristics.

Emission quantities are typically estimated using emission factors. (The impossible alternative would be direct measurement of pollutants from each emission point.) Emission factors relate the quantity of pollutants emitted to an indicator of activity such as

production capacity or quantity of fuel burned. But because emission factors are statistical averages, they are not necessarily precise indicators of emissions from an individual source. When applied to a large number of sources, however, a reasonable estimate of total emissions can be obtained. Therefore, for larger geographic areas, the percentage error should be smaller.

Table 4-1 illustrates the problems associated with the use of emission factors. "Estimates" refers to National Air Pollutant Emission Estimates, 1970-1978 (U.S. Environmental Protection Agency, 1980a). Emissions totals in that document were obtained from one calculation performed at the national level by use of total national activity levels and national average emission factors for each source category. "NEDS" (National Emissions Data System) refers to the 1977 National Emissions Report (U.S. Environmental Protection Agency, 1980b). NEDS national emissions totals were obtained by adding the emissions from individual facilities. Mistakes, biases, and omissions are more likely to affect the NEDS

TABLE 4-1. TWO EPA ESTIMATES OF 1977 EMISSIONS OF PARTICULATES AND SULFUR OXIDES (10^6 METRIC TONS PER YEAR)

Source Category	Particulates		Sulfur Oxides	
	Estimates	NEDS	Estimates	NEDS
Fuel combustion	4.8	3.6	22.2	22.7
Industrial processes	6.4	3.9	4.2	5.1
Solid waste disposal	0.5	0.4	0.0	0.0

estimate. Therefore, the "Estimates" are judged by the U.S. Environmental Protection Agency to be the most reliable national estimates presently available. The NEDS state emissions totals, presented in Section 4.5.2, are the best available at the state level, but these totals should be considered carefully for the reasons given here.

Problems are also apparent with fugitive particulate emissions, both industrial and non-industrial. Industrial process fugitive particulate emissions, or process fugitives, include most industrial particulate emissions not passing through a stack or other identifiable emission point. Process fugitives are difficult to estimate due to the lack of engineering data and adequate emission factors. One reference (Zoller et al., 1978) estimated them at 3.4×10^6 metric tons per year. However, the U.S. Environmental Protection Agency's "Estimates" include "rough estimates of fugitive particulate emissions from industrial processes." Therefore, the particulate emissions under the industrial processes category presented in this chapter probably include part of the emissions listed as process fugitives.

Estimates of non-industrial fugitive particulate emissions vary quite significantly in some cases. Cooper et al. (1979) estimated annual emissions from entrainment of dust from unpaved and paved roads at 290 x 10^6 metric tons and 7.2 x 10^6 metric tons, respectively. The U.S. Environmental Protection Agency (1980b) estimated emissions from the same categories at 35 x 10^6 metric tons and 4.7 x 10^6 metric tons. Differences are probably due to the use of different assumptions and method of calculation.

Finally, particle size and composition data are also subject to differences. Most of these data are based on emissions sampling and analysis studies. While these studies probably exhibit a high degree of accuracy on a case-by-case basis, making generalizations based on data from a small number of individual sources may not be advisable. Emission characteristics, as well as emission quantities, are highly subject to a number of source-specific factors such as source characteristics and operating conditions, and fuel characteristics. For example, the size distribution of particulate emissions from a given utility boiler can be altered significantly by changing boiler load. Therefore, the emission characteristics from a particular source could vary from the information presented in this chapter.

4.4 NATURAL SOURCES AND EMISSIONS

Knowledge of natural sources and emissions of particulate matter and sulfur, including sulfur oxides, is important for understanding air pollution. Baseline concentrations in continental and marine air represent natural exposure levels and also provide a reference for comparing concentrations in polluted air. Thus, the concentrations and biological effects of air pollutants can be compared with those of natural atmospheric components.

Significant natural sources of particulate matter and sulfur, including reduced sulfur which can become oxidized to sulfur oxides in the atmosphere (see Chapter 6), are terrestrial dust, sea spray, the biosphere, volcanoes, and wildfires. Estimates of emissions from these natural sources in the U.S. are described in more detail in subsequent sections. Table 4-2 presents a summary of natural source emission totals and characteristics.

4.4.1 Terrestrial Dust

Terrestrial dust is transferred to the atmosphere by the action of wind on the earth's soils and crustal materials. Theoretical and experimental studies (Gillette, 1974) indicate that sand grains, produced by the weathering of rocks and soils and moved by wind, cause the pulverization of soil minerals, as in sandblasting, to produce fine particles. These particles may become airborne and may be transported through the atmosphere for considerable distances. For example, dust from the Sahara Desert may be carried by air currents across the Atlantic Ocean as far as Florida and Barbados (Delaney et al., 1967; Junge, 1957).

The amounts of global terrestrial dust have been estimated at 182 x 10^6 metric tons per year (Robinson and Robbins, 1971) and 100-500 x 10^6 metric tons per year* (National Research Council, 1979). Calculations by Vandergrift et al. (1971), based on soil conservation data, resulted in estimated U.S. natural dust emissions of 57 x 10^6 metric tons per year.

TABLE 4-2. SUMMARY OF NATURAL SOURCE PARTICULATE AND SULFUR EMISSIONS[a]

Source Category	Estimated U.S. Emissions (10^6 metric tons per year)		Particulate Characteristics	
	Particulate	Sulfur[b]	Size Range Data	Chemical Composition
Terrestrial Dust	57	-	10% <1 μm	Al, Ca, Fe, K, Mg, Na, Si, organics, trace elements
Sea Spray	5.5[c]	-	22% <3 μm	Seawater, organics
Biosphere	20	1.2 - 5.5[d]	Unknown	Organic aerosols, trace metals
Volcanoes	Variable	Variable	~5% <1 μm	Al, Ca, Fe, K, Mg, Si, Trace elements
Wildfires	0.5 - 1.0	-	80% <1 μm	Organics, trace minerals
TOTAL	~84+	~5+		

[a]All data are referenced in the text.

[b]One metric ton of sulfur, when oxidized, equals two metric tons of sulfur dioxide, SO_2.

[c]Including 0.7 x 10^6 metric tons of sulfate aerosol.

[d]Predominantly reduced sulfur compounds.

Terrestrial dust in the atmosphere is composed primarily of seven major elements - silicon, aluminum, iron, sodium, potassium, calcium, and magnesium - organic material, and trace elements (Miller et al., 1972). The major elements are present in aerosol samples to nearly the same extent as in earth crustal material (Miller et al., 1972; Lawson and Winchester, 1979a). Atmospheric concentrations of many trace elements, however, are 10- to 1000- fold higher than would be expected from physical dispersion of soil materials. These anomalous trace element enrichments have been observed in many parts of the world, including northern Canada (Rahn, 1974), the South Pole (Zoller et al., 1974), and South America (Adams et al., 1977). Table 4-3 summarizes geometric mean enrichment factors, relative to aluminum, for various elements according to Rahn's compliation of all published data up to 1976 (Rahn, 1976).

The atmospheric enrichment sources of these elements are unknown, but transport from polluting industries (Rahn, 1974), natural rock volatility (Goldberg, 1976), and biogenic emanations (Barringer, 1977) have all been suggested. In general, not enough is known about element ratios in the natural atmosphere to detect a pollution component.

Most terrestrial dust particles are greater than 2 μm in diameter (EPA, 1979). The major element constitutents of terrestrial dust also occur principally as coarse particles. Size-fractionated particle samples indicate that more than 90 percent of the mass occurs on the first three impactor stages, >4, 4-2, and 2-1 μm aerodynamic diameter (Winchester et al., 1979). The low relative abundance of submicron silicon, iron, and other major dust constituents reflects the greater amount of energy needed in order for fine particles to be generated from soils by the wind-driven sandblasting mechanism. This energy is normally not provided by the atmosphere near the ground.

4.4.2 Sea Spray

Aerosol droplets are generated at the ocean surface by the action of wind, principally through a process whereby air bubbles become entrained and rise to burst at the surface. Robinson and Robbins (1971) estimated global emissions of particulates from sea spray at 900 x 10^6 metric tons per year, including 120 x 10^6 metric tons of sulfate aerosol per year (Eriksson, 1959, 1960; Robinson and Robbins, 1968). Assuming 10 percent of the annual production penetrates continental areas (Eriksson, 1959), and assuming the impact of the U.S. is proportional to the ratio of U.S. to global coastline (12 x 10^3 miles: 200 x 10^3 miles), approximately 5.5 x 10^6 metric tons of sea spray particulate per year (including 0.7 x 10^6 metric tons of sulfate aerosol per year) impact upon U.S. coastal areas.

Sea spray is composed of seawater and organic materials, and surface-active materials which may be concentrated into the 0.05 to 0.5 μm thickness of bubble surface (MacIntyre, 1974). The surface-active material may be of natural or pollutant origin and may include

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*Includes unknown amounts of indirect manmade contributions.

TABLE 4-3. AEROSOL ENRICHMENT FACTORS RELATIVE TO Al

EF[a]	Elements
0.7-7	Li, Na, K, Rb
	Be, Mg, Ca, Sr, Ba
	Sc, Y, lanthanides
	Al, Ga, Tl
	Si, Ti, Zr, Hf, Th, U
	Mn, Fe, Co, Nb
	F, P
7-70[b]	Cr, Cs, V, W, B, Ni, Ge
70-400[b]	H, In, Cu, Mo, Bi, Zn, As
400-4000[b]	I, Hg, S, Cl, Au, Ag, Sn, Sb,
	Pb, Br, Cd, Te, Se, C, N

[a]Geometric means of element ratios to Al, relative to geochemical average earth crustal material.

$$EF = \frac{(element/Al)_{aerosol}}{(element/Al)crust}$$

[b]Anomalously enriched elements arranged in order of increasing EF.

Source: Based on Rahn (1976).

organic molecular films, organic and inorganic particulate including viruses, bacteria, and large living forms (Blanchard and Parker, 1977; Duce and Hoffman, 1976). Such materials, by becoming components of sea spray aerosol droplets, may be carried through the atmosphere far from the point or origin. While not clearly understood, the potential for virus transfer from coastal waters to the atmosphere and transport by winds inland to inhibited areas has been demonstrated (Baylor et al., 1977).

Because of differences in the mechanics of droplet formation, differences in chemical composition may exist (Berg and Winchester, 1978). For example, some droplets may or may not contain the surface-active particulate matter scavenged from the water column by the rising bubbles. Chloride, bromide, and iodide also may be present (Moyers and Duce, 1972). A clear understanding of the processes through which sea spray droplets are formed and transported has not yet been achieved.

The size distribution of sea spray particles as documented by Taback et al. (1979) is as follows: >10 μm - 24 percent, 3-10 μm - 54 percent, 1-3 μm - 20 percent, <1 μm - 2 percent.

4.4.3 Biogenic Emanations

Plants emit particulate matter in the form of organic aerosols, and trace metals and nutrients. Global emissions of volatile organic compounds released from plants have been estimated at 200 x 10^6 metric tons per year (Went, 1960). The U.S. total would probably be less than 20 x 10^6 metric tons per year. Isoprene derivatives such as terpenes, carotenoids, and other compounds are believed to predominate. They are likely to be partially oxidized to CO_2 and H_2O, resulting in blue haze and submicron condensation nuclei (Went, 1960; Went et al., 1967; Rasmussen and Went, 1965; Schnell and Vali, 1972, 1973).

Trace metals have long been known to occur in fluids secreted by plants. Radiotracer strontium is transferred from plant foliage to the atmosphere, presumably in particles (Moorby and Squire, 1963) which may be affected by electric fields (Fish, 1972). Transpiration causes the transfer of both cations and anions to the atmosphere (Nemeryuk, 1970). Twenty-seven trace elements have been identified in exudates from coniferous trees (Curtin et al., 1974). Radiotracer experiments using zinc and lead show that particles greater than 5 μm in diameter contain most of the metals released (Beauford et al., 1975, 1977). Sulfur, potassium, and phosphorous have also been shown to be associated with tropical forests and to occur in large aerosol particles (Lawson and Winchester, 1979b). The metal content of plant-derived aerosols is so high that it has been suggested as an indicator for geochemical prospecting (Barringer, 1977; Curtin et al., 1974).

The terrestrial and marine biospheres, while not direct sources of sulfur dioxide, are significant sources of reduced sulfur compounds. Volatile reduced sulfur compounds are released to the atmosphere via microbiological processes and may become oxidized to SO_2 and sulfate. The compounds released included hydrogen sulfide (H_2S), dimethyl sufide (DMS), dimethyl disulfide (DDMS), carbon disulfide (CS_2), carbonyl sulfide (COS), and methyl mercaptan (CH_3SH) (Lovelock et al., 1972; Rasmussen, 1974; Lovelock, 1974; Adams et al., 1979a).

A number of previous estimates of global emissions of reduced sulfur compounds range from 64 x 10^6 metric tons per year (land) and 27 x 10^6 metric tons per year (ocean) (Robinson and Robbins, 1968) to 3 x 10^6 metric tons per year (land) and 34 x 10^6 metric tons per year (ocean) (Granat et al., 1976). Granat's estimate, scaled down to the U.S., would result in 0.2 x 10^6 metric tons per year (land) and about 2-5 x 10^6 metric tons per year (ocean) (based on Galloway and Whelpdale, 1980). These estimates, however, were derived indirectly as balances for other sulfur fluxes.

Recent field monitoring studies conducted by Maroulis and Bandy (1977), McClenny et al. (1979), and Adams et al. (1979a), result in slightly different estimates. Adams et al. (1979b) calculated a mean annual sulfur flux of 0.02 g S $m^{-2}yr^{-1}$, weighted over a number of eastern U.S. soil types, including marshes. The entire U.S. would probably average 0.02-0.05

g S $m^{-2}yr^{-1}$ (Adams, 1980). Applying these numbers to the entire earth's land area (approximately 56 million square miles) results in about 3-7 x 10^6 metric tons per year. The land area of the U.S. (3.6 million square miles) emits about 0.2-0.5 x 10^6 metric tons per year based on 0.02-0.05 g S $m^{-2}yr^{-1}$. The impact of marine biogenic activity would be limited primarily to coastal areas. Sulfur emissions from marine biogenic activity are probably on the order of 1 x 10^6 metric tons per year (based on Galloway and Whelpdale, 1980). Note that these lower estimates of sulfur emissions on a national scale do not preclude significant localized biogenic sulfur emissions, especially in areas where wetlands are prevalent (Henry and Hidy, 1980).

4.4.4 Volcanic Emissions

Emissions from volcanic eruptions and fumaroles may contribute to global atmospheric background levels of particulate matter and sulfur. Volcanoes are one of the few sources of atmospheric particulate and sulfur whose effects can be felt at great distances. Plumes from volcanoes intense enough to inject material into the upper troposphere or lower stratosphere (about 10-15 miles above the earth's surface) have been tracked great distances before removal (Fegley et al., 1980). The famous eruption of Krakatoa in 1883 injected enough dust into the stratosphere to cause brilliant sunsets thousands of kilometers away and a global reduction of incoming solar radiation (Wexler, 1951a,b).

Until recently, volcanic activity has been relatively insignificant in the United States. The Mt. St. Helens eruption was only the second this century in the contiguous United States. Mt. Lassen, California, in 1915, was the previous one. There have been about 20 other volcanic eruptions since 1900 in Hawaii and Alaska.

The average global emission rates of particulates and sulfur compounds have been estimated by a number of investigators. Robinson and Robbins (1971) estimated the average global emission rate of small particles (the persistent fraction) at 3.6 x 10^6 metric tons per year. Airborne measurements and observations made during the 1976 eruption of the St. Augustine volcano (Alaska) led to particulate emissions estimates for a one-year period for that particular volcano of 6 x 10^6 metric tons for particles of 0.01 - 66 μm in size and 0.25 x 10^6 metric tons for particles 0.01 - 5 μm in size (Stith et al., 1978).

Estimates of global volcanic sulfur emissions as documented in Granat et al. (1976), range from 0.75 - 3.75 x 10^6 metric tons per year. Emissions of SO_2 for a 1-year period at St. Augustine were estimated at 0.1 x 10^6 metric tons (or 0.05 x 10^6 metric tons of sulfur) (Stith et al., 1978). The St. Augustine volcano also emitted lesser quantities of H_2S. Stith et al. (1978) estimated global volcanic emissions of H_2S at 1 x 10^6 metric tons per year.

Particles collected from the St. Augustine eruptions were composed primarily of silicon, aluminum, magnesium, calcium, and iron. Trace amounts of potassium, titanium, and sulfur were also present (Stith et al., 1978). Samples of Mt. St. Helens ash have contained mainly silicon, aluminum, iron, calcium, sodium, magnesium, and potassium. Titanium, phosphorous, and manganese, as well as traces of sulfur, chlorine, strontium, barium, vanadium, zirconium, and zinc (among others) have also been found (Fruchter et al., 1980).

Based on the St. Augustine particulate emissions (6×10^6 metric tons total, 0.25×10^6 metric tons less than 5 μm) less than 5 percent of the particles were less than 5 μm in size (Stith, et al., 1978). According to preliminary airborne studies of Mt. St. Helens ash, significant amounts of particulate matter between 1 and 2 μm have been emitted to the atmosphere (Hobbs et al., 1980). Other preliminary studies of Mt. St. Helens ash place the fraction less than 3.5 μm at around 2 percent (Fruchter et al., 1980).

(This section could be revised depending on the availability of further information from the Mt. St. Helens eruptions.)

4.4.5 Wildfires

There are three major types of large scale fires: 1) wildfires, 2) prescription fires in natural areas, and 3) agricultural burning. The latter two types are exclusively man-caused and are mentioned in Section 4.5. Wildfires, defined by the Forest Service as "any fire that burns uncontrolled in vegetative or associated flammable material," are treated as a natural emission source, as has been done in the literature, even though man's activities cause about 90 percent of their total number; only 10 percent are truly "natural," resulting from lightning (USDA Forest Service, 1979).

Wildfire particulate emissions calculations have typically been based on three numbers: wildfire acreage, fuel burned per acre, and emissions per unit mass of fuel. Robinson and Robbins (1971) estimated yearly particulate emissions from forest fires in the U.S. as 0.7×10^6 metric tons, based on 4.5×10^6 acres burned, 18 tons of fuel per acre, and 17 pounds of particulate per ton of fuel. Yamate (1973) arrived at 0.5×10^6 metric tons per year, assuming numbers similar to those used by Robinson and Robbins.

Recent research, however, has proposed estimates of particulate emissions per unit mass of fuel at 17-67 pounds per ton (GEOMET, 1978) and 80 pounds per ton (Radke et al., 1978), based on airborne sampling studies in Oregon and Washington. Most likely, since emissions from fires are dependent on fuel conditions and fire behavior (GEOMET, 1978), an estimate in between the extremes should be chosen as an average. Assuming 40 pounds per ton, 1977 U.S. wildfire acreage of 3.15×10^6 (USDA Forest Service, 1979), and a U.S. average of 17 tons of fuel per acre (Yamate, 1973), U.S. particulate emissions from wildfires total 1.0×10^6 metric tons per year.

Chemical analysis of particulate matter from temperate forest burning indicates approximately 50 percent benzene-soluble organic matter, 40 percent elemental carbon, and 10 percent mineral matter (Ryan and McMahon, 1976). Another analysis suggests 55 percent tar, 25 percent soot, and 20 percent ash (Vines et al., 1971). About 80 percent of the mass of smoke particles from forest fires is less than 1 μm in diameter, with the average size being 0.1 μm (GEOMET, 1978; Radke et al., 1978; Vines et al., 1971).

Wildfires contribute varying amounts of other pollutants to the atmosphere. Carbon monoxide and hydrocarbons are the most significant. Wildfires are not, however, considered to be a source of sulfur oxides (Radke et al., 1978; Yamate, 1973; Vines et al., 1971).

4.5 MANMADE SOURCES AND EMISSIONS

A number of definable source categories emitting particulate matter and sulfur oxides can be attributed solely to man. They are the subjects of this section. Emissions from these source categories are summarized in Table 4-4. Manmade emissions of particulate matter result primarily from stationary point sources (fuel combustion and industrial processes), industrial process fugitive particulate emission sources, non-industrial fugitive sources (roadway dust from paved and unpaved roads, wind erosion of cropland, etc.), and transportation sources (automobiles, etc.). From Table 4-4 it is evident that non-industrial fugitive emissions are significant on a mass basis. However, these emissions normally originate away from heavily populated areas and settle out more rapidly than do point source emissions.

TABLE 4-4. SUMMARY OF ESTIMATED ANNUAL MANMADE EMISSIONS

Source Category	Emissions (10^6 Metric tons)	
	Particulate matter	Sulfur oxides
Stationary point sources	10	26.2
Industrial Process Fugitives	3.3[a]	-
Non-industrial fugitives	110-370	-
Transportation sources	1.3	0.8
TOTAL	~125-385	27.0

[a]NOTE: Approximately half of the 3.3 x 10^6 metric tons from process fugitives are probably included in the 10.5 x 10^6 metric tons from stationary point sources. See Section 4.3 for explanation.

Manmade emissions of sulfur oxides result almost exclusively from stationary point sources. The combustion of fossil fuels by electric utilities causes most sulfur oxide emissions. Transportation sources also contribute a small amount of sulfur oxide emissions.

4.5.1 Historical Emission Trends[a]

Economic conditions and the degree to which air pollution control devices are used are the two factors having the most impact on emissions totals, especially from stationary point sources (fuel combustion and industrial processes). Economic conditions affect the amounts of goods produced and, therefore, the amounts of emissions generated. The economics of relative fuel prices also affects emissions. That is, higher prices on oil and natural gas cause increased use of coal, which generally emits more particulate matter and sulfur oxides per unit energy than oil or natural gas. Increased use of control devices has resulted from the enactment of regulations such as New Source Performance Standards and State Implementation Plans.

Historical trends in particulate matter (not including fugitive emissions, which have not been documented) and sulfur oxide emissions are shown in Table 4-5. Data for the years 1940, 1950, and 1960 are from U.S. EPA (1978b), while data for 1970 through 1978 are from U.S. EPA

[a]Sources: U.S. EPA (1978b); U.S. EPA (1980a)

TABLE 4-5 (a) NATIONAL ESTIMATES OF PARTICULATE EMISSIONS[a]
(10^6 metric tons per year)

SOURCE CATEGORY	1940	1950	1960	1970	1975	1978
Stationary fuel combustion	8.7	8.1	6.7	7.2	5.1	3.8
Industrial processes	9.9	12.6	14.1	12.8	7.4	6.2
Solid waste disposal	0.5	0.7	0.9	1.1	0.5	0.5
Transportation	0.5	1.1	0.6	1.1	1.0	1.3
Miscellaneous[b]	5.2	3.7	3.3	1.0	0.6	0.7
TOTAL	24.8	26.2	25.6	23.2	14.6	12.5

Table 4-5 (b) NATIONAL ESTIMATES OF SULFUR OXIDE EMISSIONS
(10^6 metric tons per year)

SOURCE CATEGORY	1940	1950	1960	1970	1975	1978
Stationary fuel combustion	15.1	16.6	15.7	22.7	20.9	22.1
Industrial processes	3.4	4.1	4.8	6.2	4.5	4.1
Solid waste disposal	0.0	0.1	0.0	0.1	0.0	0.0
Transportation	0.6	0.8	0.5	0.7	0.8	0.8
Miscellaneous[b]	0.4	0.4	0.4	0.1	0.0	0.0
TOTAL	19.5	22.0	21.4	29.8	26.2	27.0

[a]Does not include industrial process fugitive particulate emissions, and non-industrial fugitives from paved and unpaved roads, wind erosion, construction activities, agricultural tilling, and mining activities.

[b]Includes forest fires, agricultural burning, coal refuse burning, and structural fires.

SOURCES: U.S. Environmental Protection Agency (1978b)
U.S. Environmental Protection Agency (1980a)

(1980a). Emissions estimates from the latter are considered more accurate. It should be noted that local emission trends might not necessarily coincide with national emission trends.

Nationwide emissions of particulate matter (not including fugitive emissions) have generally decreased since 1950 after a slight increase from 1940 to 1950. These emissions have resulted primarily from stationary fuel combustion (utility and industrial) and industrial processes. Particulate emissions from stationary fuel combustion decreased fairly consistently from 1940 to 1978. From 1940 through the early 1970's this was probably due to increased use of oil and natural gas. Even though the oil embargo of 1973-1974 caused increased use of coal, conservation efforts by industry and the installation of control equipment resulted in further reductions in particulate emissions through 1978.

Industrial process emissions of particulate matter increased from 1940 to 1960, then declined steadily through 1978. Increases were due to expanding production, while decreases were due to installation of controls.

Nationwide emissions of sulfur oxides have increased overall since 1940. As with particulate matter, stationary fuel combustion (primarily utility and industrial) and industrial processes (primarily ore smelting) have been the main contributors. Coal combustion was the largest stationary fuel combustion source. Coal use by industrial, commercial/institutional, and residential users has declined, corresponding with a decrease in sulfur oxide emissions from those categories. Increased coal use by electric utilities, however, has more than offset this decrease. Sulfur oxide emissions from electric utilities account for more than half the total emissions. Flue gas desulfurization (FGD) systems have seen only limited use to date and have not had a major impact on emissions. About eleven percent of U.S coal-fired electrical generating capacity is presently fitted with FGD (U.S. EPA 1980e).

From industrial processes, increased production caused most of the sulfur oxide emission increases through 1970. However, since that time significant emission reductions from non-ferrous smelters and sulfuric acid plants have occurred. For smelters, by-product recovery of sulfuric acid has significantly reduced sulfur oxide emissions. Sulfur oxide emissions from copper, lead and zinc smelters have gone from 4×10^6 metric tons per year in 1970 to about 2×10^6 metric tons per year in 1978.

Future emission trends are subject to a number of assumptions concerning economic climate, fuel use, environmental policy, and control technology. These considerations are beyond the scope of this document. (See U.S. DOE 1978 and U.S. DOE 1979.)

4.5.2 Stationary Point Source Emissions

This section presents an analysis of sources and characteristics of particulate and sulfur oxide emissions from stationary point sources; the two major categories are fuel combustion and industrial processes. A third but minor category is solid waste disposal. Table 4-6 lists calculated estimates of 1978 emissions from these source categories. Based on these estimates, fuel combustion contributed 36 percent of the particulates and 84 percent of

TABLE 4-6. 1978 ESTIMATES OF PARTICULATE AND SULFUR OXIDE EMISSIONS FROM STATIONARY POINT SOURCES[a]

Source category	Emissions (10^3 metric tons) Particulates	Sulfur oxides
Fuel combustion		
Utility		
Coal	2,350	15,900
Oil	140	1,720
Gas	10	0
Industrial		
Coal	700	1,890
Oil	90	1,150
Gas	40	0
Other fuels[b]	280	150
Commercial/Institutional		
Coal	20	40
Oil	60	900
Gas	10	0
Residential		
Coal	20	60
Oil	20	260
Gas	30	0
Industrial processes		
Metals		
Iron and steel	830	110
Primary smelting	480	1,960
Iron foundries	140	0
Other	120	0
Mineral Products		
Cement	780	670
Asphalt	150	0
Lime	150	0
Crushed rock	1,340	0
Other	910	30

TABLE 4-6. (continued)

Source category	Emissions (10^3 metric tons) Particulates	Sulfur oxides
Petroleum		
Refining	70	900
Natural gas production	0	140
Chemicals		
Sulfuric acid	0	220
Other	190	0
Other		
Grain processing	730	0
Pulp and paper	240	80
Other	60	0
Solid waste disposal	500	0
TOTAL	10,460	26,180

[a]Source: U.S. Environmental Protection Agency (1980a).
[b]Primarily wood/bark waste.

the sulfur oxides emitted by stationary point sources in 1978. Industrial processes emitted 59 percent of the particulates and 16 percent of the sulfur oxides. Solid waste disposal contributed 5 percent of the particulates.

An unknown percentage of particulates and sulfur oxides is emitted as primary sulfates. Primary sulfates consist of gaseous sulfur trioxide (SO_3), sulfuric acid (H_2SO_4), and particulate sulfates. Estimates of primary sulfate emission quantities from major sources have not been generated to date. Primary sulfates are of increasing concern because of their potential impacts, especially on health.

Geographically, the different regions of the United States, shown in Figure 4-1, emitted varying amounts of particulate matter and sulfur oxides. Table 4-7 presents state and regional estimates of population (1979), emissions (based on the 1977 NEDS inventory), emissions densities, and percentage contributions to total U.S. point source emissions. Based on this information, Regions III through VI emitted over 70 percent of the particulate matter and sulfur oxides emitted by stationary sources in the U.S. In Region III utility and industrial fuel combustion contributed most of the particulates and sulfur oxides. The mineral products industry also contributed heavily to particulate emissions. In Regions IV and V utility fuel combustion and the mineral products industry contributed most of the particulate emissions, while utility fuel combustion contributed most of the sulfur oxide emissions. The mineral products industry and total fuel combustion caused most of the

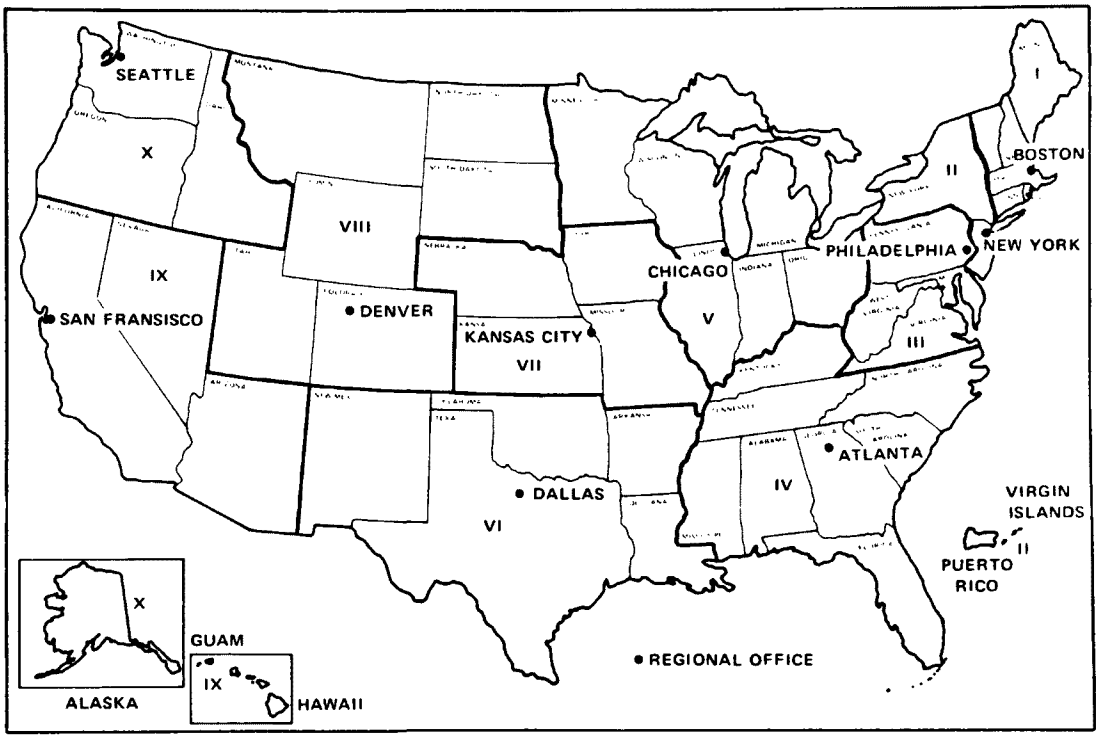

Figure 4-1. Map of EPA Regions.

TABLE 4-7. STATE-BY-STATE LISTING OF TOTAL ESTIMATED PARTICULATE AND SULFUR OXIDE EMISSIONS FROM STATIONARY POINT SOURCES (1977),[a] POPULATION, AND DENSITY FACTORS

Region and state	Population (1000's)[b]	Total area (mi^2)[c]	Population density (people/mi^2)	Particulates: Total emissions (10^3 metric tons)	Particulates: Emission density (tons/mi^2)	Particulates: State emissions (% of U.S.)	Sulfur Oxides: Total emissions (10^3 metric tons)	Sulfur Oxides: Emissions density (tons/mi^2)	Sulfur Oxides: State emissions (% of U.S.)
Region I									
Connecticut	3,099	5,009	619	26.8	5.4	0.34	71.9	14.4	0.26
Maine	1,091	33,215	33	42.2	1.3	0.53	125.3	3.8	0.45
Massachusetts	5,774	8,257	704	52.8	6.4	0.67	265.3	32.1	0.95
New Hampshire	871	9,304	94	10.8	1.2	0.14	107.9	11.6	0.39
Rhode Island	935	1,214	770	3.9	3.2	0.05	17.2	14.2	0.06
Vermont	487	9,609	51	4.5	0.5	0.06	8.9	0.9	0.03
TOTAL	12,257	66,608	184	141.0	2.1		596.5	9.0	
Percent of U.S.	5.5	1.8		1.8			2.1		
Region II									
New Jersey	7,327	7,836	935	63.6	8.1	0.81	259.4	33.1	0.93
New York	17,748	49,576	358	206.6	4.2	2.62	897.3	18.1	3.22
Puerto Rico	2,712	3,435	790	55.9	16.3	0.71	291.4	84.8	1.05
Virgin Island	62	133	466	11.3	85.0	0.14	3.7	27.8	0.01
TOTAL	27,849	60,980	457	337.4	5.5		1,451.8	23.8	
Percent of U.S.	12.6	1.7		4.3			5.2		
Region III									
Delaware	582	2,057	283	32.6	15.8	0.41	118.6	57.7	0.43
District of Columbia	674	67	10,060	2.7	40.3	0.03	21.3	317.9	0.08
Maryland	4,144	10,577	392	46.8	4.4	0.59	305.5	28.9	1.10
Pennsylvania	11,862	45,333	259	685.0	15.1	8.69	2,235.3	49.3	8.03
Virginia	5,032	40,817	126	116.4	2.9	1.48	396.0	9.7	1.42
West Virginia	1,821	24,181	77	187.2	7.7	2.38	1,109.0	45.9	3.98
TOTAL	24,143	123,032	196	1,070.7	8.7		4,185.7	34.0	
Percent of U.S.	10.9	3.4		13.6			15.0		

TABLE 4-7. Continued

Region and state	Population (1000's)[b]	Total area (mi^2)[c]	Population density (people/mi^2)	Particulates: Total emissions (10^3 metric tons)	Particulates: Emission density (tons/mi^2)	Particulates: State emissions (% of U.S.)	Sulfur Oxides: Total emissions (10^3 metric tons)	Sulfur Oxides: Emissions density (tons/mi^2)	Sulfur Oxides: State emissions (% of U.S.)
Region IV									
Alabama	3,742	51,609	73	264.5	5.1	3.36	919.7	17.8	3.30
Florida	8,594	58,560	147	191.0	3.3	2.42	873.4	14.9	3.14
Georgia	5,084	58,876	86	107.5	1.8	1.36	620.8	10.5	2.23
Kentucky	3,498	40,395	87	385.3	9.5	4.89	1,471.0	36.4	5.28
Mississippi	2,404	47,716	50	147.9	3.1	1.88	225.8	4.7	0.81
North Carolina	5,577	52,586	106	186.9	3.6	2.37	547.4	10.4	1.97
South Carolina	2,918	31,055	94	89.5	2.9	1.14	264.8	8.5	0.95
Tennessee	4,357	42,244	103	143.2	3.4	1.82	1,145.4	27.1	4.12
TOTAL	36,174	383,041	94	1,515.8	4.0		6,068.3	15.8	
Percent of U.S.	16.4	10.6		19.2			21.8		
Region V									
Illinois	11,243	56,400	199	473.4	8.4	6.01	1,522.6	27.0	5.47
Indiana	5,374	36,291	148	393.4	10.8	4.99	1,700.2	46.8	6.11
Michigan	9,189	58,216	158	233.4	4.0	2.96	1,093.3	18.8	3.93
Minnesota	4,008	84,068	48	127.9	1.5	1.62	247.1	2.9	0.89
Ohio	10,749	41,222	261	585.3	14.2	7.43	2,932.0	71.1	10.53
Wisconsin	4,679	56,154	83	249.6	4.4	3.17	594.2	10.6	2.13
TOTAL	45,242	332,351	136	2,063.0	6.2		8,089.4	24.3	
Percent of U.S.	20.5	9.2		26.2			29.1		
Region VI									
Arkansas	2,186	53,104	41	123.6	2.3	1.57	119.1	2.2	0.43
Louisana	3,966	48,523	82	303.8	6.3	3.85	311.7	6.4	1.12
New Mexico	1,212	121,666	10	81.2	0.7	1.03	516.2	4.2	1.85
Oklahoma	2,880	69,919	41	81.7	1.2	1.04	101.2	1.4	0.36
Texas	13,014	267,338	49	422.3	1.6	5.36	1,314.9	4.9	4.72
TOTAL	23,258	560,550	41	1,012.6	1.8		2,363.1	4.2	
Percent of U.S.	10.5	15.5		12.8			8.5		

TABLE 4-7. Continued

Region and state	Population (1000's)[b]	Total area (mi^2)[c]	Population density (people/mi^2)	Particulates: Total emissions (10^3 metric tons)	Particulates: Emission density (tons/mi^2)	Particulates: State emissions (% of U.S.)	Sulfur Oxides: Total emissions (10^3 metric tons)	Sulfur Oxides: Emissions density (tons/mi^2)	Sulfur Oxides: State emissions (% of U.S.)
Region VII									
Iowa	2,896	56,290	51	209.1	3.7	2.65	308.2	5.5	1.11
Kansas	2,348	82,264	29	170.6	2.1	2.16	172.1	2.1	0.62
Missouri	4,860	69,686	70	171.9	2.5	2.18	1,355.2	19.4	4.87
Nebraska	1,565	77,227	20	125.9	1.6	1.60	51.3	0.7	0.18
TOTAL	11,669	285,467	41	677.5	2.4		1,886.8	6.6	
Percent of U.S.	5.3	7.4		8.6			6.8		
Region VIII									
Colorado	2,670	104,247	26	40.4	0.4	0.51	99.6	1.0	0.36
Montana	785	147,138	5	29.8	0.2	0.38	189.8	1.3	0.68
North Dakota	652	70,665	9	33.6	0.5	0.43	113.5	1.6	0.41
South Dakota	690	77,047	9	43.1	0.6	0.55	38.7	0.5	0.14
Utah	1,307	84,916	15	91.7	1.1	1.16	198.6	2.3	0.71
Wyoming	424	97,914	4	171.8	1.8	2.18	173.5	1.8	0.62
TOTAL	6,528	581,927	11	410.4	0.7		813.7	1.4	
Percent of U.S.	3.0	16.1		5.2			2.9		
Region VII									
Iowa	2,896	56,290	51	209.1	3.7	2.65	308.2	5.5	1.11
Kansas	2,348	82,264	29	170.6	2.1	2.16	172.1	2.1	0.62
Missouri	4,860	69,686	70	171.9	2.5	2.18	1,355.2	19.4	4.87
Nebraska	1,565	77,227	20	125.9	1.6	1.60	51.3	0.7	0.18
TOTAL	11,669	285,467	41	677.5	2.4		1,886.8	6.6	
Percent of U.S.	5.3	7.4		8.6			6.8		

TABLE 4-7. Continued

Region and state	Population (1000's)[b]	Total area (mi^2)[c]	Population density (people/mi^2)	Particulates: Total emissions (10^3 metric tons)	Particulates: Emission density (tons/mi^2)	Particulates: State emissions (% of U.S.)	Sulfur Oxides: Total emissions (10^3 metric tons)	Sulfur Oxides: Emissions density (tons/mi^2)	Sulfur Oxides: State emissions (% of U.S.)
Region VIII									
Colorado	2,670	104,247	26	40.4	0.4	0.51	99.6	1.0	0.36
Montana	785	147,138	5	29.8	0.2	0.38	189.8	1.3	0.68
North Dakota	652	70,665	9	33.6	0.5	0.43	113.5	1.6	0.41
South Dakota	690	77,047	9	43.1	0.6	0.55	38.7	0.5	0.14
Utah	1,307	84,916	15	91.7	1.1	1.16	198.6	2.3	0.71
Wyoming	424	97,914	4	171.8	1.8	2.18	173.5	1.8	0.62
TOTAL	6,528	581,927	11	410.4	0.7		813.7	1.4	
Percent of U.S.	3.0	16.1		5.2			2.9		
Region IX									
Arizona	2,354	113,909	21	64.4	0.6	0.82	1,118.2	9.8	4.02
California	22,294	158,693	140	235.4	1.5	2.99	515.8	3.3	1.85
Hawaii	897	6,450	139	17.5	2.7	0.22	56.0	8.7	0.20
Nevada	660	110,540	6	89.5	0.8	1.14	298.2	2.7	1.07
Guam	85	212	401	4.5	21.2	0.06	53.7	253.3	0.19
TOTAL	26,317	389,880	68	411.3	1.1		2,041.9	5.2	
Percent of U.S.	11.9	10.8		6.2			9.0		
Region X									
Alaska	403	589,757	1	23.1	<0.01	0.29	15.6	<0.01	0.06
Idaho	878	83,557	11	25.2	0.3	0.32	45.7	0.5	0.16
Oregon	2,444	96,981	25	81.2	0.8	1.03	39.3	0.4	0.14
Washington	3,774	68,192	55	112.8	1.7	1.43	235.7	3.5	0.85
TOTAL	7,499	838,487	9	242.3	0.3		336.3	0.4	
Percent of U.S.	3.4	23.0		3.1			1.2		
U.S. TOTALS	220,951	3,620,000	61	7,882	2.2		27,834	7.7	

[a]Source: U.S. Environmental Protection Agency (1978b). The accuracy of these data may not warrant the number of significant figures shown.
[b]Source: U.S. Department of Commerce (1979).
[c]Source: The World Almanac and Book of Facts 1980 (1980).

particulate emission in Region VI. The primary metals and petrochemical industries, along with fuel combustion contributed most of the sulfur oxides emissions in Region VI.

In other regions grain processing (Region VII) and mineral products (Region IX) emitted large amounts of particulate matter. Fuel combustion (Regions II and VII) and the primary metals industry (Region IX) contributed significant amounts of sulfur oxides.

The quantity and characteristics (size and composition) of particulate matter emissions from stationary sources may be affected by several factors. Among these are source type, operating conditions and practices, fuel characteristics (if the source is a fuel combustion source), and type of emission control equipment, if any. The chemical composition of emitted particles can determine possible reactions that occur during transport and the final effects upon receptors (see Chapters 5 and 6). Particle size affects suspension time and transport distance. It is also an important factor in determining any possible health effects (see Chapters 13, 14, and 15).

Table 4-8 presents a summary of particle size and chemical composition data for uncontrolled particulate emissions from stationary sources. Note that these data are for uncontrolled emissions. This is significant because control devices exert strong influence on the particle size distribution of emissions. Table 4-9 illustrates that, for coal-fired boilers, most control devices are more efficient at removing larger particles. Therefore, even though the total mass of smaller particles decreases, the percentage increases. [Refer to U.S. EPA (1980b) for further discussion on the effects of control devices on emissions characteristics.] Therefore, applying the particle size percentages shown in Table 4-8 to the emission quantities listed in Table 4-6 and 4-7 would probably result in an underestimation of the finer particle fractions since Tables 4-6 and 4-7 were arrived at assuming the application of control devices.

As a further example, control devices have helped reduce the mass flow of particulate emissions in California's South Coast Air Basin by 95 percent or more from what prevailed under uncontrolled conditions. However, over 90 percent of the remaining emissions (both point sources are miscellaneous area sources) have particle sizes less than 10 μm (Taback et al., 1979).

A final point with respect to Table 4-8 is that the particle size and chemical composition data represent an overall source category. Therefore, in the iron and steel industry, for example, not all of the many different processes emitting particulate matter would necessarily have emissions exhibiting that exact characteristics shown. The reader should refer to the documents cited for more detailed information.

The same factors mentioned earlier may affect the quantity and characteristics of sulfur oxide emissions. By volume, over 90 percent of total national sulfur oxide emissions are in the form of sulfur dioxide, SO_2. Primary sulfates account for most of the other 10 percent. Little is known about primary sulfates, but combustion of coal and oil is thought to be a major source. Primary sulfates are of increasing concern because of their potential impacts on visibility, acidic deposition, and health.

TABLE 4-8. EXAMPLES OF UNCONTROLLED PARTICULATE EMISSION CHARACTERISTICS[a]

Source category	Particle size data[b] (weight % less than stated size) 15 μm	2.5 μm	1.0 μm	Chemical Composition Data[c] Major elements and compounds	Trace elements (less than 1% by weight)
Fuel combustion					
Utility					
Coal	15-90	5-70	1-15	Al,Ca,Fe,Si, sulfates,organics	As,B,Ba,Be,Cd,Cl,Co,Cr, Cu,F,Hg,K,Mg,Mn,Na,Ni, P,Pb,S,Se,Ti,V,Zn,Zr
Oil	95	70-95	95	Al,Ca,Fe,Mg,Na, sulfates,organics	As,Ba,Br,Co,Cr,Cu,K, Mn,Mo,Ni,Pb,Se,Sr,Ti,V
Industrial					
Oil			65-95	Al,Fe,Mg,Si, sulfates,organics	As,Ba,Ca,Cd,Co,Cr,Cu,Hg, K,Mo,Ni,Ph,Se,Sr,Ti,V,Zn
Gas			100	Cl,Na,sulfates, organics	
Com/Inst/Res					
Oil				Al,Ca,Mg,Zn, sulfates	As,Ba,Cd,Cr,Cu,Hg,K, Ni,Pb,Sb,C
Gas			100	Cl,Na,sulfates organics	

TABLE 4-8. (continued)

Source category	Particle size data[b] (weight % less than stated size) 15 μm	2.5 μm	1.0 μm	Chemical Composition Data[c] Major elements and compounds	Trace elements (less than 1% by weight)
Industrial processes					
Metals					
Iron and steel		35-99	40-95	Al,C,Ca,Cr,Fe,K,Mg, Mn,Pb,Si,Zn, sulfates,organics	Ag,As,Br,Cd,Cs,Cu,F,I, Mo,Ni,Rb,Se,Sn,Sr,V,Zr
Primary aluminum	90	75	35-45	Al,C,Ca,F,Fe,Na	
Primary copper		20-95	70	Cu,Pb,S,Zn	Ag,Al,As,Cd,Hg,Sb,Se, Si,Te
Primary lead		80		Pb,Zn	As,Cd,Se,Te
Primary zinc		90-98		Cd,Fe,Pb,S,Zn	Cu,Hg,Mn,Sn
Iron foundries	70-95	65-90	65		
Mineral products					
Cement	80	30	5-35	Al,C,Ca,Cl,K,Mg, Na,Si,carbonates, sulfates	Ag,Ba,Cd,Cr,Cu,F,Fe,Mn, Mo,Ni,Pb,Rb,Se,Ti,Zn
Asphalt	10	1	0-30	Al,C,Ca,Fe,K,Mg, Si,sulfates	Ag,As,Ba,Cr,Ti
Lime		25-50	5	Ca,Fe,Mg,Se,Si, carbonates	
Gypsum			20	Al,C,CA,Mg,Na, sulfates	As,Ba,Br,Cd,Cl,Cr,Cu, Fe,K,Mn,Mo,Ni,Pb,Se, Sr,Y.Zn

TABLE 4-8. (continued)

Source category	Particle size data[b] (weight % less than stated size) 15 μm	2.5 μm	1.0 μm	Chemical Composition Data[c] Major elements and compounds	Trace elements (less than 1% by weight)
Crushed rock			1-2	Ca,Si,P	Ba,Cu,Fe,K,Mn,Sr
Petroleum			50-90	Asphalt, coke dust, sulfuric acid mist, flyash, soot	
Chemicals					
sulfuric acid		40-95	10-55	Sulfuric acid mist	
Others					
Grain processing		2	0	Organics	
Pulp and paper	90-95	70-80		Ca,Mg,Na,carbonates, sulfates	
Solid waste disposal					
Incinerators	45	35			

[a]Sources: Surprenant et al. (1979); Taback et al. (1979); U.S. Environmental Protection Agency (1980c); U.S. Environmental Protection Agency (1980d).

[b]Since a number of references were cited, some characterizing different processes, discrepancies may exist in the ranges shown.

[c]Elements and compounds listed were included in at least one of the references cited.

4.5.2.1 Fuel Combustion--Stationary fuel combustion includes all boilers, heaters, and furnaces. Utilities, industry, and commercial/institutional and residential establishments are the fuel combustion source categories. In the utility and industrial sectors, coal, and to a lesser degree, oil combustion contribute most of the particulate and sulfur oxides emissions (see Table 4-6). Oil combustion causes most of these emissions from commercial/institutional and residential establishments.

Coal is a slow-burning fuel with a relatively high ash content. Coal combustion particulates consist primarily of carbon, silica, alumina, and iron oxide. See Table 4-9. Particulate sulfates and trace elements are also included. A large percentage of the trace elements in raw coal remain in the solid waste or bottom ash. Table 4-10 (based on 1974 emissions data) shows this. The roughly 940,000 metric tons of trace elements emitted to the atmosphere represent about 15 percent of total particulate emissions.

Uncontrolled, the quantity and particle size distribution of coal fly ash depend on the amount and type of coal burned, the unit type, and the ash content of the coal. Cyclone and pulverized-coal furnaces, typically used in utility boilers, discharge finer particles than stoker-fired boilers, used mainly by industry. The combustion of low-ash coal produces less particulate matter than the combustion of high-ash coal. High-sodium lignite causes less combustion particulate formation than does low-sodium lignite (U.S. Environmental Protection Agency, 1977).

In the combustion of most coals (most commonly bituminous), greater than 90 percent of the coal sulfur is converted to gaseous SO_2 about 1 to 2 percent of the emitted sulfur oxides are in the form of primary sulfates (Homolya and Cheney 1978a; Homolya and Cheney, 1979).

Lignite is being utilized where it is plentiful at relatively low cost. The alkali content (mostly sodium) of lignite ash has a major effect on the amount of coal sulfur retained in bottom ash. A high-sodium lignite may retain over 50 percent of the available sulfur, while a low-sodium lignite may retain less than 10 percent (U.S. Environmental Protection Agency, 1977).

Several factors can affect the formation of primary sulfates from coal-fired boilers. The higher excess oxygen levels commonly used in industrial boilers increase the oxidation of SO_2 to SO_3 and H_2SO_4 (Homolya and Cheney, 1978a; Bennett and Knapp, 1978). Most gaseous SO_3 is hydrated to gaseous or aerosol H_2SO_4 before exiting the boiler stack (Homolya and Cheney, 1979). Dirty equipment may also increase primary sulfate emissions from coal-fired boilers since boiler deposits can act as catalysts in the oxidation of SO_2 to sulfates. Conversely, the relatively low flame temperatures used in most coal-fired boilers lessen the formation of SO_3 from SO_2.

After coal, oil combustion in the utility and industrial sectors contributes the greater amounts of emissions. In direct contrast to coal, however, oil is a fast burning, low ash fuel. The low ash content results in formation of less particulate matter, but the size of particles formed by oil combustion is generally smaller than of particles formed by coal

TABLE 4-9. SIZE SPECIFIC PARTICULATE EMISSIONS FROM COAL-FIRED BOILERS[a]

Control device	Inlet size distribution (uncontrolled) (Mass percent less than)		Outlet size distribution (controlled) (Mass percent less than)		Removal Efficiency (%) (at)		
	15 μm	2.5 μm	15 μm	2.5 μm	15 μm	2.5 μm	overall
ESP	15-50	5-20	70-95	15-70	65-99+	60-95	85-99+
Wet scrubber	30-95	10-70	80-95	50-90	75-95	50-90	80-95
Fabric filter[b]	55-65	20-45	~80	20-90	~99	~99	~99

[a]Source: U. S. Environmental Protection Agency (1980d).

[b]Based on limited data.

TABLE 4-10. TRACE ELEMENT AIR EMISSIONS VS. SOLID WASTE: PERCENT FROM CONVENTIONAL STATIONARY FUEL COMBUSTION SOURCES, AND TOTAL (METRIC TONS PER YEAR)[a]

Element	Air emissions (fly ash)					Solid waste (bottom ash)				
	Util	Indust	Com/Inst	Res	Total	Util	Indust	Com/Inst	Res	Total
As	90	8	2	<1	2,990	89	9	1	1	12,250
Ba	88	9	3	<1	2,770	83	13	2	2	15,970
Be	89	9	2	<1	240	83	12	2	3	740
B	90	9	1	<1	4,990	85	13	1	2	16,240
Br	84	13	2	1	6,080	0	0	0	0	0
Cd	61	21	18	<1	300	83	14	1	2	110
Cl	83	13	2	2	644,100	0	0	0	0	0
Cr	84	11	5	<1	1,630	75	12	5	8	5,040
Co	63	23	14	<1	460	69	9	8	14	1,920
Cu	72	16	12	<1	2,540	78	12	4	6	4,280
F	83	13	2	2	33,570	0	0	0	0	0
Fe	77	20	3	<1	154,200	87	9	2	2	1,369,900
Pb	92	7	1	<1	1,180	81	15	2	3	2,530
Mn	89	10	1	<1	4,630	98	1	1	<1	12,520
Hg	81	14	3	2	50	78	20	2	<1	10
Ni	60	21	19	<1	7,350	81	12	3	4	4,700
Se	85	13	2	1	790	76	22	1	1	370
Ti	89	9	2	<1	56,250	83	13	2	2	178,700
U	86	10	4	<1	1,540	84	13	1	2	4,510
V	63	20	17	<1	9,980	84	12	1	2	8,450
Zn	89	10	1	<1	2,090	83	13	2	3	6,890
Zr	78	20	2	<1	2,090	86	11	1	2	17,240
					939,820					1,662,370

[a]Source: Suprenant et al. (1976).

combustion (see Table 4-8). Also, while coal combustion contributes most of the trace elements associated with particulate emissions, oil combustion is the source of 50 to 80 percent of cadmium, cobalt, copper, nickel, and vanadium emissions (Suprenant et al., 1976).

Oil-fired boilers generally convert over 90 percent of available fuel sulfur to gaseous SO_2 emissions. However, high flame temperatures used in the combustion of oil exacerbate the formation of primary sulfates. Tests have shown that about 7 percent by weight of sulfur oxide emissions from oil combustion is emitted as primary sulfates (Homolya and Cheney, 1978b). Increasing excess oxygen and increasing the oil vanadium content will increase the formation of primary sulfates (Homolya and Cheney, 1978b; Bennett and Knapp, 1978; Dietz et al., 1978). Vanadium acts as a catalyst in the oxidation of SO_2 to SO_3.

Low sulfur oil and natural gas are the fuels typically used for space heating in the commercial/institutional and residential sectors. Total emissions are minor compared with the utility and industrial sectors. However, most commercial/institutional and residential sources are in areas of high population density and release emissions at or near ground level, thereby providing for high population exposure (Suprenant et al., 1979). Also, emissions are concentrated primarily during the winter heating season.

There has currently been a trend toward homeowners burning coal or wood in auxiliary space heaters to lower fuel bills. Should this trend continue, the increased emissions from this sector could significantly affect urban air quality.

4.5.2.2 Industrial Processes--Major industrial process sources of particulate and sulfur oxide emissions include the metals, mineral products, petroleum, and chemicals industries. Others are grain processing and pulp and paper production. See Table 4-6.

The most significant emitters in the metals industry are iron and steel, and primary smelting. The iron and steel industry involves coke, iron, and steel production. Coking is the process of heating coal in a low-oxygen atmosphere to remove volatile components, which are recovered. Coke is used in the production of iron. Both particulates and sulfur oxides result from charging of coal to the hot ovens, door and topside leaks, underfiring, pushing (removal of hot coke), and quenching. Some fine particles consist, at least partly, of condensed organic components.

Particulate emission sources of iron production include the combustion gases, tapping operations, and blast furnace slips (operations that require bypassing the control device). The emitted particles are probably all fine particles that either escape the control device or result from tapping (see Table 4-8). Blast furnace flue dust is composed primarily of iron, silicon dioxide, and aluminum oxide, among others.

Steel is produced several different ways. The basic oxygen furnace produces steel from a furnace charge composed of about 70 percent molten pig iron and 30 percent scrap. A stream of commercially pure oxygen is used to oxidize impurities, principally carbon and silicon. The tremendous agitation produced by the oxygen lancing produces high dust loadings consisting

mostly of iron and small amounts of fluorides. Most of the particles are less than 5 μm. One source reports that the particles contained 80 ppm cadmium, 4600 ppm lead, and 45,000 zinc.

From 1960 to 1975, steel production in open hearth furnaces declined from 90 percent of the U.S. total to 20 percent (Desy, 1978). Open hearth furnaces are being replaced by basic oxygen furnaces which produce 272 or more metric tons of steel per hour compared to the 27 to 54 metric tons per hour typically produced in an open hearth furnace. The composition of particulate emissions is similar to the basic oxygen furnace. Most of the emissions before control are less than 5 μm and probably 90 percent are fine particles after control.

Two types of electric furnaces, the arc furnace and the induction furnace, are used to produce steel. The arc furnace is used to produce high-alloy steel, as well as a considerable amount of mild steel. Particulate emissions consist primarily of oxides of iron, manganese, aluminum, calcium, magnesium, and silicon. Particulate fluorides are also emitted. Emissions are primarily fine particles. The induction furnace produces primarily specialty and high alloy steels with no real emission problems.

The primary metals industry includes the smelting of copper, lead, and zinc, along with aluminum production. Sulfur in unprocessed copper, lead, and zinc ores is converted to SO_2 in the smelting processes (U.S. Environmental Protection Agency, 1977). A relatively small portion of the sulfur is emitted as particulate sulfate and sulfuric acid. The bulk of SO_2 is formed in the roasting, smelting, sintering, and converting processes (U.S. Environmental Protection Agency, 1974). Particulate matter emitted from the same processes is mostly fine particles, less than 2.5 μm in diameter.

Aluminum production involves mainly bauxite calcining, reduction, and grinding. Particulate emissions are primarily alumina with about 25 percent particulate fluoride (U.S. Environmental Protection Agency, 1977). Before control, 35 to 44 percent of the particles are below one micron in diameter.

Emissions from the mineral products industry result primarily from the production of Portland cement, asphalt, and crushed rock. Others include lime, glass, gypsum, brick, fiberglass, cleaned coal, phosphate rock, and potash. Emission points such as crushing, screening, conveying, grinding, drying or calcining, and loading are common to most mineral products industries. Fugitive dust from most of these processes tends to be larger than 15 microns. However, drying and calcining produce relatively finer particulates. The composition of particulate emissions is similar to the mineral being processed.

More than 30 raw materials are used to make cement. They can be divided into four basic categories: lime (calcareous), silica (siliceous), alumina (argillaceous), and iron (ferriferous). The kiln and associated clinker cooler are potentially the largest sources of particulate and sulfur oxides emissions (U.S. Environmental Protection Agency, 1977). Kiln emissions also include primary sulfates (Dellinger et al., 1980). Probable particle size distribution and chemical composition are shown in Table 4-8.

Asphalt concrete is a mixture of aggregate, asphalt cement, and occasionally mineral filler. Commonly, asphalt concrete is produced in conjunction with crushed and broken stone production facilities. The rotary dryer typically used to dry and heat the aggregate is potentially the largest particulate emission source (U.S. Environmental Protection Agency, 1977).

Emissions from the production of crushed rock result primarily from the processes mentioned earlier. The chemical composition of particulate emissions is similar to the material processed. The particles emitted are normally relatively coarse.

The major sources of sulfur oxide emissions in the petroleum industry are the catalytic cracking and sulfur recovery processes and off-gas flares (U.S. Environmental Protection Agency, 1977); Dickerman et al., 1977). SO_2 emissions from the catalytic cracking process are emitted during the catalyst regeneration step.

Major sour gas streams are usually treated in a sulfur plant. Most sulfur plants utilize a modified Claus process which consists of multi-stage oxidation of hydrogen sulfide to elemental sulfur. The sulfur recovery efficiency of these sulfur plants ranges from 92 to 97 percent depending on the number of catalytic stages. Sulfur plant tail gas is usually incinerated so that most of the remaining sulfur species are oxidized to SO_2. Some plants have installed tail gas clean-up systems to further reduce SO_2 emissions. These units along with a sulfur plant can achieve up to 99.8 percent sulfur recovery.

Minor off-gas streams and recovered vapors are often combusted in flares. Most of the sulfur species present in these vapors are oxidized to SO_2.

A variety of processes make up the chemical production industry. Chemical process industries that contribute significant amounts of sulfur oxide emissions are sulfuric acid plants, elemental sulfur plants, and explosives manufacturing.

Sulfuric acid is manufactured primarily by the contact process. The three types of raw materials charged to sulfuric acid plants are elemental sulfur, spent acid and hydrogen sulfide, and sulfide ores and smelter gases. The amount of SO_2 emissions in acid plant exit gases is an inverse function of the sulfur conversion efficiency of the process (U.S. Environmental Protection Agency, 1977). Sulfuric acid mist is generated by the process SO_2 absorbers. The quantity and size distributed of the acid mist are dependent on the type of sulfur feedstock used, the strength of the acid produced, and the conditions in the absorber.

The manufacture of TNT and nitro cellulose explosives produces emissions of SO_2 and sulfuric acid mist. A major raw material in the production of these explosives is sulfuric acid. Sulfuric acid concentrators, sellite exhaust, and incinerators are the major sulfur oxides sources in these processes. Sulfur oxide emissions may vary considerably depending on the efficiency of the process and the operating conditions (U.S. Environmental Protection Agency, 1977).

Particulate emissions from grain processing typically result from handling, cleaning, drying, and milling (U.S. Environmental Protection Agency, 1977). Grain processing particulates are normally coarse, and are composed of the parent organic material.

Chemical wood pulping by the kraft or sulfite processes involves cooking wood chips under pressure to dissolve the lignin that binds the cellulose fibers, in addition to washing, milling, bleaching, and drying (U.S. Environmental Protection Agency, 1977). Particulate emissions occur primarily from the recovery furnace (used to recovery cooking chemicals) and the lime kiln (lime is used in cooking). Sulfur dioxide emissions result mainly from oxidation of reduced sulfur compounds in the recovery furnace.

4.5.3 Industrial Process Fugitive Particulate Emissions

Fugitive dust emissions result from wind erosion of storage piles and unpaved plant roads and from vehicular traffic over plant roads. Fugitive process emissions result from industry-related operations such as materials handling, loading, unloading, and transfer operations. Point sources controlled incompletely, such as furnace charging and tapping, and equipment that is maintained poorly, such as leaking furnaces and coke oven doors, are also fugitive process emission sources.

Process fugitives are not emitted from a definable point such as a stack. They are difficult to collect, measure, and control. For a given industry, there are generally a large number of fugitive particulate emission sources. For example, 20 separate sources have been identified for foundries (Jutze et al., 1977). In terms of total emissions, however, one or two of these sources may predominate.

Even though fugitive particulate emission totals may appear small when compared with totals from large point sources, they may take on importance because of the concentration of control efforts on point source emissions. In the integrated iron and steel industry, where fugitive particulate emissions are characterized relatively well, fugitives are estimated to account for about 10 percent of all uncontrolled emissions. However, since fugitive particulate emissions are poorly controlled, they account for greater than 60 percent of total controlled emissions (Spawn, 1979). Also, in situations where point sources are controlled well or use high stacks, fugitive particulate emissions exert the primary effect on local air quality. Extremely high suspended particulate levels have been measured in areas where process fugitives are predominant (Lynn et al., 1976; Lebowitz, 1975).

Table 4-11 presents estimates of uncontrolled industrial process fugitive particulate emissions. Particle size and composition characteristics are also presented. Unfortunately, many of the emission factors used to estimate process fugitives are based on engineering judgement or extrapolation from similar processes. Often, there is little test data available to support these estimates since process fugitives are difficult to measure. Therefore, the accuracy of these estimates is questionable. Also note that some of the emissions presented in Table 4-11 may have already been accounted for in Table 4-6 (Section 4.5.2). This overlap is due to using different references (see Section 4.3).

As is evident from Table 4-11, three broad categories account for nearly all of the potential process fugitives in the United States. They are mineral products, food and

TABLE 4-11. UNCONTROLLED INDUSTRIAL PROCESS FUGITIVE PARTICULATE EMISSIONS[a]

Source category	Annual uncontrolled fugitive particulate emissions (10^3 metric tons)	Size characteristics	Major components
Mineral products			
Crushed rock Extraction, Surface coal mining	730	10-50%<10 μm 1-2%<1 μm	Same as parent material (important for toxic minerals such as asbestos, beryllium, silica)
Portland cement	700	10-15%<10 μm	Limestone, clay, shale, gypsum, iron-bearing and siliceous materials
Asphalt concrete	100	50-70%<4 μm	Sand, crushed stone, limestone, hydrated lime
Lime manufacturing	50	45-70%<5 μm	Limestone, lime
Concrete batching	30	10-20%<5 μm	Cement dust
Food and agriculture			
Grain elevators	1,250	1%<10 μm	Grain dust
Primary metals			
Coke/iron/steel	250	Coke mfg: 27-80% <10 μm, 15-26% <2 μm; iron mfg: 1-10%<5 μm; Steel mfg: 50% <5 μm	Polycyclic organic matter, coal dust, code dust, iron oxide dust, kish (graphite material), metal fume (primarily iron oxide)
Foundries	125	50%<15 μm	Metal oxide fume Primarily oxides of silicon and iron), fine carbonaceous fume

TABLE 4-11. (continued)

Source category	Annual uncontrolled Fugitive particulate emissions (10^3 metric tons)	Size characteristics	Major components
Aluminum	60	50-90%<10 μm	Particulate fluorides, alumina (Al O), carbon dust, condensed hydrocarbons, tars
Copper	40	10-50%<5 μm	Cu, Fe, S, SiO from ore concentrate; metal fume consisting of oxides of As, Pb, Zn, Cu, Cd
Lead	15	10-90%<5 μm	Metal fume consisting of oxides of Pb, Cd, Zn, Sb
Secondary metals	10	80-100%<5 μm	Oxides of Al,Cu,Pb, Sn,Zn; Oxides of alkali metals; $AlCl_3$, NH_4Cl,NaCl, $ZnCl_2$; flourides, and carbonaceous materials
Wood products	10	40-90% 10 μm	Sawdust
TOTAL	3,370		

[a]Sources: Taback et al. (1979)
Zoller et al. (1978)
Jutze et al. (1977)

agriculture, and primary metals. In the mineral products industries, fugitive particulate emissions tend to reflect the composition of the parent materials. The limited amount of particle size data indicate that most particles are relatively coarse.

Grain elevator operations account for the fugitive particulate emissions in the food and agriculture industry. These emissions consist almost entirely of grain dust from loading and unloading, drying and cleaning operations, conveyor belts, and transfer points. Only about one percent of these particles are less than 10 μm in size.

Primary metals production encompasses six separate industries. Fugitive particulate emissions in this category result from the handling and transporting of raw materials and from the smelting and refining of these raw materials into their finished metal products. While emissions of the first type are not characterized well, emissions of the second type often consist of fine metal fumes. This is particularly significant because of the quantities of toxic trace metals than can be concentrated and volatilized in metal melting operations. Some of these toxic components of particulate emissions are presented in Table 4-12.

The remaining two categories, secondary metals and wood products, account for less than one percent of the national total of industrial process fugitive particulate emissions. Fugitive metal fume particulates from secondary metal melting operations also include toxic components. These are presented in Table 4-12.

4.5.4 Non-Industrial Fugitive Particulate Emissions

This section addresses the subject of non-industrial fugitive particulate emissions, or fugitive dust. These emissions are caused by traffic entrainment for dust from public paved and unpaved roads, agricultural operations, construction activities, surface mining operations, and fires. With the exception of fires, all of these sources may be classified as open-dust sources; that is, they entail dust entrainment by the interaction of machinery with aggregate materials and by the forces of wind on exposed materials.

A number of factors can affect the degree of emissions from open sources. These factors could generally be classified under three headings: material, equipment, and climate. Material encompasses such factors as silt content and moisture content. For example, increasing the silt content and decreasing the moisture content of unpaved road material would probably result in more dust being generated. Equipment factors generally refer to vehicle weight and speed. For example, increasing the speed or weight of a vehicle travelling over an unpaved road would tend to increase emissions. Climatic factors are wind speed and precipitation. Increased wind speed and decreased precipitation would both tend to increase emissions from any open-dust source.

Estimated U.S. annual particulate emissions from non-industrial fugitive dust sources are difficult to pin down. As shown in Table 4-13, fugitive dust emissions from unpaved roads tend to be quite significant. The two available estimates, however, vary by almost an order of magnitude. Fugitive dust from wind erosion of cropland and construction activities as documented by Cooper et al. (1979) also appears significant. However, no other estimates with

TABLE 4-12. TOXIC COMPONENTS OF FUGITIVE (AND STACK) PARTICULATE EMISSIONS IN THE PRIMARY AND SECONDARY METALS INDUSTRIES[a]

Industry	POM[b]	As	Be	Pb	Cr	Cd	Hg	Se	Ag	Co	Ni	Fluorides
Primary metals												
1. Coke	++[c]	+	+	+	+	+		+		+	+	
2. Iron				+								+
3. Steel				+	+							+
4. Foundaries				+	+				+	+	+	
5. Aluminum	+											++
6. Copper		++		++		+		+	+			
7. Lead		+		++		+		+	+			
8. Zinc				++		+	+					
Secondary metals												
1. Lead				++								
2. Aluminum												++
3. Copper (brass/bronze)				++		+						
4. Zinc				+	+	+					+	

[a]Sources: Daugherty and Coy (1979), U.S. Environmental Protection Agency (1978a), Bohn et al. (1978), Jutze et al. (1977), Steiner (1977), Nelson et al. (1977), and Vandegrift et al. (1971).

[b]Polycyclic Organic Matter

[c]The symbol (+) is used to indicate the presence of a toxic component in the particulate emissions. If the toxic component is present in large quantities (>5 percent by weight), the symbol (++) is used.

TABLE 4-13. ESTIMATED ANNUAL PARTICULATE EMISSIONS FROM NON-INDUSTRIAL FUGITIVE SOURCES

Source Category	Estimated Emissions (10^6 metric tons/year[a])	
	Cooper et al. (1979)	U.S. EPA (1980b)
Unpaved roads	290	35
Paved roads	7.2	4.7
Wind erosion of cropland	40	-
Agricultural tilling	2.9	-
Construction activities	25	-
Minerals extraction	3	-
Mineral tailing	0.7	-
Prescribed fires[b]	0.4	0.2

[a]Particles less than 30 μm in diameter.

[b]Includes prescribed forest burns and agricultural burning.

which to compare are available. Total fugitive emissions range from approximately 112 x 10^6 metric tons per year to 369 x 10^6 metric tons per year. The lower figure assumes the U.S. Environmental Protection Agency's estimate of fugitive emissions from paved and unpaved roads, while the higher figure assumes the estimate of Cooper et al. Because of the disparity between comparable estimates, the estimated emissions presented in Table 4-13 should be considered with a degree of caution.

Information on particle size distribution is also limited. Some limited data are presented in Table 4-14 but they are representative only of California's South Coast Air Basin and should not be extrapolated to the nation as a whole. Dust from unpaved roads, agricultural tilling, construction, and road building is composed primarily of silicon, phosphorous, aluminum, iron, calcium, and potassium. Trace elements include barium, cobalt, copper, lead, manganese, nickel, titanium, vanadium, and zinc (Taback et al., 1979).

Finally, it is estimated that fugitive dust emissions exceed particulate emissions from stationary point sources in 90 percent of the Air Quality Control Regions that are not meeting the ambient standards for total suspended particulates (Carpenter and Weant, 1978). However, the impact of fugitive dust emissions on populated areas may be lessened bacause of several

TABLE 4-14. ESTIMATED PARTICLE SIZE DISTRIBUTIONS FOR SEVERAL NON-INDUSTRIAL FUGITIVE SOURCE CATEGORIES[a] IN CALIFORNIA'S SOUTH COAST AIR BASIN

Source Category	Weight Percent in Size Range			
	>10 μm	3-10 μm	1-3 μm	<1 μm
Unpaved road dust	54	16	12	18
Agricultural tillage dust	40	21	17	22
Road building and construction dust	36	24	16	24
Agricultural burning	<1	2	8	90

[a]Source: Taback et al (1979).

factors: 1) a major portion of these emissions consists of large particles which settle to the ground a short distance from the source, and 2) most fugitive dust sources, like unpaved roads, exist mainly in rural areas, and their emissions are spread over large land areas of low population density (U.S. Environmental Protection Agency, 1980b).

4.5.5 Transportation Source Emissions

Transportation source emissions may be divided into two categories: engine-related emissions from vehicle exhaust, and other highway vehicle-related particles from tire wear and clutch and brake lining wear (Bradow et al., 1979; U.S. Environmental Protection Agency, 1978b; Dennis, 1974; and Jacko and DuCharme, 1973). Total transportation source emissions for 1978, including emissions from highway vehicles, aircraft, railroads, and vessels, were estimated at 1.3×10^6 metric tons (particulate matter) and 0.8×10^6 metric tons (sulfur oxides) (U.S. Environmental Protection Agency, 1980a). About 75 percent of the particulate emissions and 50 percent of the sulfur oxide emissions in 1978 were from highway vehicles.

Engine-related particulate emissions from transportation sources are composed primarily of lead halides, sulfates, and carbonaceous matter (including absorbed organics). Highway vehicle-related particulates are emitted at the rate of about 0.01-0.30 grams per mile by gasoline engines and 0.5-3.0 grams per mile for diesel engines (Bradow et al., 1979). The major components are lead (except for vehicles using unleaded gasoline), carbon, organics, and sulfates. Vehicles burning leaded gasoline also emit inorganic compounds of lead (mostly PbBrCl), bromine, and chlorine (Springer, 1978). Particulate matter from catalyst-equipped vehicles using unleaded gasoline is dominated by sulfate and carbonaceous material.

Diesel particulates can include traces of iron, copper, calcium, and zinc, along with carbon, lead, organics, and sulfates (Lee and Duffield, 1979). Particulate emission rate and

composition for diesel engines are sensitive to many parameters, including vehicle size, operating conditions (speed, load), and fuel characteristics. Normally, carbon-containing species dominate, including a material similar to lubricating oil (Black and High, 1978).

Engine-related particles are mostly under 1 μm in diameter. For vehicles burning leaded gasoline, the available data indicate a mass medium diameter of about 0.25 μm (Moran et al., 1971). Due to the predominance of sulfates, catalyst-equipped vehicles burning unleaded gasoline emit smaller particles having a mass mean diameter of about 0.05 μm (Groblicki, 1976). The size distribution of diesel particulate matter suggests a mass median diameter of about 0.2 μm (Dolan and Kittleson, 1979).

Very little data exist on non-engine particulates from highway vehicles. About 40 percent of particles from tire wear are less than 10 μm (about 20 percent are less than 1 μm); they are composed primarily of carbon (Taback et al., 1979). Particles from brake lining attrition are all less than 1 μm and are composed mainly of asbestos (80 percent) and carbon (Taback et al., 1979).

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5. ENVIRONMENTAL CONCENTRATIONS AND EXPOSURE

5.1 INTRODUCTION

This chapter has two functions. One is to show the concentrations of sulfur dioxide and of particles suspended in the air to which all living things and valuable objects are exposed. The second is to show how the various sources of air pollutants contribute to these exposures.

The first goal is to demonstrate the concentrations of these two air pollutants in a way relevant to the effects they might cause. Measurements of sulfur dioxide, of TSP, and of some chemical components of particulate material in the ambient air have been made for a long time, mostly with methods and procedures which have some imperfections. In Chapter 3, the most current information relative to sources of error in measurement are covered in detail. Here, only those issues which influence interpretation are mentioned and then only briefly. The reader is cautioned to consult Chapter 3 for more detail.

Despite imperfections in measurement methods, state and local monitoring data stored by EPA is the largest source of information relative to long-term trends in pollutant concentrations and of the geographical distributions of the pollutant levels. Therefore, the existing monitoring data are presented first to gain this overall perspective with respect to SO_2 and particles in that order.

The pollutant called particulate matter is exceedingly complex both with respect to its physical properties and chemical composition. In Chapter 2 those characteristics of particles which are generally observed in most atmospheres are covered in detail. Consequently, in this section only those features of chemical composition and physical size are treated which influence data interpretation. The reader is directed to Chapter 2 for more detail on these subjects.

Recently, particle measurements have been collected and analyzed to estimate the relative contributions of important sources. In this case, the complexity of the particles proves to be valuable since many source types have nearly unique chemical signatures. Consequently, it is often possible to make at least approximate assignments of the relative amounts of suspended particulate material derived from road dust, power plants, automobiles, and other common sources provided that an adequate description of the source signature is available. Since this technique is still new, only a few studies are available some of which are discussed to show the approximate source contributions in representative cases. For a more complete description of particle emission factors and inventories, Chapter 4 should be consulted.

Ultimately, the importance of the ambient air measurements of pollutant concentrations is in estimating harmful effects. When the effect considered is visibility reduction, the important factors are concentrations of light scattering and attenuating particles over the geographical scale of several miles. In materials damage, concentrations of SO_2 and of

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soiling particles are important over time scales of months or years. But when considering harmful influences of air pollutants on living things, the important matter is the dose. Dose incorporates concentration, time and absorption and the relationship among these parameters. Throughout their lifetime people inhale a complex mixture of gases and particles. Other living things, vegetation and animals, are also exposed to the same complex mixtures, whose composition varies with time at any given location because of changing atmospheric conditions and source contributions. The effects of air pollution on health and welfare are function of dose delivered to the receptor and the ability of the receptor to cope with the resultant stress. In humans, the stress experienced by a critical organ or receptor tissue from particle inhalation depends on particle size, composition, morphology, acidity or basicity, and other physical-chemical properties of the aerosol. The delivered dose is also a function of the anatomical features of the receptor as well as manner of breathing, breathing rate, and integrity of bodily defense systems.

It is almost impossible to measure directly the air pollution dose to a population or even to an individual except in the laboratory. As an alternative to direct measurement of dose, exposure can and often must be used as an approximation of dose for studies on air pollution risk and effects. The exposure-response relationship for air pollution is most important for establishing standards. Unfortunately, to extrapolate from measurements of ambient levels at a few locations to an individual or population exposure is a very difficult task at present. The outdoor air's contribution to indoor concentrations is still being investigated. The additional exposures to gases and particles from nonoccupational indoor sources are not adequately quantified.

Indoor air quality and activity patterns complicate air pollution exposure estimates and are discussed later in this chapter. First, the ambient outdoor concentrations of sulfur dioxide and particulate matter are examined.

5.2 AMBIENT MEASUREMENTS OF SULFUR DIOXIDE

Ambient concentrations of sulfur dioxide are determined by the following factors: (1) the density of emissions sources; (2) the source characteristics such as stack height, exit velocity, and source strength (3) the local meteorological conditions (4) the local topography and surrounding buildings (5) the reaction rate of sulfur dioxide in plumes, and (6) the removal rates by precipitation, deposition at surfaces, and other reactions. These factors interact in such a way that in urban and industrialized areas with high densities of SO_2 emissions, the SO_2 concentrations are much higher than in surrounding rural areas. It is quite common to find gradients in SO_2 concentration within these industrialized and areas, with a central core area reporting the highest SO_2 concentrations. This pattern is shown diagrammatically in Figure 5-1.

Where SO_2 emissions are dominated by a single or a few point sources, the pattern of SO_2 concentrations could be different from the pattern displayed in Figure 5-1. Depending on

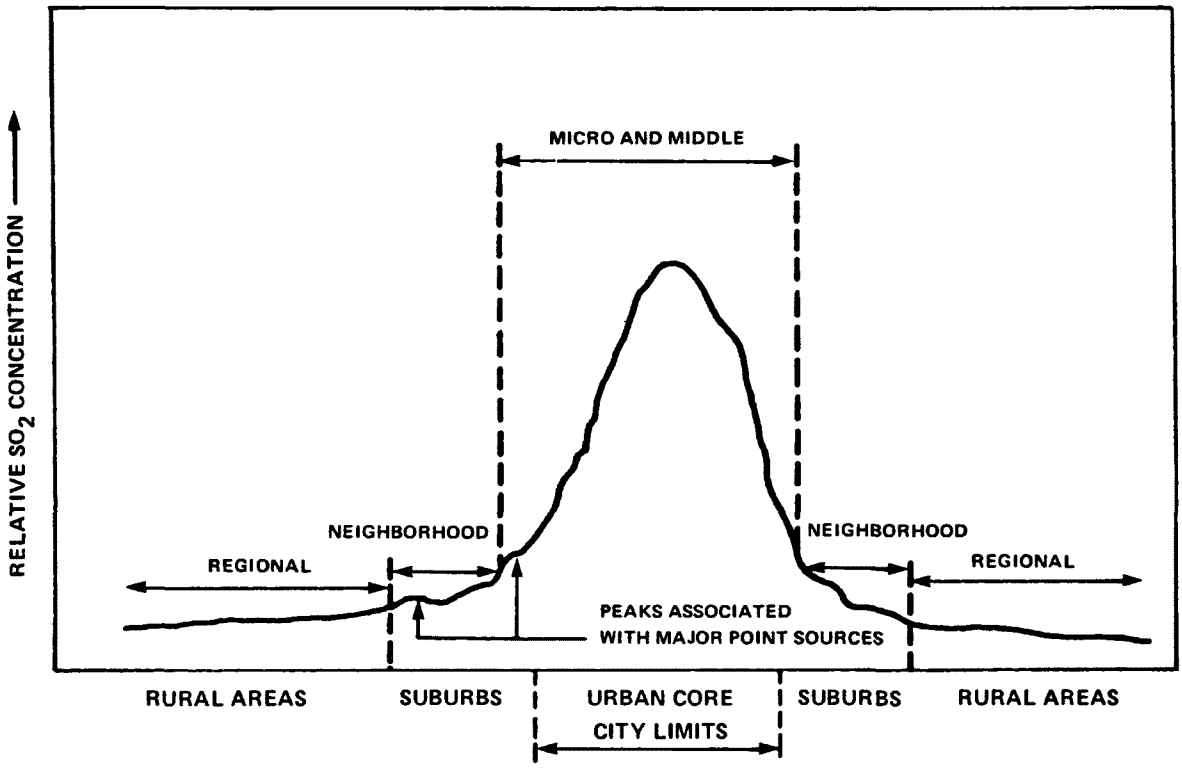

Figure 5-1. Relative locations for sites measuring concentrations represent several spatial scales of measurement in an urban complex, with respect to annual averaging times.

topography, meteorology, and source characteristics, the concentration patterns may be asymmetrical and the temporal distribution may be skewed to low mean values with a few intermittent high peaks. These differences in concentration patterns may be important to the effects experienced in exposed human populations.

Most urban areas have experienced dramatic improvements in air quality as a result of: (1) restrictions on sulfur in fuel (2) better controls on new and existing sources; (3) displacement of sources and the building of new sources in less populated regions; and (4) the building of taller stacks.

This section presents SO_2 concentration data for specific locations and areas where levels are currently high. The national status of SO_2 concentrations is reviewed, along with trends data. A comparison is made between SO_2 levels in six cities in the early 1960's and the concentration in the late 1970's. Insights on factors that are important determinants of population exposures are presented in the discussion of diurnal and seasonal SO_2 concentration patterns. Since SO_2 can be measured by a variety of methods (see chapter 3), a brief discussion of SO_2 monitoring and instruments precedes the substantive sections on concentrations.

5.2.1 Monitoring Factors

The Environmental Protection Agency is now in the process of revising federal, state, and local air monitoring networks. By 1981, states will be operating a selected number of sites in the National Air Monitoring Station (NAMS) Network. These sites are to be located in the areas of highest pollution concentrations and areas of high population density. They are designed to serve in assessing the trends and progress in meeting standards. By 1983, the state and local agencies are to be operating the State and Local Air Monitoring Station (SLAMS) Network. This network is designed to be part of each state's implementation plan. It is expected that this will mean fewer sites than are currently in operation; however, the effort of federal coordination of air monitoring should provide the much-needed quality control. The trend to reduction in the number of stations is already apparent in the 1977 sulfur dioxide data. There were 117 fewer monitoring sites reporting data in 1977 than in 1976 (2365 vs. 2482). Many States terminated all or most of their 24-hr West-Gaeke bubbler sampling in 1978, and most remaining bubbler stations are being fitted with temperature controls to avoid sample degradation (see Chapter 3). However, state and local agencies, where they can, are relying primarily on continuous monitoring equipment.

Nationally, SO_2 monitoring is not as extensive as TSP monitoring. In 1978 there were 947 sites with continuous monitoring equipment and 1298 bubbler sites. Every state conducted SO_2 monitoring. All reported sites are considered to have produced useful information on short-term (1 to 24 hour) SO_2 concentrations. However, only those sites reporting a specified number of hourly or daily observations per year are considered valid in terms of their annual mean. EPA's minimum criteria for a valid annual mean are: 6570 hourly values from a continuous monitor or 5 24-hour values in each quarter from a bubbler monitor.

It is with respect to the number of SO_2 sites with valid annual means that the national coverage appears inadequate. Only 99 of the 1298 bubbler sites (or 7.6 percent) have valid annual means in 1978; only 385 of the 947 (or 40.7 percent) continuous sites are considered valid. There are 7 states with no valid annual SO_2 data for 1978. EPA is currently taking steps to improve the quality of SO_2 data and increase the number of representative sites reporting valid data.

For valid bubbler sites, the average number of 24-hr observations in 1978 was 60. The number of observations per site ranged from 28 to 322. For the valid continuous sites the mean number of observations was 7806 hourly measurements. This ranged from a minimum of 6578 hr to a maximum of 8755 hr.

5.2.2 Sulfur Dioxide Concentrations

Although there are natural sources of SO_2 such as volcanoes (see chapter 4), they are of minor importance. Sulfur dioxide has a rather short half-life in the troposphere (see chapter 6). Background levels are often below the monitor's detection limit. Therefore it is not surprising that the annual mean SO_2 concentration is 3 $\mu g/m^3$ in some nonurban locations.

Monitoring in urbanized areas near industrial sources that use sulfur-bearing fuels shows rather high concentrations of SO_2. In 1978 the annual mean concentrations obtained by SO_2 bubblers ranged from 3 to 79 $\mu g/m^3$. The valid continuous monitors registered 1978 annual mean concentrations ranging from 3 to 152 $\mu g/m^3$.

The concentration of SO_2 like that of TSP is affected by meteorological variables influencing transport, dispersion, and removal, as well as by topography and the configuration of sources. Spatial and temporal variations in these parameters are reflected in the range of maximum and 90th percentile concentrations reported across the Nation. For bubbler sites, the lowest 24-hr maximum value reported by a site was 3 $\mu g/m^3$ and the highest was 907 $\mu g/m^3$. For the valid continuous sites the spread of 24-hr maximum values was greater, ranging from 10 $\mu g/m^3$ at one site to 2512 $\mu g/m^3$ at another site. Among all continuous sites reporting in 1978, regardless of validity, the extreme 24-hour value was 3931 $\mu g/m^3$.

Figure 5-2 presents the distribution of annual averages for all valid continuous monitoring sites in 1978. On this time scale, the most commonly measured values are between 20 and 30 $\mu g/m^3$ with most values below 60 $\mu g/m^3$. Most monitoring stations are situated specifically to detect higher urban or source-specific levels of SO_2, however, and the data in Figure 2 may be judged more nearly representative of high population density areas than of the bulk of U.S. land area. The following section discusses the effect of site location.

5.2.3 Sulfur Dioxide Concentration By Site and Region

5.2.3.1 Analyses by Various Site Classifications--In this section the distributions of annual mean and 90th percentile concentrations by site descriptors are presented for bubbler and for continuous methods. As with TSP, a two-descriptor code has been associated with each site. Distributions for every combination of Type 1 (population, source, background) and for Type 2

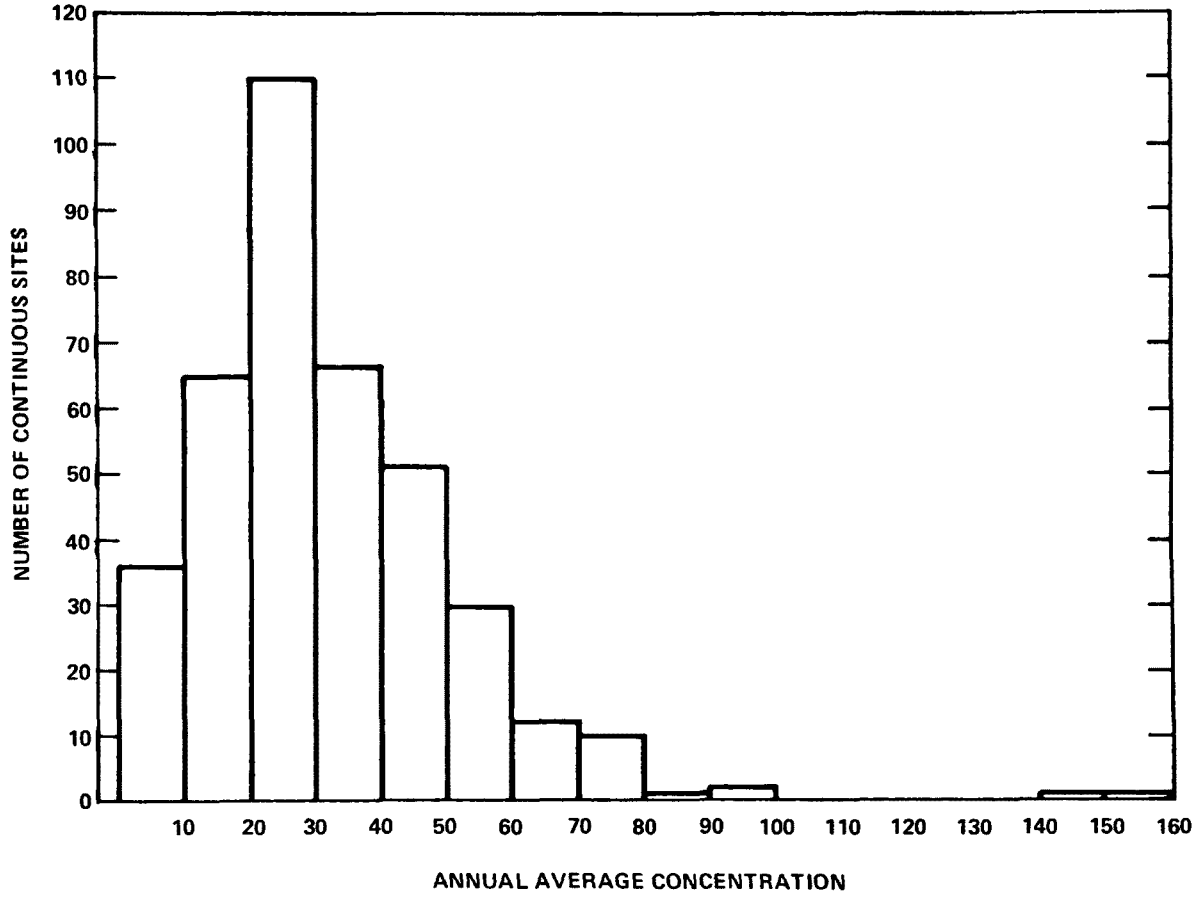

Figure 5-2. Histogram shows annual average sulfur dioxide concentrations for valid continuous sites, 1978.

(central city, suburban, rural, remote) will not be presented. In some cases the designations are contradictory, such as "population-remote" or "background-central city." The purpose of presenting these distributions is to permit comparison of these two categories of sampling methods and to examine the SO_2 concentrations as a function of location.

In Table 5-1 the cross-tabulation of mean concentrations by method is presented for center-city sites that are primarily either population oriented or source oriented. The third and fourth numbers in each cell are the column percentage and total percentage of sites having concentrations within the designated range. Examination of each of these numbers reveals that bubblers are, on the average, reporting lower concentrations than the continuous instruments, an expected result because of the method biases reported in Chapter 3. In Table 5-1, 14.4 percent of the "population-oriented" continuous monitors report mean concentrations above 62 $\mu g/m^3$ while only 1.6 percent of the bubblers report these higher concentrations. Of the "source-oriented" sites, a higher percentage (7.1 percent) of the bubblers are above 62 $\mu g/m^3$, but this is still less than the 12.5 percent of the continuous monitors in this category.

5.2.3.2 Regional Comparisons--Regional differences in SO_2 concentrations are not striking. In part, this is the result of the locational dependency of the monitor. In previous sections it was shown that high SO_2 levels are found around smelters in otherwise clean areas. In the eastern and northern states, most continuous SO_2 monitoring is in urbanized areas. Mean concentrations across all continuous monitors in Regions I, II, III, IV, and V range from 23 $\mu g/m^3$ to 51 $\mu g/m^3$ (see Table 5-2). The maximum annual mean among the valid sites in these regions ranges from 59 $\mu g/m^3$ in Region I to 140 $\mu g/m^3$ in Region III. In the less industrialized or less populated regions (VI through X), the mean annual concentration across all sites in each region ranges from 8 $\mu g/m^3$ to 40 $\mu g/m^3$.

Even with the summary of the 1978 continuous SO_2 data, it is difficult to speculate on regional differences in SO_2 concentrations. Concentrations are influenced primarily by local sources. The locations of monitors have clearly not been randomly chosen in each region, nor have they been systematically deployed for source population or background sampling. Therefore, a better indicator of regional differences in SO_2 concentrations and population exposures can be obtained from examining sulfur emission patterns (see Chapter 4).

The data base used in compiling Figure 5-3, collected between 1974 and 1976, offers finer spatial resolution of national SO_2 concentrations on a county scale. The second highest 24-hr average SO_2 concentration by county is displayed. Some areas in the west with extremely high concentrations were still problem areas in the late 1970's (see Table 5-3). Several counties and cities are still reporting high concentrations; however, one should not infer that the reported concentration prevails throughout the county. High readings may exist at one or more monitoring sites (for example, Deer Lodge County, MT), but it is likely that there are substantial gradients across the county, and almost certainly across an air quality control region (AQCR).

TABLE 5-1. CROSSTABULATION OF ANNUAL MEAN SO_2 CONCENTRATION BY METHOD (BUBBLER OR CONTINUOUS) FOR POPULATION-ORIENTED AND FOR SOURCE-ORIENTED CENTER CITY SITES

Annual mean SO_2 concentration, $\mu g/m^3$	Purpose of Site: Population			Purpose of Site: Source		
	Bubbler	Continuous	Row Total	Bubbler	Continuous	Row Total
2-7						
Number of sites	139	15	154	9	3	12
Percent of row	90.3	9.7		75.0	25.0	
Percent of column	27.6	5.3		16.1	6.3	
Percent of total	17.7	1.9	19.6	8.7	2.9	11.5
7-18						
Number of sites	159	32	191	18	10	28
Percent of row	83.2	16.8		64.3	35.7	
Percent of column	31.6	11.3		32.1	20.8	
Percent of total	20.2	4.1	24.3	17.3	9.6	26.9
18-33						
Number of sites	106	86	192	12	14	26
Percent of row	55.2	44.8		46.2	53.8	
Percent of column	21.1	30.3		21.4	29.2	
Percent of total	13.5	10.9	24.2	11.5	13.5	25.0
33-62						
Number of sites	91	110	201	13	15	28
Percent of row	45.3	54.7		46.4	53.6	
Percent of column	18.1	38.7		23.2	31.3	
Percent of total	11.6	14.0	25.5	12.5	14.4	26.9
>62						
Number of sites	8	41	49	4	6	10
Percent of row	16.3	83.7		40.0	60.0	
Percent of column	1.6	14.4		7.1	12.5	
Percent of total	1.0	5.2	6.2	3.8	5.8	9.6
Column total						
Number of sites	503	284	787	56	48	104
Percent of total	63.9	36.1	100.0	53.8	46.2	100.0

TABLE 5-2. CONTINUOUS SO_2 MONITOR RESULTS BY REGION.

Region	Type	Number of sites	Number of observations per site				Arithmetic Means				90th Percentile			
			Min.	Mean	Max.	s.d.	Min.	Mean	Max.	s.d.	Min.	Mean	Max.	s.d.
I	Valid	22	6665	7519	8416	567	16	33	59	12	34	65	147	27
	All	72	185	4582	8416	2720	8	39	138	23	14	77	340	52
II	Valid	51	6597	7540	8697	546	15	37	78	16	35	72	159	30
	All	87	140	5815	8697	2380	15	41	94	19	35	78	173	33
III	Valid	26	6578	7562	8638	670	12	51	140	23	34	97	282	46
	All	108	94	4381	8638	2534	7	45	140	21	14	86	282	40
IV	Valid	100	6678	8305	8755	574	5	23	63	12	9	54	135	27
	All	203	421	5754	8755	2848	3	23	77	13	3	49	180	29
V	Valid	111	6580	7640	8715	625	7	36	84	16	10	70	167	30
	All	254	129	5512	8715	2327	3	37	192	25	5	73	501	50
VI	Valid	13	6631	7443	8452	607	3	13	31	7	3	31	69	19
	All	32	1669	5461	8452	2072	3	12	56	13	3	29	160	38
VII	Valid	13	6769	7540	8325	439	6	31	47	14	13	62	94	25
	All	38	334	4676	8325	2624	4	25	82	20	5	52	155	41
VIII	Valid	12	6741	7739	8624	514	3	40	152	47	3	100	488	146
	All	49	373	4694	8624	2358	3	34	152	39	3	89	488	113
IX	Valid	19	6857	7952	8638	507	3	8	29	6	3	16	48	12
	All	52	105	4973	8638	2525	3	24	87	20	3	49	213	49
X	Valid	18	6651	7854	8677	464	13	34	78	18	35	90	150	38
	All	29	625	6158	8677	2526	13	33	78	17	29	72	150	38

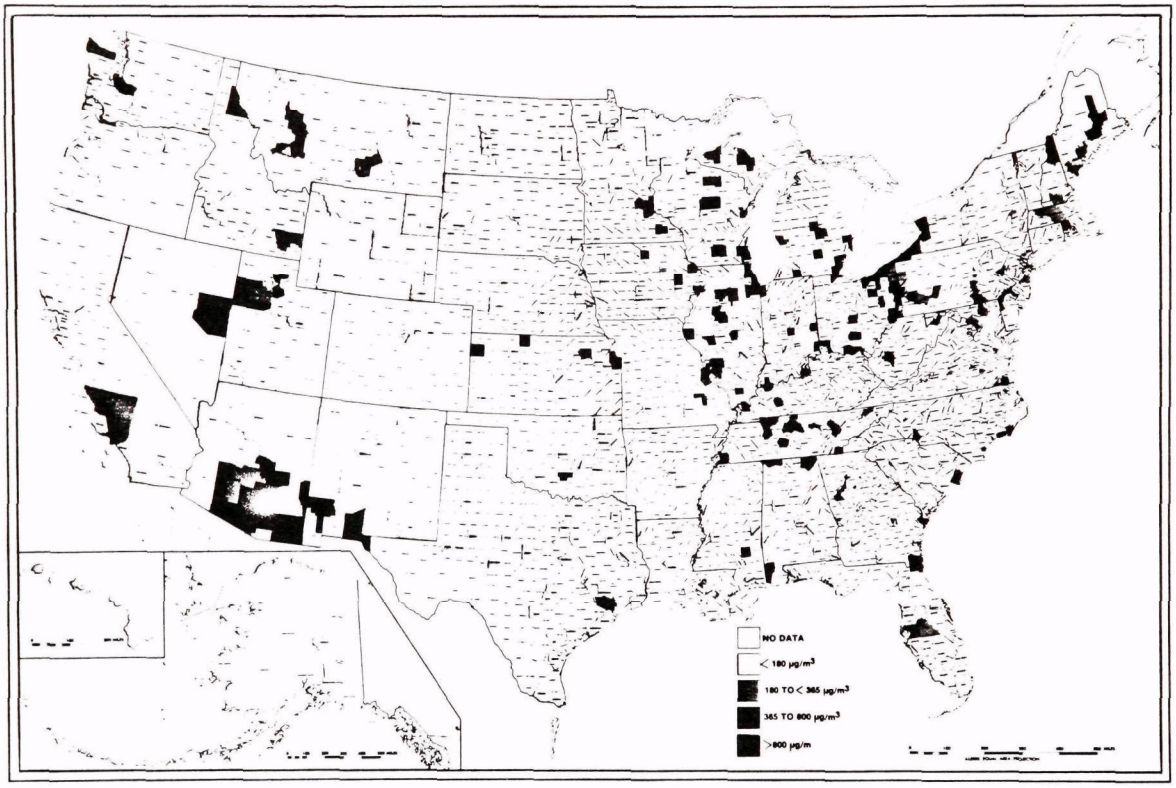

Figure 5-3. Characterization of 1974-76 national SO_2 status is shown by second highest 24-hr average concentration. (The current 24-hr primary national ambient air quality standard is 365 $\mu g/m^3$, which is not to be exceeded more than once per year.)

Source: Monitoring and Reports Branch, Monitoring and Data Analysis Division, Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency.

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TABLE 5-3. ELEVEN SO_2 MONITORING SITES WITH THE HIGHEST ANNUAL MEAN CONCENTRATIONS IN 1978 (VALID CONTINUOUS SITES ONLY)

Location	Annual Means $\mu g/m^3$	Maximum 24-hr, $\mu g/m^3$	Description
Helena, Deer Lodge Co., Montana	152	2512	Rural-mine smelter
Pittsburgh, Pennsylvania	140	602	Center city industrial
Helena, Deer Lodge County, Montana	95	1450	Rural-industrial 1.6 miles east of smelter
Magna, Salt Lake Co., Utah	93	811	Suburban-industrial
Toledo, Ohio	84	915	Center city industrial
Pittsburgh, Pennsylvania	79	376	Suburban-industrial
Buffalo, New York	78	267	Suburban-industrial
Kellogg, Shoshone Co., Idaho	78	294	Suburban-residential
Shoshone Co., Idaho	77	493	Suburban-industrial
New York City, New York	77	296	Center city residential
Mingo Junction, Ohio	76	329	Center city industrial

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5.2.4 Peak Localized SO_2 Concentrations

5.2.4.1 1978 Highest Annual Average Concentrations--The reasons for SO_2 variability have been mentioned in earlier sections. This section examines the locations with the highest annual averages and the highest maximum concentrations, and analyzes the distribution of SO_2 concentration nationally by site descriptors. However, because of the differences in SO_2 concentrations between bubbler and continuous monitoring, the distributions by site descriptor will be treated separately for each method.

Table 5-3 lists the annual mean and the maximum 24-hr concentration for the 11 valid continuous monitoring sites with the highest annual means in 1978. The highest annual mean concentration was 152 $\mu g/m^3$. This site in Montana was situated 2 miles northeast of a smelter. It also had the highest 24-hr concentration (2512 $\mu g/m^3$) of any valid continuous monitor. The maximum hour was 7205 $\mu g/m^3$, and the second highest hour was 6026 $\mu g/m^3$ at this site. Of the highest 11 sites, 5 are associated with smelters, 5 are associated with industrialized areas or towns, and one, New York City, is a densely populated city. In New York City, SO_2 emissions from space heating, power plants, and a variety of industrial sources resulted in a high annual mean concentration. Keep in mind that these are peak reporting sites; the urban sites do not typify an entire city. Conversely, there may be unmonitored neighborhoods incurring even higher concentrations.

5.2.4.2 1978 Highest Daily Average Concentrations--About fifty monitoring sites in the United States have consistently reported maximum 24-hour average SO_2 levels in excess of 300 $\mu g/m^3$ in recent years. Almost all of these have very high second and third highest values also. Many of the sites having high daily averages are located near specific industrial sources such as smelters, steel plants and paper mills. In fact the highest SO_2 values recorded are from sites specifically located for the purpose of monitoring community exposures from intense local sources. Monitors around smelters have frequently reported 24-hour values of 1000 to 3000 $\mu g/m^3$, the highest levels in the United States.

High 24-hour SO_2 values occur in 17 states emcompassing all major regions of the country. Ten of the highest sites are in Montana, six in Wisconsin, and six in Minnesota; most of these are close to intense sources. However, several urban sites and, especially, center-city sites in industrialized communities such as Philadelphia, and Pittsburgh, Pennsylvania, New York, New York, Toledo, Ohio and Hammond, Indiana, sill have high maximum 24-hour values, above 250-300 $\mu g/m^3$.

5.2.4.3 Highest 1-hour SO_2 Concentrations 1978 NADB Data--Single hourly SO_2 values greater than 1000 $\mu g/m^3$ (0.4 ppm) have been measured in about 100 cities and counties in 28 states in recent years. Such values are very widespread across the country; Maine, Florida, Montana, Texas, Arizona, and Washington all have sites in this category. Of these top 100 sites, all but 15 also had second highest values in excess of 1000 $\mu g/m^3$.

Hourly measurements this high are comparatively infrequent and for most of these 100 high sites, less than 1 percent of hourly values are in this category. But for a few sites, notably those close to metals smelting operations in a few cities, such values are observed up to 5 percent of the time. Highest 1-hour values are found in Deer Lodge County, Montana, where several measurements over 5000 $\mu g/m^3$ were recorded in two sites in 1978. Anaconda, Montana; Miami and San Manuel, Arizona; Newark, Delaware; Buffaloe County, Wisconsin; St. Charles County and North Kansas City, Missouri, all report at least one value in excess of 4000 $\mu g/m^3$.

5.2.5 Temporal Patterns in SO_2 Concentrations

5.2.5.1 Diurnal Patterns--In some locations SO_2 concentrations have distinct temporal patterns. These patterns depend on the variability of meteorological factors and on the variability of source emissions.

Diurnal variations in SO_2 concentrations reflect the changing dispersion characteristics of the lower atmosphere and variations in mixing height. If emissions are predominantly from low-level sources such as residential and and institutional space heating, the highest hourly concentrations will frequently occur at night and in the early-morning hours. At these times, low mixing height and decreased wind speeds lead to higher concentrations. During the day more vertical mixing usually occurs and wind speeds increase; this results in the dilution of low-level emissions. Figure 5-4 gives the composite diurnal pattern of hourly concentrations for SO_2 for the month of December 1978 in Watertown, MA. The pattern just described is apparent.

In locations where SO_2 emissions from taller stacks are the major SO_2 source, a different diurnal pattern can occur. In these situations, typical of power plants and smelters, the highest concentrations usually occur in the morning hours just after sunrise. Levels can be almost zero at night if the source is emitting into a stratified region above a lower level inversion. Upon inversion breakup, when heating at the surface causes vertical mixing, an elevated plume can be mixed to the ground. Fumigation conditions lasting from several minutes to several hours can occur. Two composite diurnal patterns of hourly SO_2 concentrations at a site in Kingston, TN, illustrate this point (See Figure 5-5). In January of 1975, a nearby 1500-MW power plant was emitting through nine stacks less than 320 ft high. In 1978 the emission had been switched over to two 1000-ft stacks. Montgomery and Coleman (1975) analyzed the effects of tall stacks on the peak-to-mean ratios for different averaging times and discussed the influence of inversion breakup. In essence, even with tall stacks, inversion breakup that catches the plume and brings it to the surface can occur. So the peak-to-mean ratio is almost independent of stack height. The frequency of occurrences on the other hand would most likely be less with taller stacks.

In Figure 5-5 the diurnal plot of hourly values in Kingston reveals a pattern different from that found in Watertown, MA. The maximum hours occur in midday. The hourly

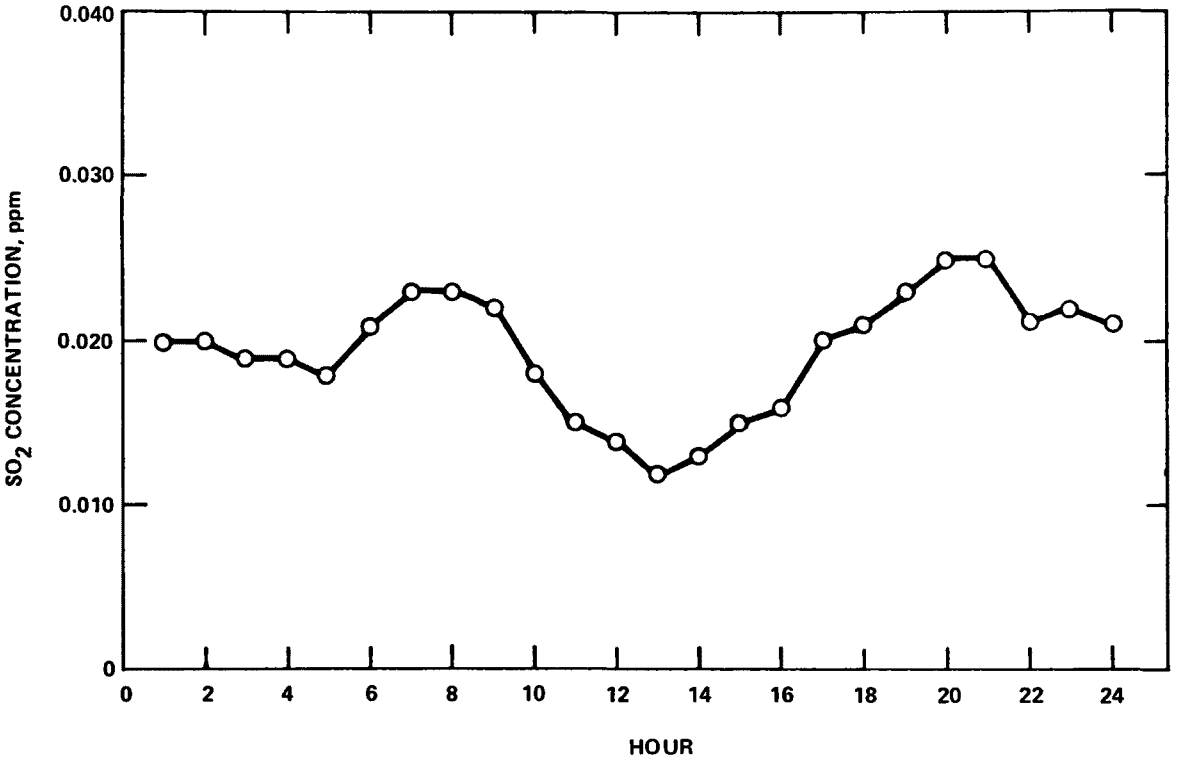

Figure 5-4. Composite diurnal pattern of hourly sulfur dioxide concentrations are shown for Watertown, MA, for December 1978.

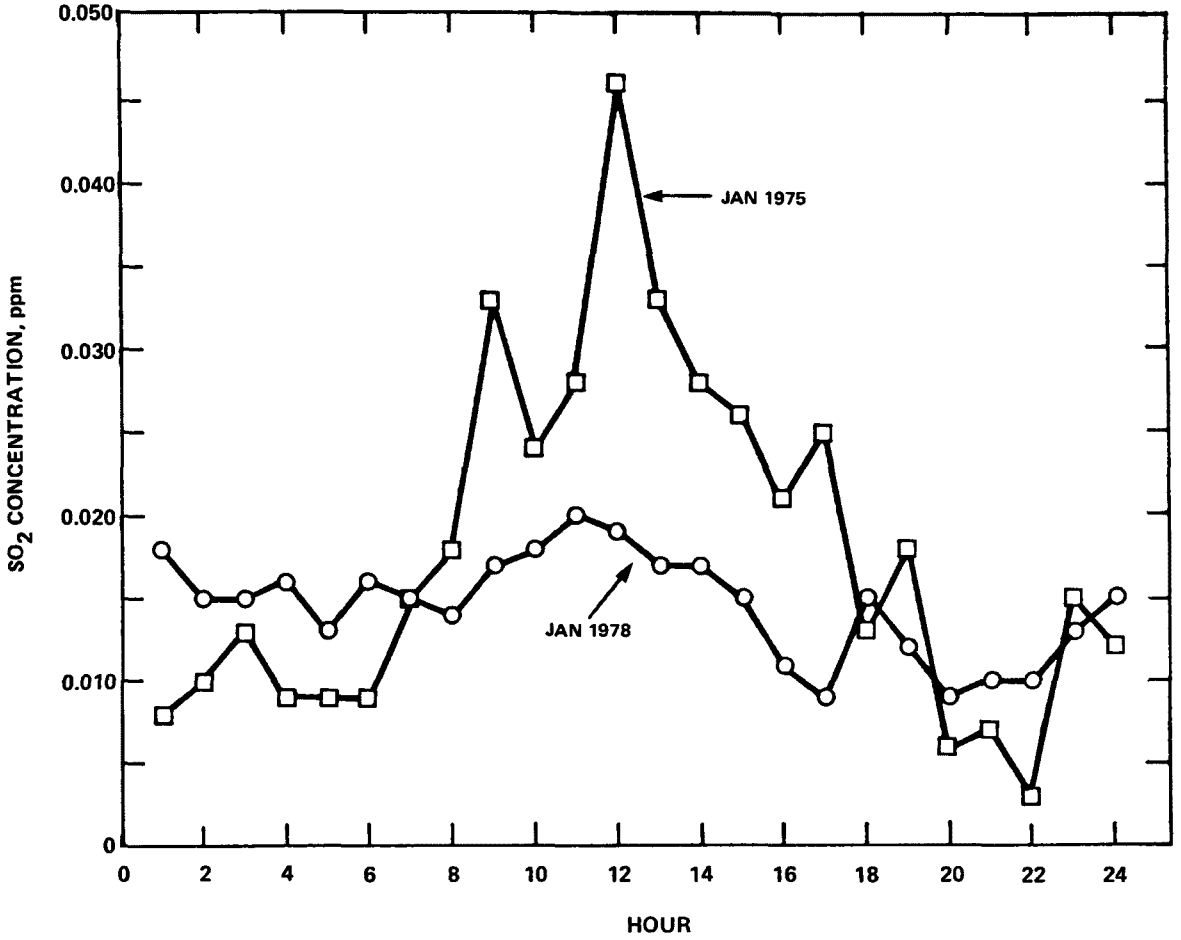

Figure 5-5. Monthly means of hourly sulfur dioxide concentrations are shown for Kingston (TVA site 44-1714-003, "Laddie Village") for January 1975 and 1978.

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observations in January 1978 show a less pronounced diurnal cycle. Some similarity can be found in comparing the diurnal pattern of hourly averages for Watertown, Massachusetts (Figure 5-4), and St. Louis, Missouri (Figure 5-6). In February, 1977, a major local source of SO_2 was still in operation in St. Louis. The midmorning and late night maxima are again associated with diurnal variations of meteorological factors. By February, 1978, the source had shut down and the SO_2 levels at the monitoring stations reflect this fact. The absence of low-level stacks emitting into a stable layer of air near the surface at night is noticeable. Concentrations do not build up at night as in the previous year.

Diurnal patterns of hourly SO_2 values for the industrialized river valley town of Steubenville, OH, are shown in Figure 5-7. In June of 1976, a distinctive maximum in the diurnal pattern appears. In July of 1977 there is no apparent variation across the hours.

In concluding this section it can be said that the variations in hourly concentrations are influenced by source configuration and meteorological dispersion. Therefore, it is difficult to generalize about the diurnal pattern of the hourly concentrations. It has been shown that, although there may be some similarities, the daily patterns in SO_2 concentrations are different for different locations and can change in time for a given location.

5.2.5.2 Seasonal Patterns--Concentrations of SO_2 display seasonal variability. The variability is most pronounced in areas in which there is strong seasonal variation in the emission-source strength or in meteorological conditions. Obviously, in urban areas where space heating is the major source of SO_2, the levels will be much higher during the heating season. Figure 5-8 illustrates just such situations in Watertown, MA and Steubenville, OH. The highest monthly mean concentrations occur in the winter months.

Figure 5-8 also shows the data for St. Louis, Missouri, where the seasonal pattern is different. Here a local industrial source dominates SO_2 concentration patterns around the monitor. The higher monthly mean concentrations occur in the months with the higher frequency of south winds. The source is to the south of the monitoring station. Any increase in SO_2 concentrations as a result of the winter heating season is not apparent.

5.2.5.3 Yearly Trends--The SO_2 levels in most urban areas in the United States have improved steadily since the mid-1960's. The trend of decreasing SO_2 concentrations can be resolved into three distinct periods. From 1964-69 the improvement was gradual. In the middle period, between 1969 and 1972, the improvement in most urban areas was more pronounced. Since 1973 the improvement has again become slower. The 1977 EPA trends report states: "In most urban areas, this is consistent with the switch in emphasis from attainment of standards to maintenance of air quality; that is, the initial effort was to reduce pollution to acceptable levels followed by efforts to maintain air quality at these lower levels." From 1972 through 1977 annual averaged SO_2 levels dropped by 17 percent, or an annual improvement rate of about 4 percent per year. Figure 5-9 summarizes the annual average SO_2 concentrations for 32 urban NASN stations for the years 1964-71. In this figure the first two periods are apparent. In

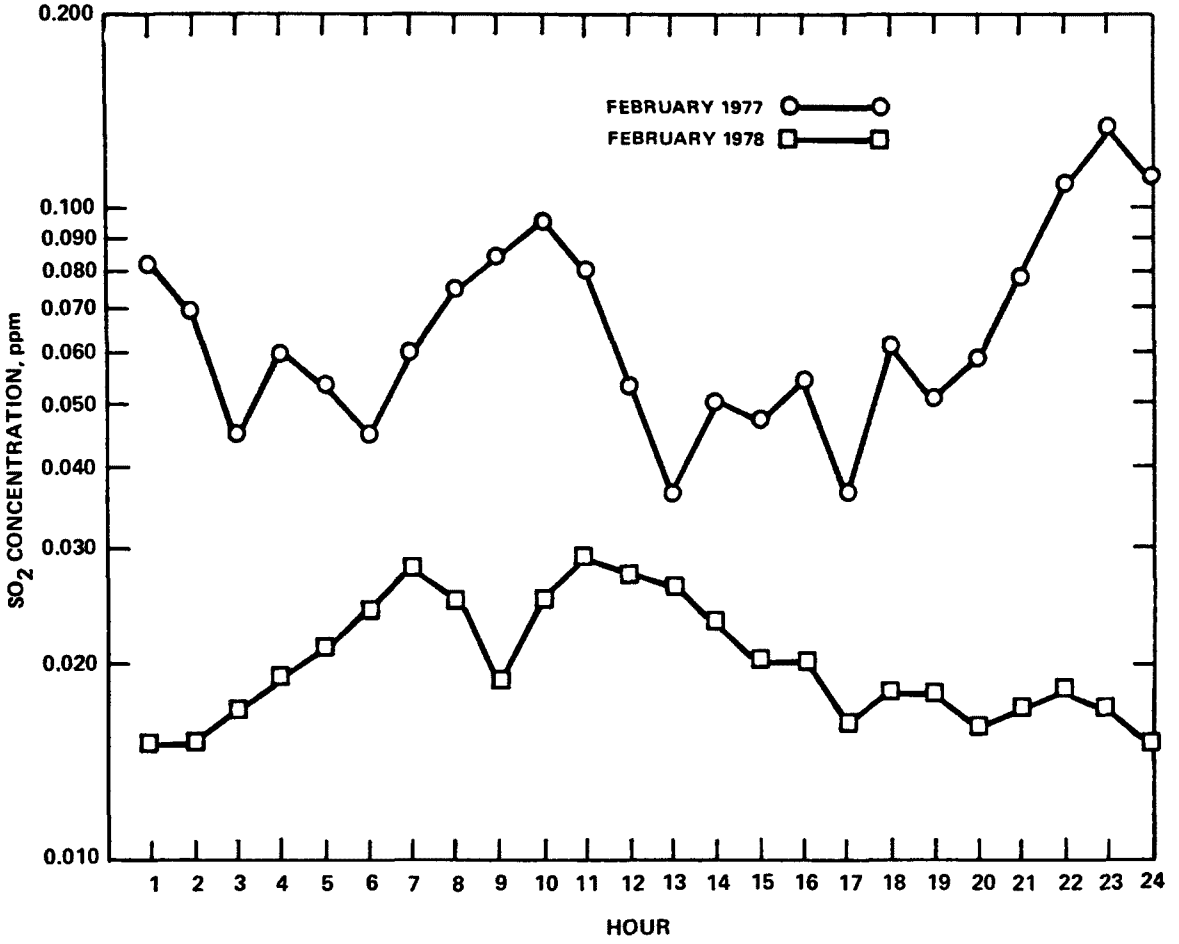

Figure 5-6. Monthly means of hourly sulfur dioxide concentrations are shown for St. Louis (city site no. 26-4280-007, "Broadway & Hurck") for February 1977 and 1978.

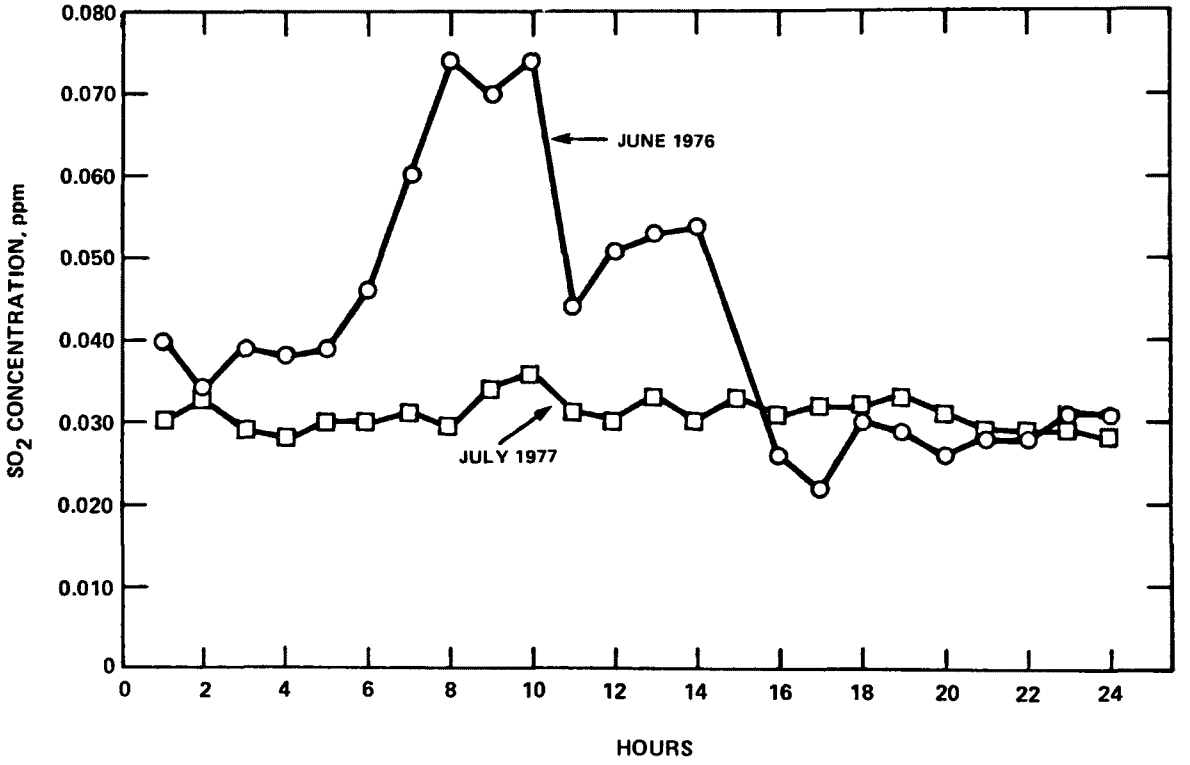

Figure 5-7. Monthly means of hourly sulfur dioxide concentrations are shown for Steubenville, OH (NOVAA site 36-6420-012) for June 1976 and July 1977.

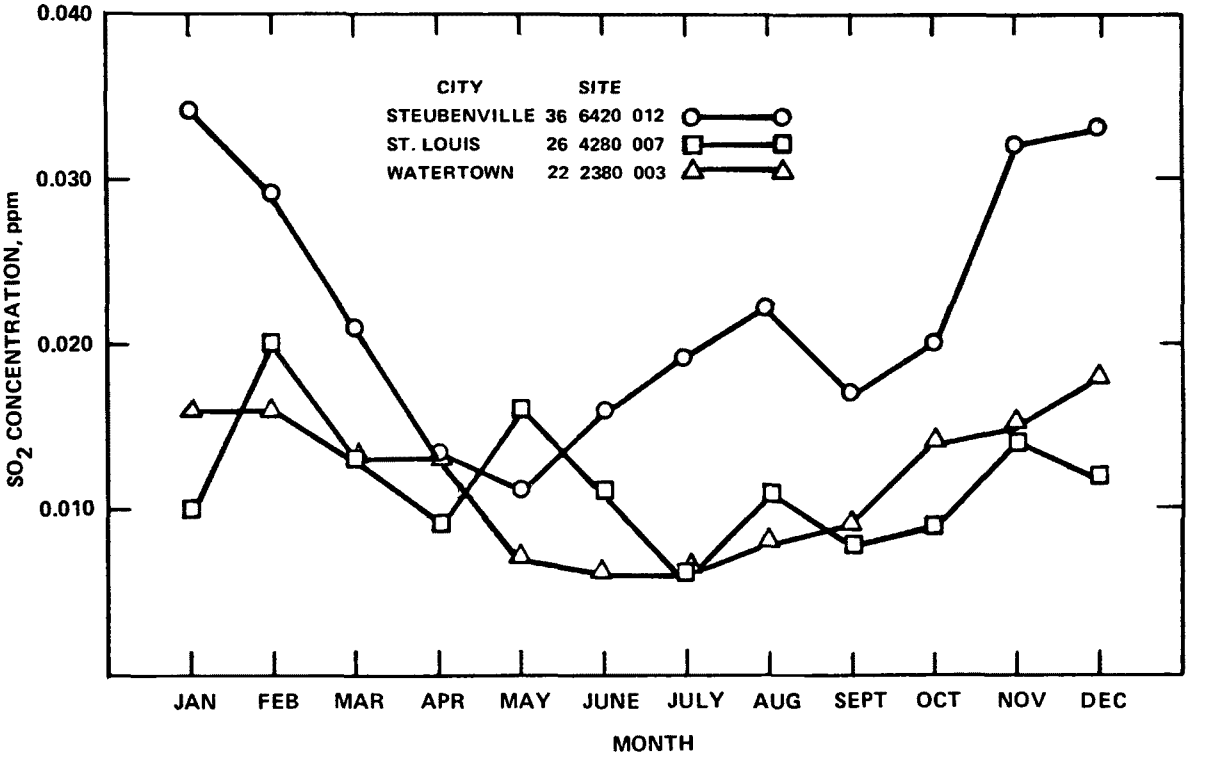

Figure 5-8. Seasonal variations in sulfur dioxide levels are shown for Steubenville, St. Louis, and Watertown.

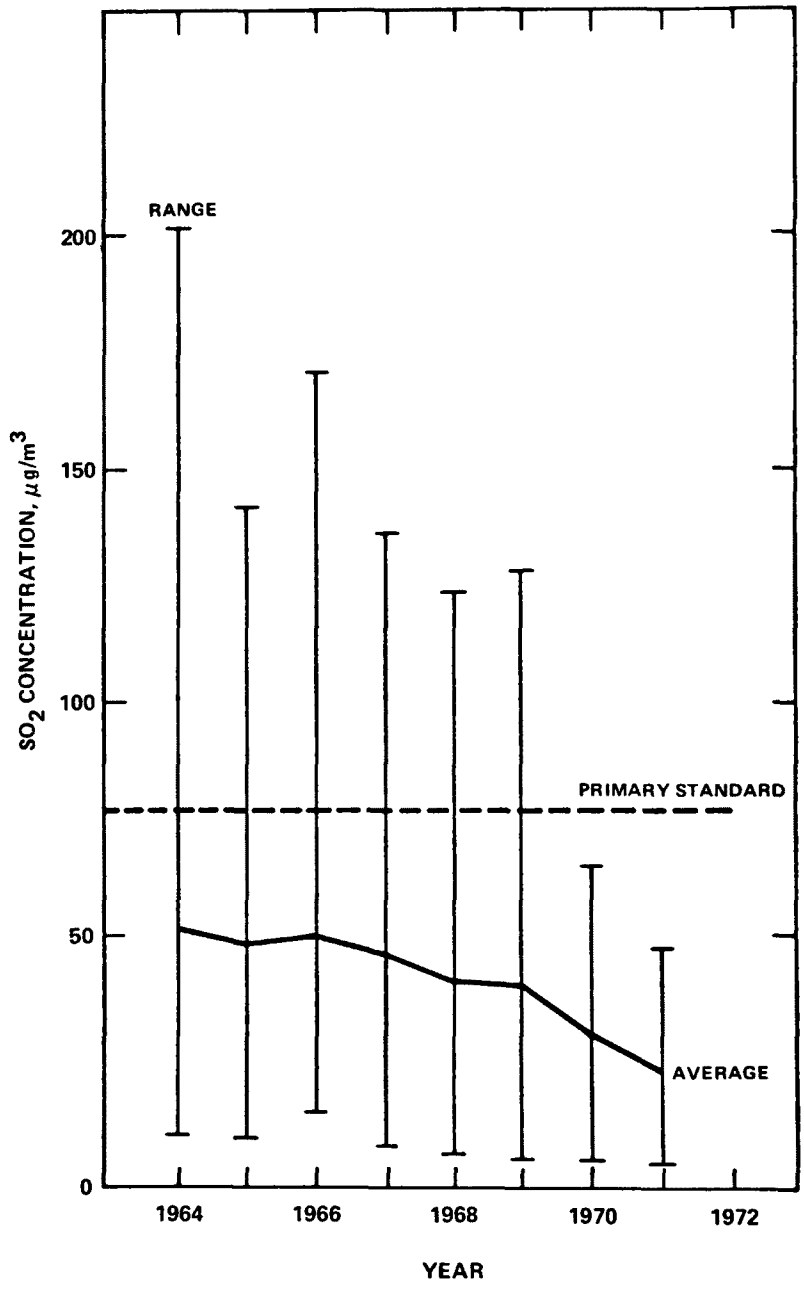

Figure 5-9. Average sulfur dioxide concentrations are shown for 32 urban NASN stations.

Source: National Academy of Sciences (1975).

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Figure 5-10 the national trends in annual average SO_2 concentrations from 1972-1977 at 1333 sampling sites are displayed. In Figure 5-10, the diamond symbolizes the composite annual average concentration; the triangle is the median value, while the dots are extreme values and the thick band covers the 10-90th percentile range.

Over the period of 1970-77 SO_2 emissions are reported to have decreased only slightly (EPA, 1978). In 1970 the estimated annual manmade SO_2 emissions were 29.8 million metric tons. By 1977 this was reduced only to 27.4 million metric tons. The improvement in the ambient air quality levels for SO_2 reflects displacement of sources from urban areas to rural areas, the restriction of sulfur content of fuels used in low-level area sources, the building of newer sources with taller stacks, and source emissions controls.

The first air quality criteria document for sulfur oxides, published in 1969, presented the frequency distributions for sulfur dioxide levels in selected American cities for 1962-1967 (U.S. Department of Health, Education, and Welfare, 1969). The 1960's data came from the Continuous Air Monitoring Project (CAMP), which operated continuous monitors in a few of the largest U.S. cities. The cities are: Chicago, Philadelphia, St. Louis, Cincinnati, Los Angeles, and San Francisco. Improvements in sulfur dioxide levels in each of the six cities are demonstrated by comparing their 1962-1967 data with data for 1977 (Table 5-4). In each city there is more than one continuous monitor now operating. The station reporting the highest levels in 1977 was used in order not to overemphasize any improvement. The comparison is only an approximation because the locations of the monitors and the instrumental methods used were not the same as those reported in the 1969 document.

TABLE 5-4. COMPARISON OF FREQUENCY DISTRIBUTION OF SO_2 CONCENTRATION (PPM) DURING 1962-67[a] AND DURING 1977[b].

		Frequency Distribution of SO_2 (ppm)					
City	Year	Percentile 30	50	70	90	99	Maximum
Chicago	1962-67	0.03	0.08	0.17	0.32	0.65	0.95
	1977	0.01	0.022	0.032	0.06	0.12	0.25
Philadelphia	1962-67	0.03	0.05	0.09	0.21	0.45	0.85
	1977	0.01	0.02	0.04	0.08	0.23	0.44
St. Louis	1962-67	0.02	0.03	0.05	0.11	0.26	0.72
	1977	0.005	0.01	0.03	0.1	0.37	0.67
Cincinnati	1962-67	0.01	0.018	0.03	0.07	0.18	0.53
	1977	0.013	0.02	0.025	0.04	0.085	0.29
Los Angeles	1962-67	0.01	0.015	0.02	0.04	0.08	0.25
	1977	0.01	0.02	0.02	0.03	0.05	0.09
San Francisco	1962-67			0.01	0.03	0.07	0.17
	1977		0.001	0.01	0.01	0.03	0.03

[a]Concentrations from CAMP stations as reported in Air Quality Criteria for Sulfur Oxides document, U.S. Dept. of Health, Education, and Welfare, NAPCA, 1969.

[b]Concentrations from NADB, U.S. Environmental Protection Agency, 1977.

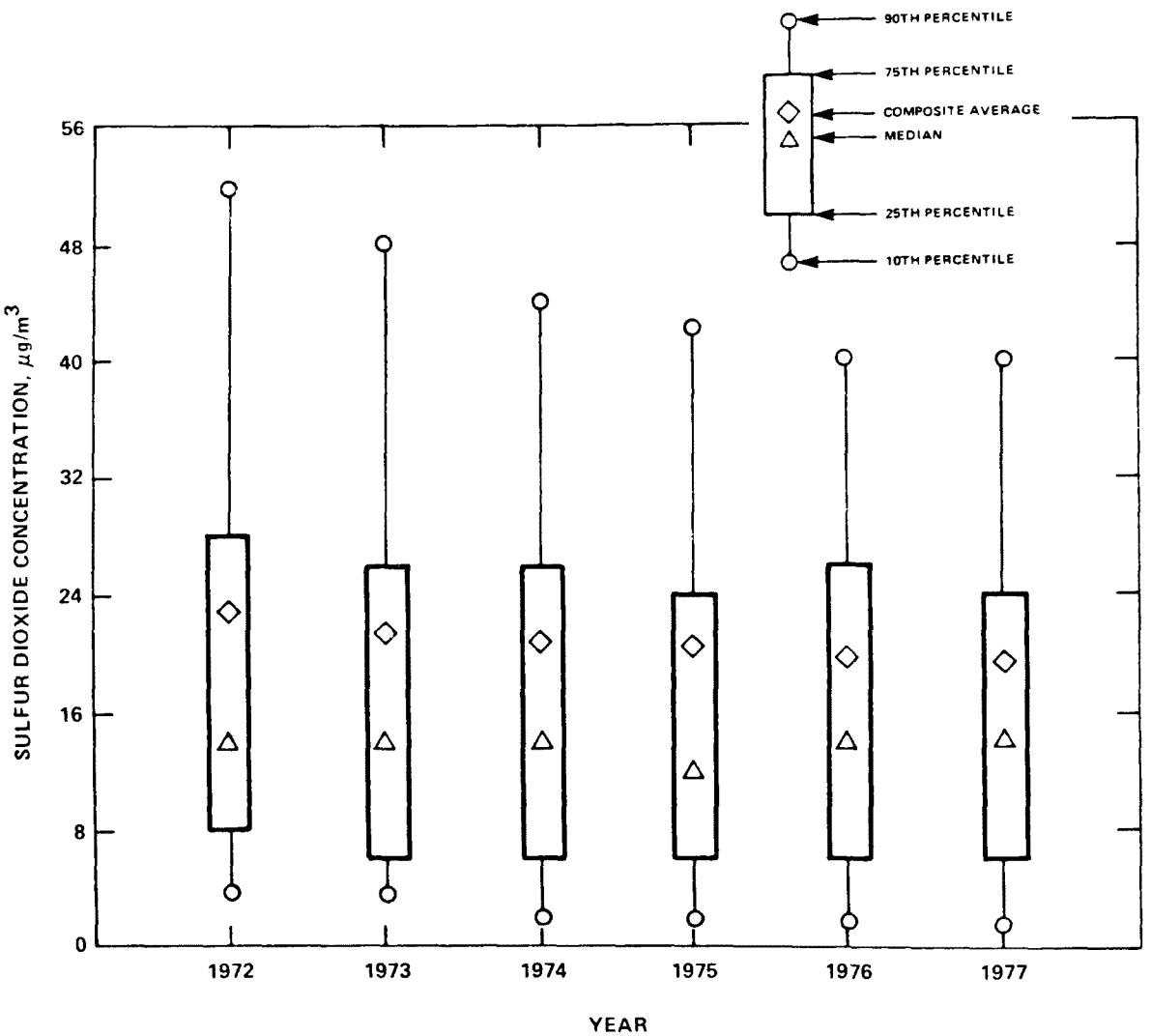

Figure 5-10. Nationwide trends in annual average sulfur dioxide concentrations from 1972 to 1977 are shown for 1233 sampling sites.

Source: U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards (1978a).

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In each city the peak concentration has decreased. In most cities the peak is less than one-half of the earlier values. The only exception is St. Louis, where the earlier peak was 0.72 ppm and the 1977 peak was 0.67 ppm. The result is not unexpected in that the earlier summary is a composite frequency distribution of 5 years of monitoring.

More stable indicators of improved air quality are provided by the 50th, 70th, and 90th percentile concentrations. In Chicago, the 50th percentile concentration dropped from 0.08 ppm to 0.022 ppm. In Philadelphia the levels have improved substantially; the 50th, 70th, and 90th percentile concentrations are less than one-half the earlier values. Modest improvement is shown for St. Louis and Cincinnati; their 50th percentile concentrations are lower now than they were in the mid-1960's. The highest concentrations occur as frequently in St. Louis as they did before, but in Cincinnati they occur less frequently. Review of the St. Louis SO_2 data shows improved air quality for most of the city. The high concentrations now reported are typical of only a smaller section of the city. Los Angeles shows improvement in reducing the high concentrations, but the 50th percentile concentration is actually slightly higher than it was the previous decade. Similarly, San Francisco has trimmed the peaks, but it has a very low median value.

In summary, the frequency of peak levels has been reduced in most urban areas. The steady improvement of SO_2 ambient air quality has been slowed somewhat in recent years. Only 1 percent of the sulfur dioxide monitoring sites show levels above 80 $\mu g/m^3$, the current annual NAAQS. In 1974 the annual mean sulfur dioxide standard was exceeded in 3 percent of the monitoring stations (31 of 1030), compared with 16 percent in 1970. In 1977 and 1978, 2 percent of the sites reported violations of the 24-hr standard. In 1974 this standard was exceeded in 4.4 percent of the reporting stations (99 of 2241), compared with 11 percent in 1970. Many of these sites reporting violations of the 24-hr standard are in remote areas near large point sources.

5.3 AMBIENT MEASUREMENTS OF SUSPENDED PARTICULATE MASS

The general character of matter designated atmospheric suspended particles has been described in Chapter 2. These particles range in size from about 5×10^{-9}m, roughly corresponding to agglomerates of a few tens or hundreds of molecules, up to about 10^{-4}m, specks of material discernable to the human eye. A useful division of these particles by size into fine and coarse fractions occurs in the range of 1 to 2×10^{-6}m or 1 to 2 micrometers (μm) as was discussed in Chapter 2.

The mass of suspended particles, generally concentrated in particles above about 0.1 μm, is usually estimated by filtration of known volumes of air. The goal of this filtration process is the separation of the gas phase from liquid and solid condensed phases of atmospheric aerosol. Thus, the mass of material accumulated on a filter is taken to represent the volume of aerosol treated, and results are presented in 10^{-6} grams, i.e., micrograms (μg) of particulate matter/cubic meter of aerosol, abbreviated "$\mu g/m^3$".

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Chapter 3 discusses some of the complications of commonly used filtration methods including retention of reactive gases such as SO_2 and HNO_3 and loss by evaporation of water and other moderately volatile liquids. While commonly used filtering media are highly efficient for collection of fine particles, determining coarse particle concentrations has involved major problems in sampler design. Despite these complications, which were discussed in detail in Chapter 3, the largest body of information on the distribution of suspended particulate mass in time and space has been obtained with the hi-vol or TSP (total suspended particulates) method. Routine monitoring information is available from the National Aerometric Data Bank maintained by EPA for many sites; some are EPA sites, many are operated by state and local agencies.

The following discussion relies mainly on NADB data; analyses are to be found in the 1976 and 1977 National Air Quality and Emissions Trends reports, in Trends in the Quality of the Nations Air reports in 1980, and in the document "Deputy Assistant Administrator's Report on Ambient Monitoring Activities - Air Portion." (EPA 1977, 1978a, 1980, 1980a).

5.3.1 Monitoring Factors

The accuracy and precision of particulate monitoring are limited by three general considerations: (1) sampling methods, including instrumentation, analytical methods, and quality assurance; (2) sampling frequency; and (3) location of monitors. Chapter 3 discusses the first of these considerations; the second and third are discussed in this chapter. Sampling frequency affects the confidence limits on mean TSP concentrations and annual or seasonal trends. It is appropriate to discuss this limitation at the beginning of this section before the 1978 national TSP data base is presented. The siting of TSP monitors influences significantly the levels measured, and hence the interpretation of data. These considerations are presented with examples in several sections of this chapter.

5.3.1.1 Sampling Frequency--In 1978 there were 4105 TSP monitoring sites in the United States and its territories that reported data to the National Aerometric Data Bank (NADB) of the U.S. Environmental Protection Agency. Of these, only 2882 had enough observations per quarter and per year for the data to be considered valid for estimating annual averages. The number of sites reporting valid data range from zero in Delaware and American Samoa to 318 in Ohio. The most populous state, California, had 60 and New York had 236.

The U.S. Environmental Protection Agency has established a uniform sampling schedule to be followed by all State and local agencies. It requires a 24-hr sample (midnight to midnight) every 6th day. Hence, in 1 year there are 60 or 61 possible sampling days from which to derive the mean value and distribution, and to determine attainment of current standards. In 1978 14 percent of all reporting sites had 60 or more observations.

Sampling days are missed and samples must be voided for a variety of reasons. Therefore, a minimum requirement has been established for considering the data from any site as valid in

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determining an annual average: there must be at least five observations during each quarter of a calender year. Of the Federal, State, and local TSP sites reporting data to NADB, 70 percent met this requirement.

The distribution of observations for the 2882 valid monitoring sites in 1978 is shown in Figure 5-11. Ten (10) percent of these sites had less than 47 observations; 50 percent had more than 56 observations. However, 80 percent of the monitoring sites collected fewer than 60 samples. Three percent of the monitors sampled at an equivalent frequency of 1 day in 3, and fewer than 2 percent collected samples at a frequency of 1 day in 2.

The current NAAQS for TSP consists of an annual geometric mean and a once-per-year daily value. Frequency of monitoring is a fundamental parameter of the air quality data used for comparison with the standards. The period of determining an annual average for comparison is a calendar year. If the number of 24-hr observations is less than 365, then the true mean concentration for the year can only be expressed as residing within a range of values. By assuming that the actual distribution of values is log normal, then confidence intervals can be calculated from the geometric mean and the geometric standard deviation. Figure 5-12 shows the effect of sample size on the 95 percent confidence intervals for a hypothetical site whose true annual geometric mean is equivalent to 75 $\mu g/m^3$ the current annual standard. From this example we can only conclude that the annual geometric mean is 75 ± 7 $\mu g/m^3$, if the mean for that year was determined from a sample size of 61. Increasing the sampling frequency to 1 day in 2 reduces the level of uncertainty so that the annual mean can be expressed as 75 ± 3 $\mu g/m^3$.

A critical factor in evaluating compliance with once-a-year standards is the effect of sampling frequency. Figure 5-11 shows that in 1978 the majority of valid sites (80 percent) had fewer than 60 sampling days. The sites with more frequent sampling had a greater chance of sampling the higher concentrations as Figure 5-12 shows. Assuming that there are a number of days on which the observations are above the standards, the probability of selecting 2 or more days on which standards are exceeded is a function of sampling frequency. If there are 10 days above the standards, there is only a slightly better than 50 percent chance of actually monitoring on 2 of those days given a sampling frequency of 61 out of 365 days. When the sampling frequency is doubled to 122 sampling days, the probability of capturing 2 days out of 10 that exceed the standards increases to 80 percent. In actuality, samples are not taken randomly; they are taken systematically, usually at a rate of once every 6 days. The probability of capturing the highest period is further complicated in that the log normal distribution of TSP concentrations does not apply uniformly to all sites.

An additional complication occurs when the meteorological regimes affecting the TSP concentrations are considered. Attainment of standards may depend on the number of "clean"

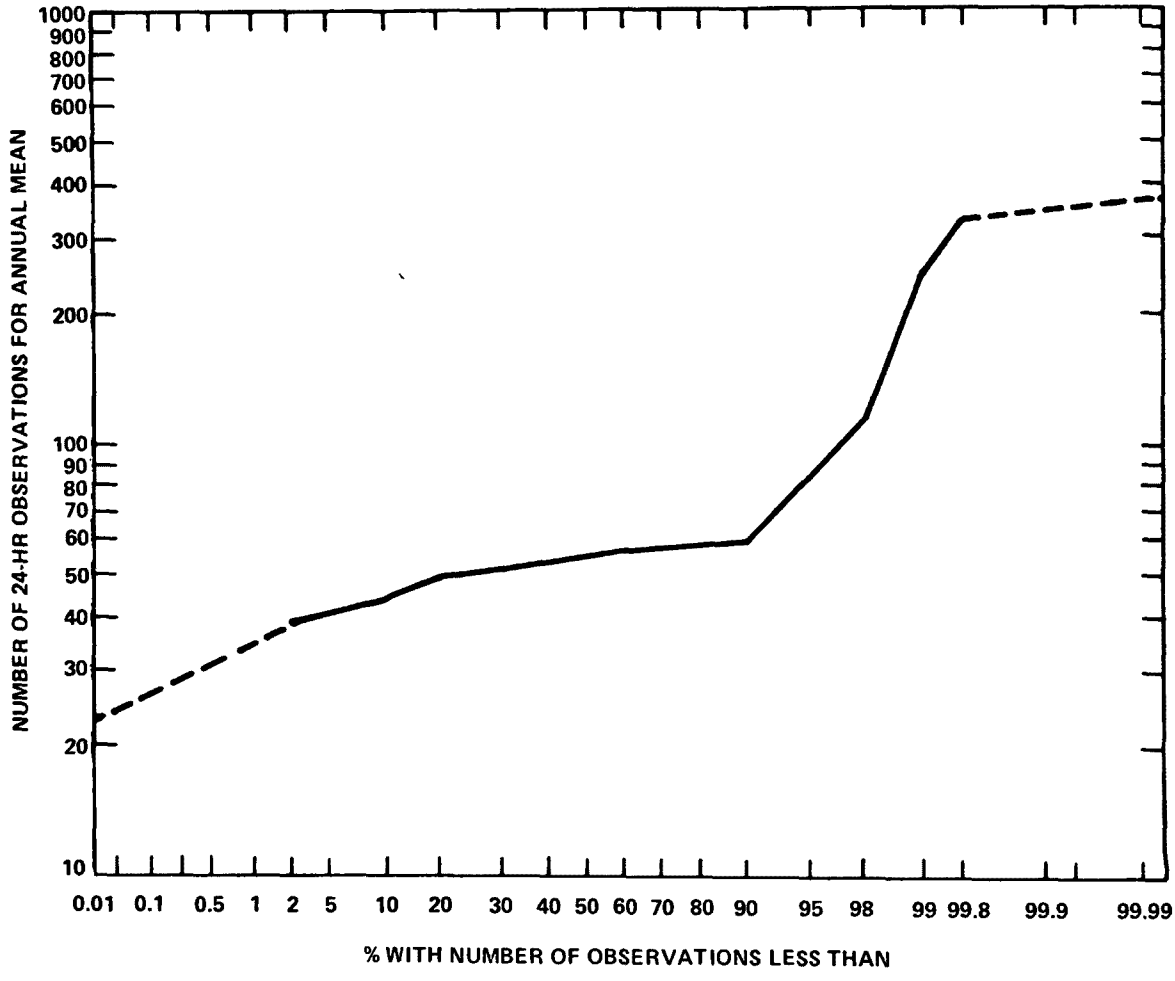

Figure 5-11. Distribution shows the number of observations per valid site in 1978; total is 2882 sites.

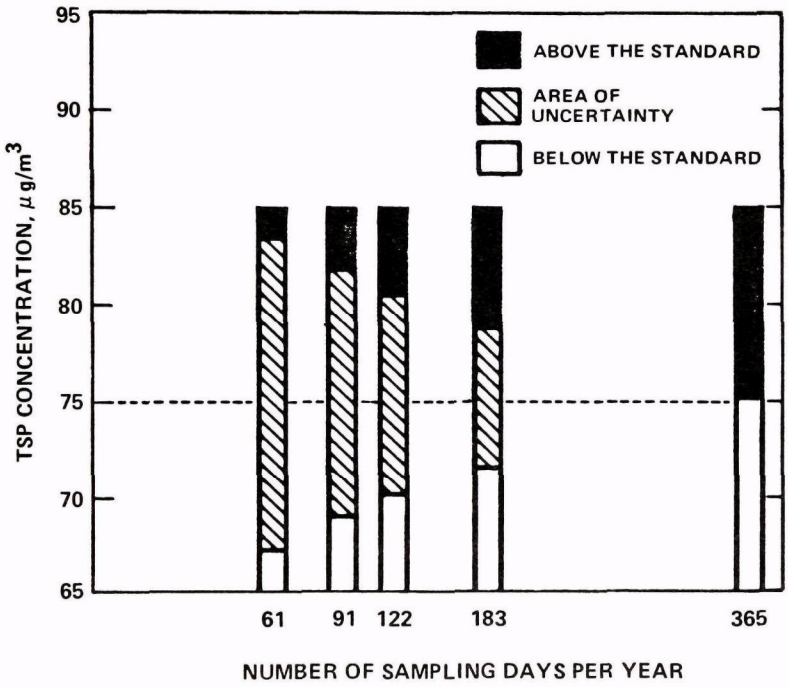

Figure 5-12. The 95 percent confidence intervals about an annual mean TSP concentration of 75 $\mu g/m^3$ is shown for various sampling frequencies (assume the geometric standard deviation equals 1.6).

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sampling days versus the number of "dirty" sampling days. Watson (1979) exemplifies this problem with Portland, OR, TSP data. The annual geometric mean TSP data show a decreasing trend from 1973 through 1975, with a significant increase in 1976. If these data are reexamined and weighted by the meteorological regimes actually sampled in each year, the conclusions are changed. The stratified mean TSP values show a large drop in concentrations occurring between 1974 and 1975, with the levels being constant for the year before and after. Since these means are determined from a sample set varying from 49 samples in 1974 to 79 samples in 1976, a statistical test is required to determine whether the means of any year are significantly different from those of any other year. The 95 percent confidence intervals for all stratified means do overlap. Watson concludes, then, that there is a reasonable chance that the true means do not really vary from year to year.

5.3.1.2 Monitor Location--The choice of sampling location can obviously affect the concentrations measured. Remotely located monitors typically record low concentrations; urban monitors characteristically record higher concentrations. The positioning of a monitor at a chosen location can also affect measured concentrations. For example, at a specific location, the height of the monitor above the ground influences sample concentrations. If the monitor is elevated above surface sources, lower concentrations of coarser particles might be measured.

Some studies indicate that TSP concentrations decrease with increasing monitor elevation (Record and Bradway, 1978; Lioy et al., 1980a, Pace, 1978), with distance from a roadway and with distance from other nearby sources. However, monitor elevation does not appear to be systematically biasing the national TSP data in the aggregate. Other siting considerations are discussed later.

The inferences drawn about air quality levels, trends, and population exposures from the TSP data presented in this chapter are made in full knowledge of the following limitations of TSP monitoring: (1) sampling sites are not standardized; (2) frequency of sampling is quite varied; (3) the vast majority of sites reporting have fewer than 60 sampling days per year; (4) the frequency of sampling is not randomized with respect to meteorological conditions. (5) no spatial averaging is used in analyzing or reporting data; and (6) though the ambient air monitor is stationary, the population it is intended to represent is highly mobile and spends a portion of its time indoors.

5.3.2 Ambient Air TSP Values

The distribution of 1978 annual arithmetic means for valid TSP monitoring sites is plotted in Figure 5-13. Half of all the Nation's sites had annual arithmetic mean values less than 60 $\mu g/m^3$. Annual mean values range from 9 to 288 $\mu g/m^3$. Only 14 valid sites had annual

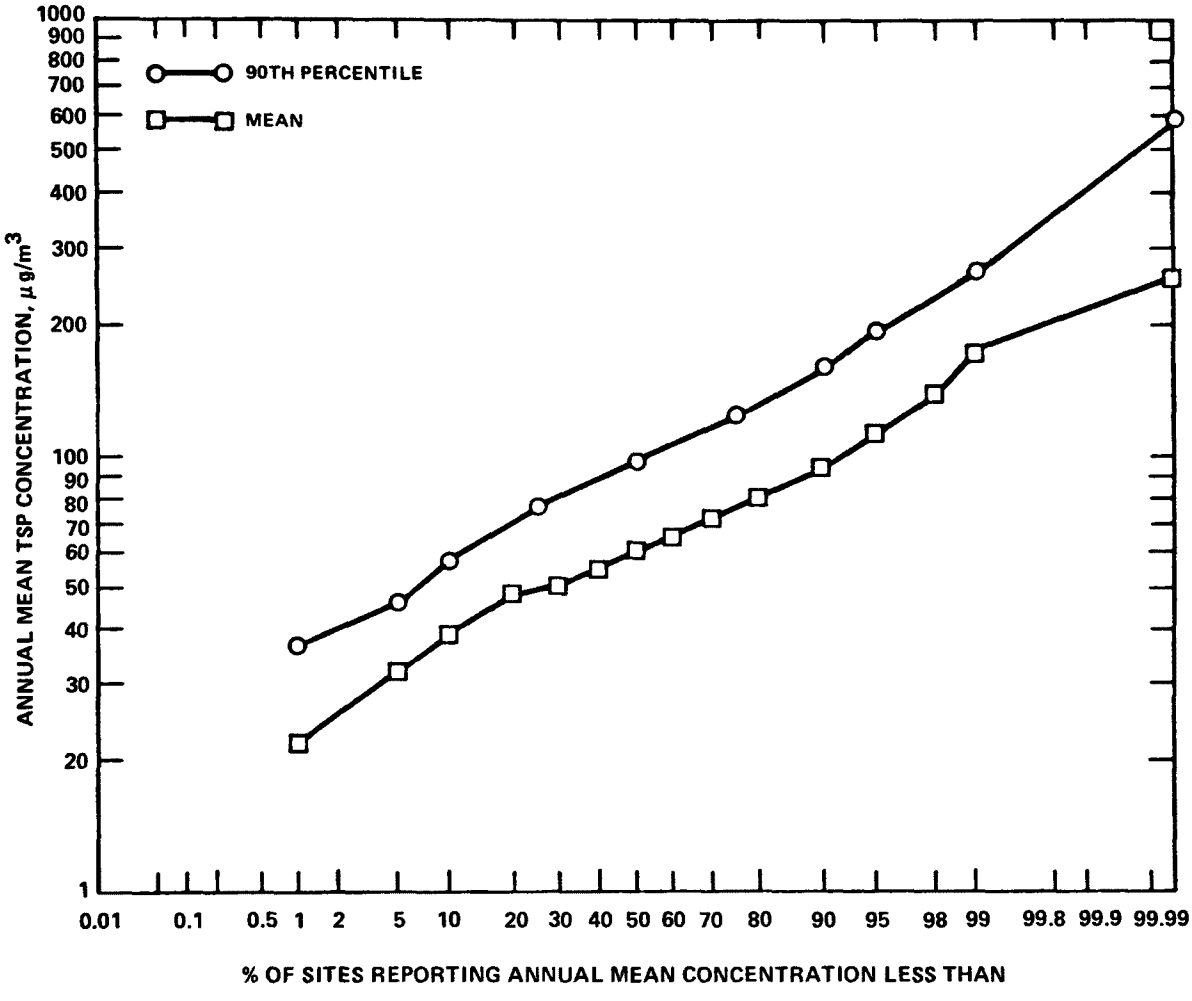

Figure 5-13. Distribution of mean and 90th percentile TSP concentrations is shown for valid 1978 sites.

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mean concentrations equal to or less than 16 $\mu g/m^3$. These lower values are associated with remote monitoring sites. Two background sites, Glacier National Park and Acadia National Park, had 1977 annual averages of 11 and 21 $\mu g/m^3$ respectively. At the other end of the distribution, 25 percent of sites had annual means greater than 76 $\mu g/m^3$ and 10 percent were greater than 96 $\mu g/m^3$. Higher annual concentrations are found in many populated and industrialized areas. About 30 sites reported annual averages in 1978 above 150 mg/m^3. Topping the list are four central-city sites in commercial, residential, or industrial settings. A Phoenix, AZ, site (0136) had the highest annual mean of 256 $\mu g/m^3$, followed by a site in Calexico, CA at 201 $\mu g/m^3$ and an industrial site in Granite City, IL, at 197 $\mu g/m^3$.

These extremely high annual TSP concentrations are associated with commercial and industrial locations. Of the top 30 sites, 15 are industrial. Many of the higher concentrations (19 of 30) were found at central-city locations. Only four were classified as rural sites, most of which are also residential areas. It is also likely that arid climates and dusty conditions in the vicinity of some monitoring sites might lead to suspension of surface material. However, it is impossible to ascertain the contribution of fugitive or resuspended dust to the concentrations measured at these 30 sites without more detailed analysis. The histogram of sites against concentrations (Figure 5-14) shows that over a third of all monitoring sites had annual mean values between 40 and 60 $\mu g/m^3$. Slightly less than another third had annual averages between 60 and 80 $\mu g/m^3$.

The distribution of 90th percentile values is also plotted in Figure 5-13. To interpret this distribution, consider that half of all valid monitors had a 90th percentile value in excess of 97 $\mu g/m^3$. For 10 percent of the monitors, 10 percent of the observations exceeded 160 $\mu g/m^3$. For one monitor, 10 percent of the observations exceeded 600 $\mu g/m^3$.

Daily, or 24-hr, TSP concentrations have a wide range. In remote areas such as the Pacific islands, daily values may be as low as a few micrograms per cubic meter. Over the continental United States, concentrations from 5 to 20 $\mu g/m^3$ are routinely reported. In other locations, daily TSP values can exceed 10 times the levels found in remote areas, on occasion exceeding 3000 $\mu g/m^3$. Values exceeding 1000 $\mu g/m^3$ are observed in remote arid regions as well as in populated urban areas. Daily TSP levels approaching these higher values, 500 to 1500 $\mu g/m^3$, are frequently associated with adverse meteorological conditions: low-level inversion, stagnation, or high winds resuspending surface material.

Thirty valid TSP monitoring sites report highest 24-hr values above 600 $\mu g/m^3$. Only a few of these sites are in the top 30 in annual average. In cities like Topeka, KS, and Libby, MT, which are not densely populated or industrialized, these high concentrations may result from chance occurrences, such as fires or dust storms. In other cities like El Paso, TX, and Granite City, IL, which are industrialized, the maximum concentrations are more likely to be related to persistent sources of pollution.

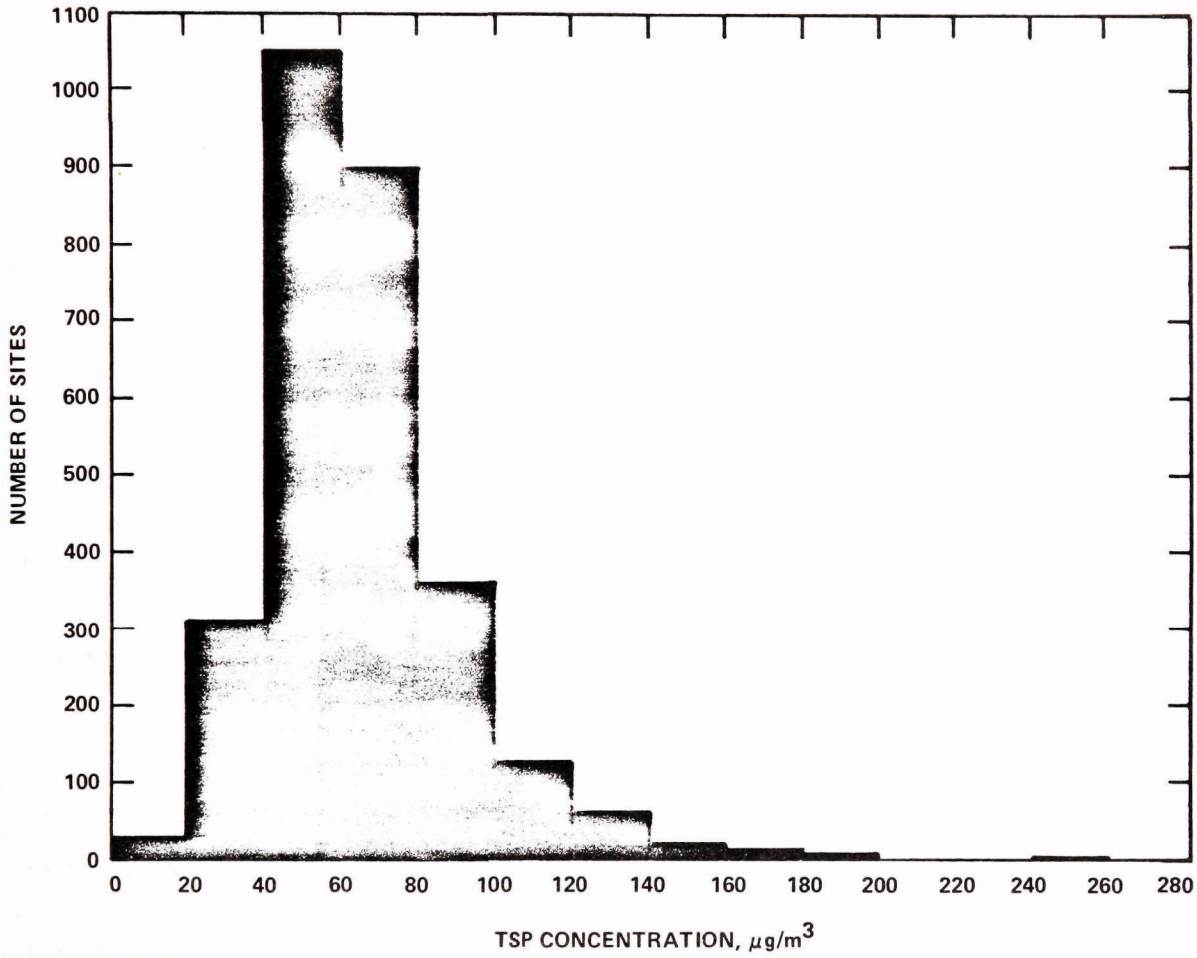

Figure 5-14. Histogram of number of sites against concentration shows that over one-third of the sites had annual mean concentrations between 40 and 60 $\mu g/m^3$.

5.3.3 TSP Concentrations by Site and Region

Ambient TSP can be simply considered as arising from the particulate emission of three broad source categories: 1) readily identifiable large point sources such as smoke stacks, 2) fortuitous sources such as dusty roads and plowed fields, 3) natural sources. The relative contributions of these three sources are affected by meteorological conditions and location. Hence it is not surprising to see a wide variation in daily measurements at a single site, variation over an urban area, or variation among regions of the country. This section will, by illustration, examine these differences in TSP concentrations by location.

5.3.3.1 TSP by Site Classifications--Evidence that fugitive dust contributes significantly to both Western arid sites and many urban sites is quite extensive. Discussion of the general influence of fugitive dust may be found later in this chapter in the section on coarse particles.

The general differences in annual TSP concentration among locations is seen in Figure 5-15. These differences reflect the character of the neighborhoods where the monitors are located. This figure summarizes the mean concentrations from 154 sites in 14 cities. Residential neighborhoods in and near cities have TSP levels between 50 and 70 $\mu g/m^3$. Commercial sites have a wider range of concentrations (60 to 110 $\mu g/m^3$). Industrial locations generally range between 80 to 150 $\mu g/m^3$.

The 1978 data base also has been analyzed on the basis of two additional sets of descriptors. One description scheme classifies monitoring sites by their purpose: population exposures, source receptors, or background sites. The other scheme identifies sites by the amount of development: central city, suburban, rural, or remote. These classifications are not mutually exclusive.

When sites are grouped by descriptors, a distinct weighting becomes apparent. Almost 80 percent of the sites are population oriented; approximately 15 percent are source related, and less than 6 percent are background monitors. The distribution by development also reflects its population emphasis. Of the total monitors, 83 percent are at either central-city or suburban sites, 15 percent are at rural sites, and 2 percent are at remote sites. In these data 38 percent of the background sites had median values less than or equal to 27 $\mu g/m^3$, whereas only 4.4 percent of all sites had these low values. Only 30 percent of the background sites had median values above 44 $\mu g/m^3$, and none had values above 97 $\mu g/m^3$, whereas 75.5 percent of source sites had median values above 44 $\mu g/m^3$. The pattern is consistent for the distribution of the 90th percentiles cross-tabulated by site purpose. Cross-tabulations of site median values and site 90th percentile values with the development-related site descriptors is further confirmation of the influences of siting on measured TSP concentrations. Rural and remote sites have lower median values and lower 90th percentile values. The suburban sites reflect the overall national distribution. The central-city category has proportionately more sites in the higher concentration ranges.

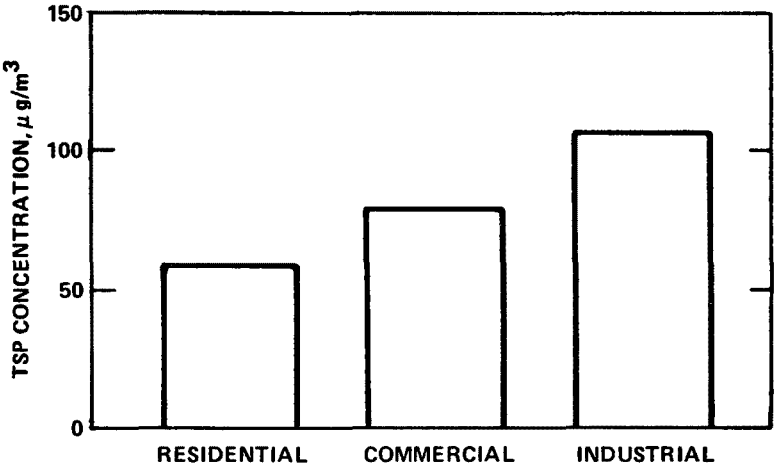

Figure 5-15. Histogram of mean TSP levels by neighborhood shows lowest levels in residential areas, higher levels in commercial areas, and highest levels in industrial areas.

Source: U.S. Environmental Protection Agency (1976).

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5.3.3.2 Intracity Comparisons--Because of the strong neighborhood influence on TSP concentrations, it is not unusual to find considerable variation in peak and mean concentrations across a community. It is instructive to examine intracity differences because it illustrates the difficulty in estimating population exposures to TSP.

Data on the nine cities having the highest annual TSP concentrations in 1977 are given in Table 5-5. Only sites having enough observations per quarter to report an annual mean are used. Although TSP concentrations in these cities were generally high, in 1977 the less developed or less industrialized areas in each city had annual geometric mean concentrations below 75 $\mu g/m^3$, (currently the annual primary NAAQS), with the exception of Granite City, IL. The annual mean concentration for the dirtiest sites can be two to four times higher than that for the cleanest sites within the same city.

TABLE 5-5. RANGE OF ANNUAL GEOMETRIC MEAN CONCENTRATIONS IN AREAS WITH HIGH TSP CONCENTRATIONS IN 1977

City	Number of sites	Number of sites with annual average >75 $\mu g/m^3$	Annual range, $\mu g/m^3$	Range of maximum 24-hr value, $\mu g/m^3$
Tucson, AZ	7	3	67-156	178-591
Pocatello, ID	4	3	65-218	344-1371
Chicago, IL	25	12	50-170	152-1106
Granite City, IL	8	8	85-185	227-485
Taos County, NM	1		168	577
Middletown, OH	3	2	64-192	157-707
Cleveland, OH	23	13	48-152	128-705
Youngstown, OH	5	4	66-172	163-602
El Paso, TX	14	10	60-158	205-691

5.3.3.3 Regional Differences in Background Concentrations--It has been demonstrated that TSP concentrations can vary across an urban area and among cities with different sources and meteorology. Superimposed on this intercity difference may be regional differences in the natural or transported fraction of TSP concentrations. Figure 5-16 shows the contribution of these sources to nonurban levels. It was assumed that the global and local contributions in the average would be similar. The greatest difference among regions is the contribution from "continental" and transported emissions. These two categories of particles contribute in such a way that nonurban sites in the West typically report annual geometric means of 15 $\mu g/m^3$, in the Midwest, 25 $\mu g/m^3$, and in the East, 35 $\mu g/m^3$. Except for the Acadia National Park site (18 $\mu g/m^3$) and Millinocket (23 $\mu g/m^3$), all sites in Maine had 1977 annual geometric means

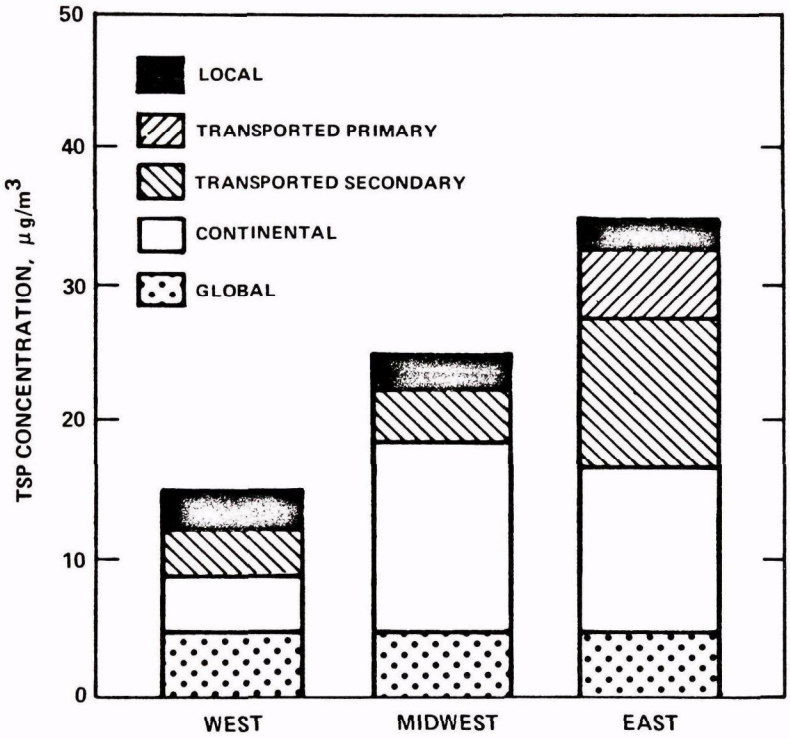

Figure 5-16. Average estimated contributions to nonurban levels in the East, Midwest, and West are most variable for transported secondary and continental sources.

Source: GCA.

above 30 μg/m^3. Nonurban sites in Wisconsin typically had mean TSP levels less than 25 μg/m^3. Nonurban sites in Montana had levels less than 20 μg/m^3 in 1977; the individual means were: Big Horn County, 17 μg/m^3; Custer County, 15 μg/m^3; Powder River County, 14 μg/m^3.

5.3.3.4 Peak TSP Concentrations--To indicate the severity of TSP ambient exposures, the 90th percentile concentration of the 24-hr measurements was examined for all 4008 sites in the 1977 NADB. The concentrations of TSP and other air pollutants have been widely reported to be log normally distributed (Larsen, 1971). This statistical relationship, however, appears inappropriate at the high and low ends of the distribution (Mage and Ott, 1978). Because the extreme values at the high end are subject to wide scatter, the 95th or 99th percentile was found to be less representative of the severity of high TSP levels. The 90th percentile was therefore chosen as being a more stable indicator, the TSP value which is exceeded 36 days of the year.

Figure 5-17 shows the number of AQCR's whose monitors have their 90th percentile TSP concentration within the various categories. Of the country's 254 AQCR's, only 20 reported every station with a 90th percentile below 100 μg/m^3. One hundred and fifty-four AQCR's had 90th percentile values in at least one site between 100 to 200 μg/m^3. These data suggest that most of the U.S. population might experience ambient TSP concentrations exceeding 100 μg/m^3 for at least 36 days of the year.

5.3.4 Temporal Patterns in TSP Concentrations

5.3.4.1 Diurnal Patterns--TSP concentrations vary with local emissions strength, meteorological conditions, and the changes in the contributions from background particles. The particle emissions loadings to the atmosphere in general increase during the day and decrease at night The atmosphere undergoes greater vertical mixing during the day, and wind speeds near the surface increase as a result. Greater vertical mixing coupled with increased source emissions cause particle mass loadings to increase. At night, decreased mixing and the resultant decreased surface winds permit settling of larger particles. With increased atmospheric stability, local elevated sources are not as likely to mix to the ground. The final result is that diurnal patterns in TSP are frequently not pronounced. Trijonis (1980) found no clear diurnal trend in sub-15 μm particle mass in 6-hour samples from the St. Louis Regional Air Pollution Study (RAPS). Stevens, et al. (1980) have found slightly higher daytime levels of sub-15 μm particle mass in a remote site in the Smoky Mountains; however, Pierson, et al. (1980) noted no significant diurnal pattern in a forested region in Pennsylvania.

It is likely that day-night patterns are somewhat obscured by averaging times. Heisler, et al. (1980) found peaks in light scattering and in particle mass corresponding to rush hours in Denver in the winter of 1978; minimum values were found in mid-afternoon corresponding with mixing height maxima. Unfortunately, diurnal cycles are not well established because the standard sampling procedure for TSP measurements yields a 24-hr sample, midnight to midnight.

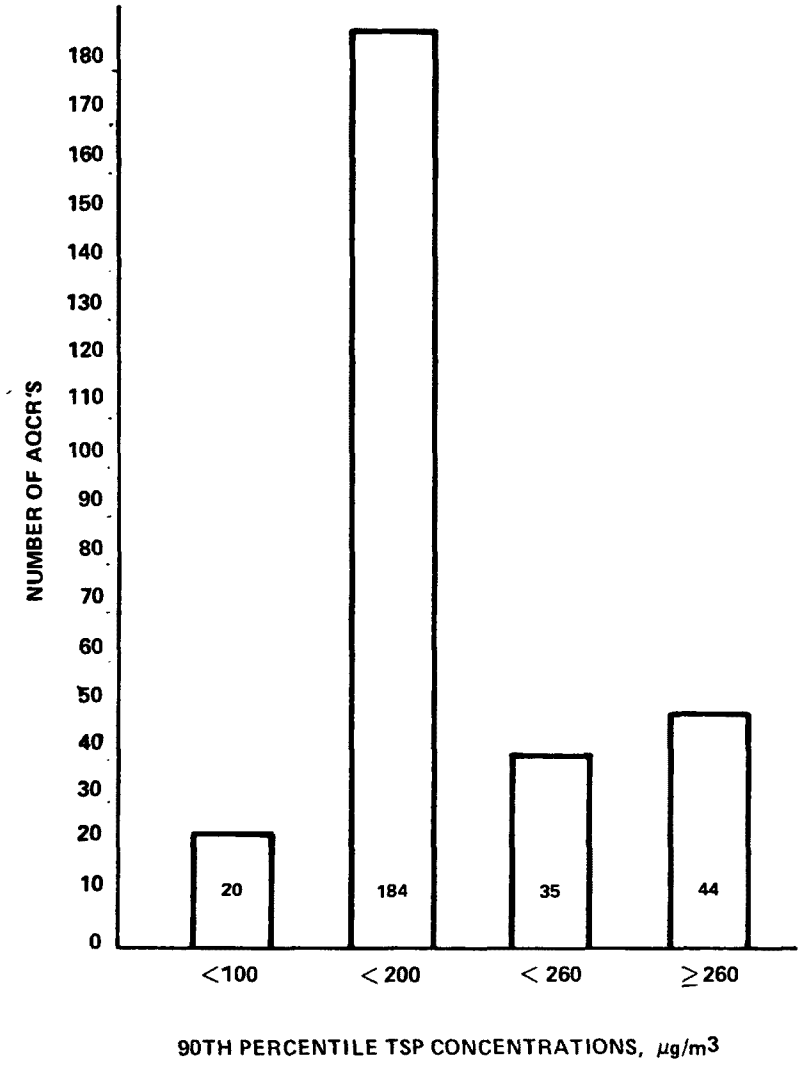

Figure 5-17. Severity of TSP peak exposures is shown on the basis of the 90th percentile concentration. Four ACQR's did not report.

5.3.4.2 Weekly patterns--Since human activity follows distinct weekly cycles, it is likely that anthropogenic sources of particles will also have weekly patterns. The most distinct weekly patterns are weekdays versus weekends. Trijonis et al. (1980) have examined the St. Louis TSP and dichotomous data base for weekend-weekday differences in particle loadings. They concluded that there was only a slight (-9 percent) difference between weekend TSP values and weekday values for the average of five urban sites in St. Louis. For three suburban sites the difference was -5 percent and for two rural sites the difference was -12 percent. The urban difference was dominated by readings from one monitor in a heavily industrial and commercial area.

5.3.4.3 Seasonal Patterns--Analyzing temporal patterns can frequently provide insight into the nature and source of particulate matter. Meteorological parameters affect the generation and dispersion of particles. These parameters include, among others, degree-days, mixing height, ventilation factors, frequency of calms and stagnations, and precipitation. There are also seasonal patterns in some sources emissions.

Because meteorological parameters are so important, it is likely that seasonal patterns in one area cannot be generalized to other areas. Trijonis et al. (1980) found a modest seasonal pattern of higher TSP concentrations in the summer months in St. Louis. Figure 5-18 supports this observation. It is a comparison between the TSP monthly mean values and the data from dichotomous sampling. The really distinct seasonal pattern is in the fine aerosol fraction. Summer fine-particle concentrations are twice as great as winter values. As discussed later, sulfates aerosol makes up most of the fine-fraction particles and shows a distinct seasonal pattern.

To illustrate the geographic specificity of these seasonal cycles, 3 years of monthly averaged TSP data are presented in Figure 5-19. The data are from Steubenville, OH, an industrialized site in the upper Ohio River Valley. Each monthly mean is derived from 20 or more sampling days. The TSP concentrations are considerably higher than the St. Louis values. The months with the highest TSP in Steubenville were March, April, and May in 1977, July, August, September, and November in 1978, and February and June in 1979. No clear seasonal pattern emerges from this 3-year period.

5.3.4.4 Yearly Trends--In 1957, a National Air Sampling Network (NASN) began to operate routinely on a national basis. The U.S. Public Health Service, with cooperation from State health departments, operated 231 urban and 37 nonurban stations. Some of these stations operated every other year, so in a given year there were 143 urban and 37 nonurban TSP high-volume monitoring sites in operation. These sites collected one 24-hr sample every other week for a total of 26 samples per year. In 1977, over 4000 stations, most of them in state and local networks, reported TSP values to the National Aerometric Data Bank of the U.S. EPA. Not only has the number of sites greatly increased, but the sampling frequency has been 1 day in 6 since 1971. For some cities there are now data for more than 20 years of TSP monitoring.

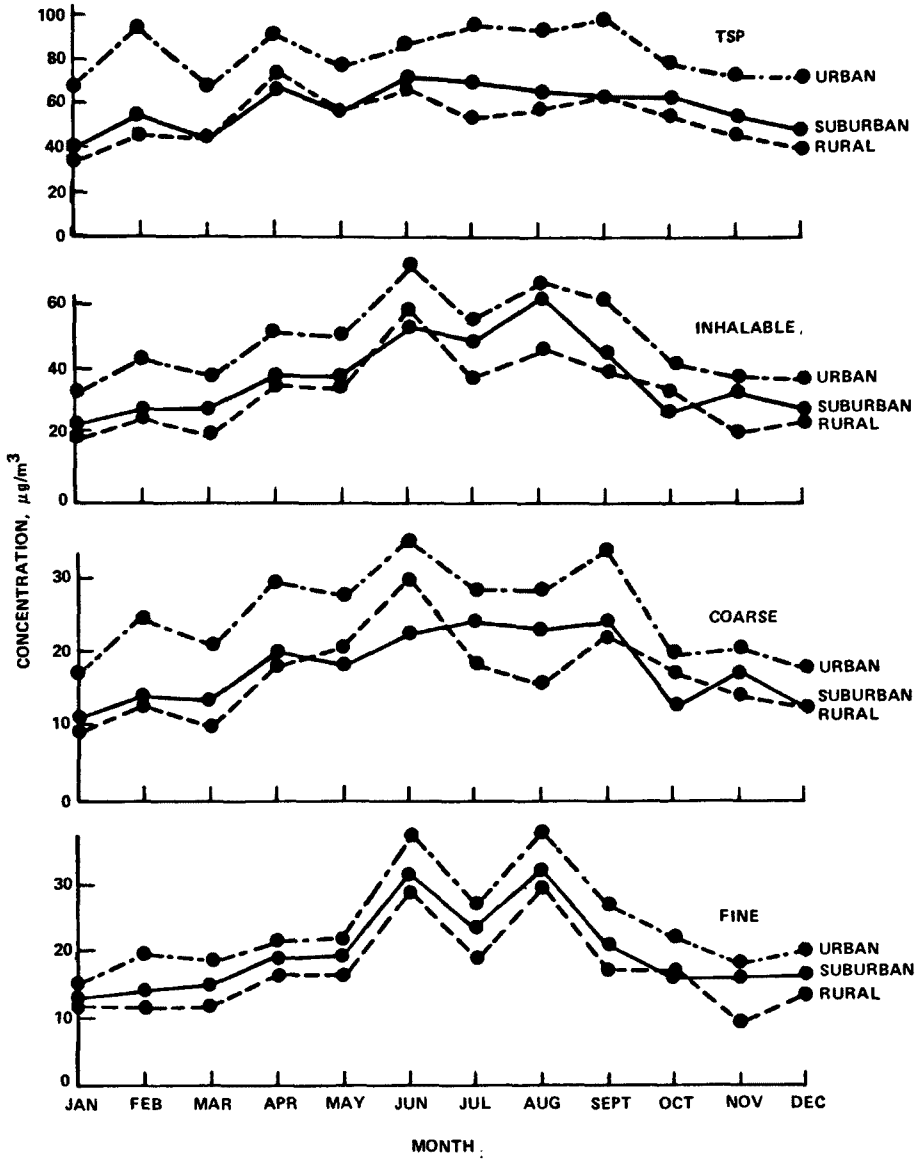

Figure 5-18. Seasonal variations in urban, suburban, and rural areas are shown for four size ranges of particles.

Source: Trijonis et al. (1980).

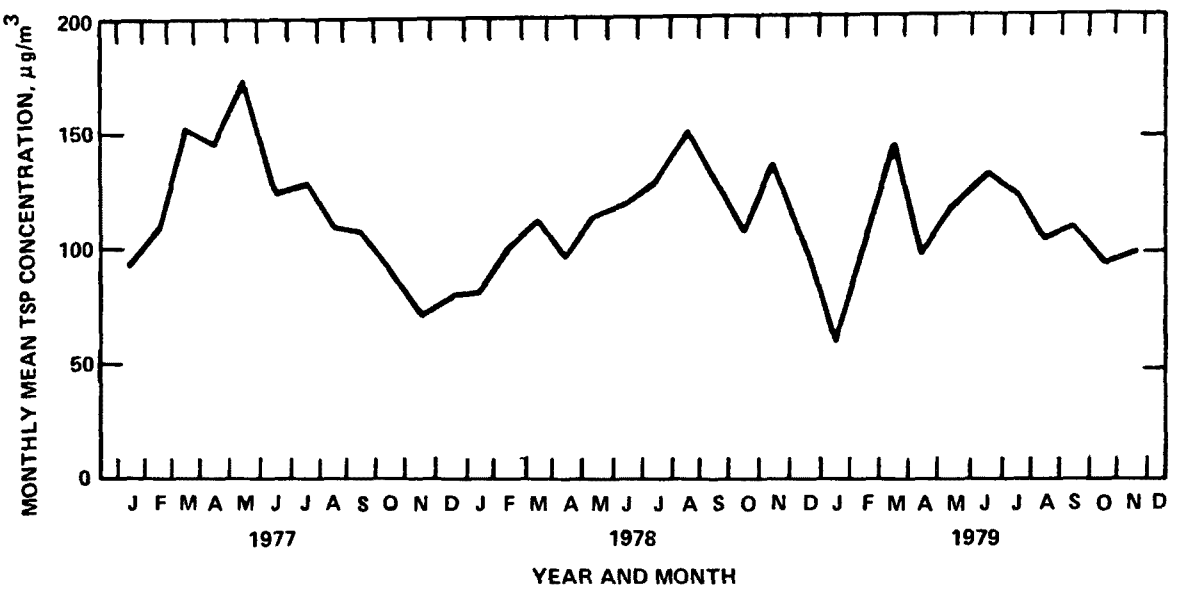

Figure 5-19. Monthly mean TSP concentrations are shown for the Northern Ohio Valley Air Monitoring Headquarters, Steubenville, OH. No clear seasonal pattern is apparent.

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Although the sites may not be in exactly the same locations for every city, general trends in TSP concentrations can be obtained. Figure 5-20 plots the annual geometric mean TSP concentrations for three groups of cities. In 1958, these five cities, classified as industrial, had annual mean TSP concentrations between 140 and 170 $\mu g/m^3$. By 1974 the annual mean concentrations had dropped to between 80 and 110 $\mu g/m^3$. Similarly, three of four cities classified as moderately industrialized showed substantial decreases. Only the Denver station recorded an increase. The four cities classified as lightly industrialized showed less overall change.

Examining the expanded data set for TSP from high-volume samplers shows that for 2707 sites, the composite median concentration has remained about 60 $\mu g/m^3$ between 1972 and 1977. The geometric mean over this period has decreased by approximately 8 percent. The decrease in the 90th percentile of the annual average concentrations is most pronounced over this period (see Figure 5-21). Lowering the TSP concentrations in locations with very high levels has been a target of State air pollution control strategies. In addition, displacing sources to rural regions, building new sources with taller stacks, converting to cleaner fuels, and restricting open burning have decreased the number of locations experiencing annual concentrations of over 100 $\mu g/m^3$.

For the period 1970-77 EPA reported an almost 50 percent reduction in TSP emissions. Most of this reduction occurred in the early 1970's as State air pollution control programs started many major emitters on compliance schedules. The rather modest composite overall reduction of 8 percent in annual TSP levels may be explained by the fact that direct emissions from stationary sources contribute only a fraction of the TSP loadings in the atmosphere.

Another perspective on regional differences is gained from observations of the 1978 data. Table 5-6 provides a statistical summary for the 50th and the 90th percentiles for valid monitors. Region IX ranks first for the mean 50th and 90th percentiles, followed by Region VII, Region VI and Region V. Regions I and II had consistently lower values.

The column presenting the standard deviations of the mean values for the 50th and 90th percentiles is also of interest. Smaller standard deviations suggest that there is more uniformity in reported concentrations among monitoring sites. Regions I, II, and IV have less variance among sites than other regions. This could be interpreted as either more uniform distribution of pollution levels or more uniformity and consistency in placing monitoring sites. The larger standard deviations in other regions, particularly in the West, probably mean that there is greater variation in pollution levels.

There are distinct regional differences in the trends of TSP concentrations. The distribution of site means and the actual rate of change in TSP levels differ among regions of the country. These trends are shown in Figures 5-22 and 5-23; it should be realized that the differences between years and even over the entire period have not been tested for significance. Therefore, intraregion and interregion comparisons are presented qualitatively.

TABLE 5-6. REGIONAL SUMMARIES OF TSP VALUES FROM VALID MONITORS

Number of sites	Region	Median				90th percentile			
		Minimum	Mean	Maximum	SD[a]	Minimum	Mean	Maximum	SD[a]
128	I	14.0	49.2	100.0	14.6	32.0	87.3	181.0	27.7
315	II	10.0	43.2	114.0	15.3	29.0	85.0	286.0	30.6
300	III	27.0	59.8	171.0	20.3	52.0	105.7	296.0	42.1
534	IV	22.0	55.3	137.0	17.2	41.0	93.5	256.0	30.9
781	V	13.0	64.1	189.0	22.0	26.0	122.4	383.0	42.8
294	VI	12.0	65.0	166.0	20.9	37.0	110.4	436.0	45.8
136	VII	34.0	69.7	154.0	20.2	58.0	123.6	359.0	44.2
152	VIII	7.0	54.8	164.0	32.8	18.0	107.8	412.0	64.0
89	IX	16.0	76.5	226.0	38.0	37.0	133.4	381.1	66.0
113	X	11.0	60.3	129.0	24.5	23.0	123.6	361.1	52.5
15	Alaska	11.0	48.1	94.0	22.7	35.0	137.1	250.0	68.7
9	Hawaii	25.0	39.7	70.0	13.7	40.0	63.6	99.0	18.9
10	Puerto Rico	32.0	54.3	85.0	13.9	66.0	90.7	134.0	18.9
2882	Total[b]	7.0	58.9	226.0	22.8	18.0	107.9	436.0	44.9

[a]SD, Standard deviation of the mean.
[b]Including American Samoa and Guam.

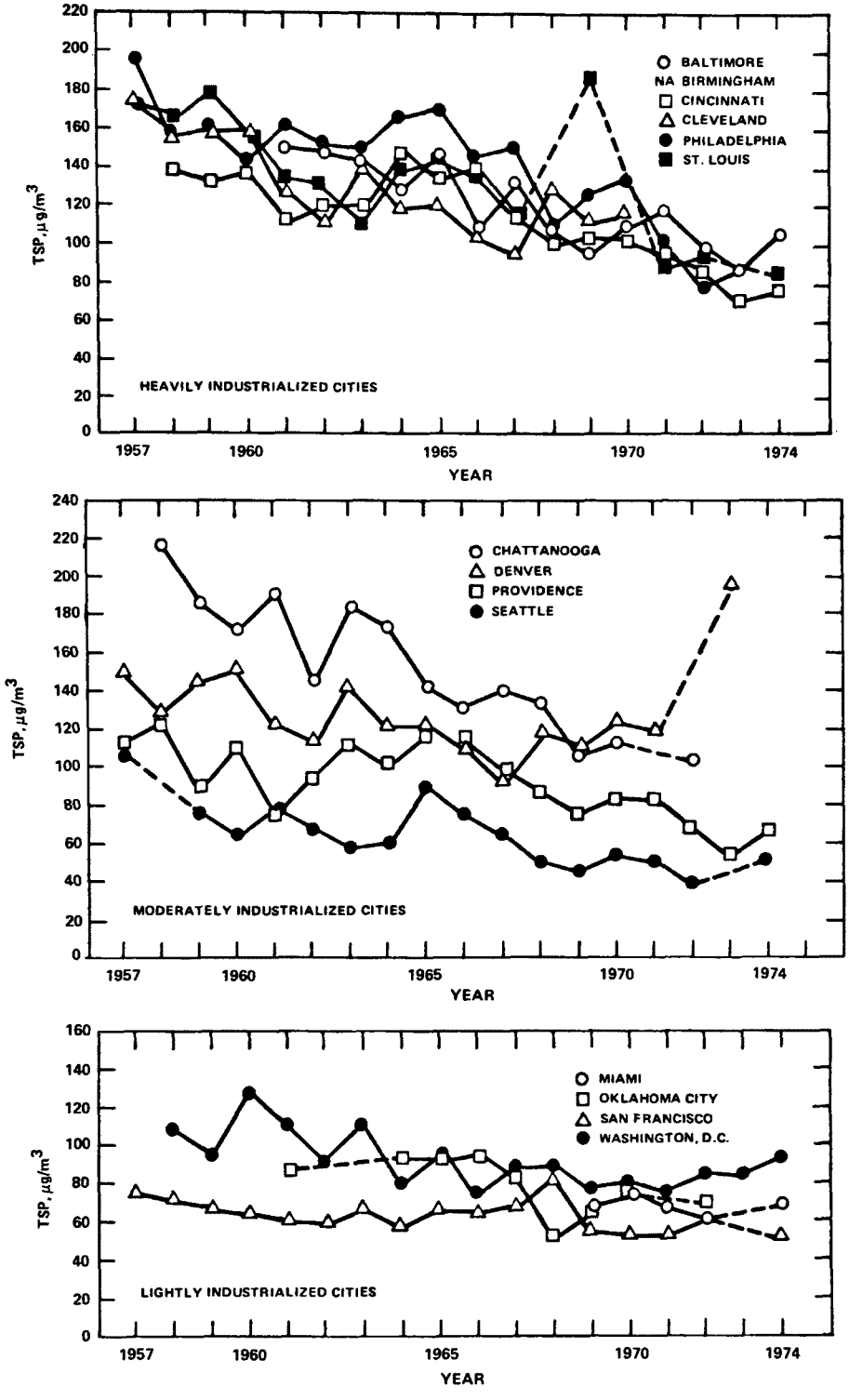
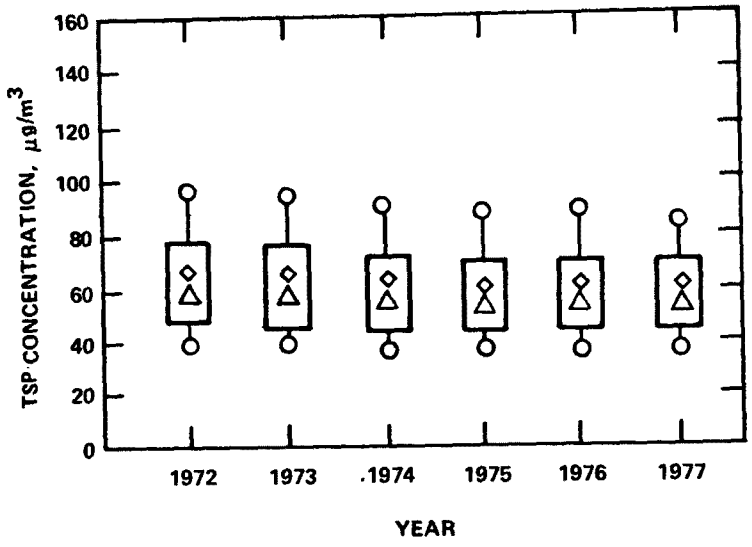


Figure 5-20. Annual geometric mean TSP trends are shown for selected NASN sites.



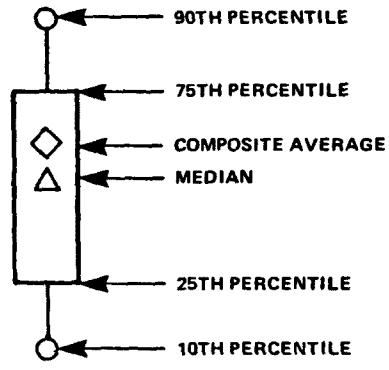
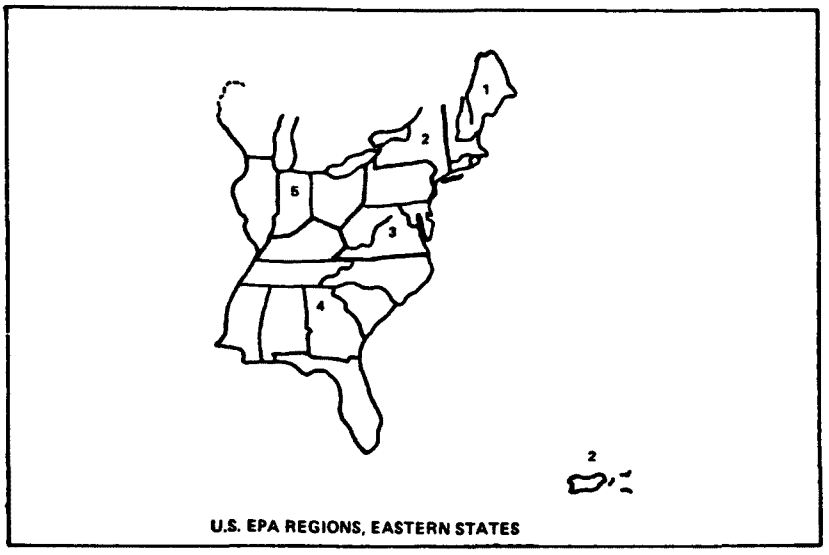


Figure 5-21. (Top) Nationwide trends in annual mean total suspended particulate concentrations from 1972 to 1977 are shown for 2707 sampling sites. (Bottom) Conventions for box plots.



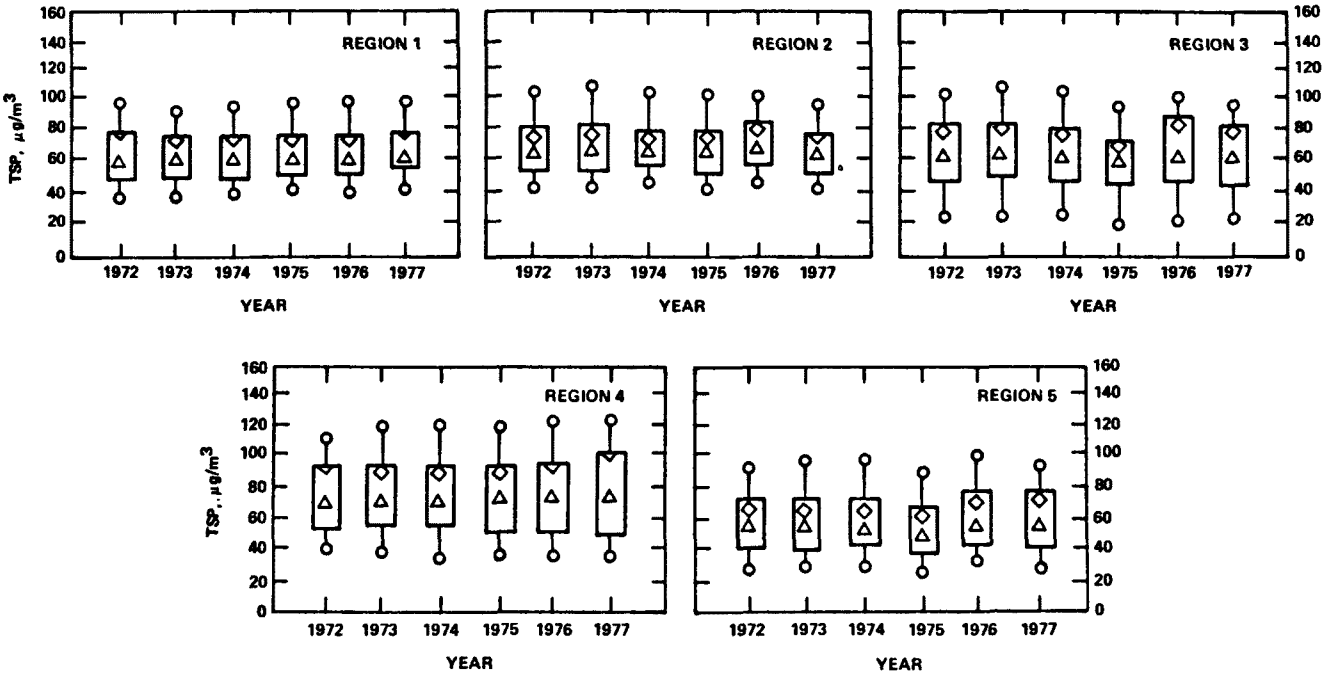
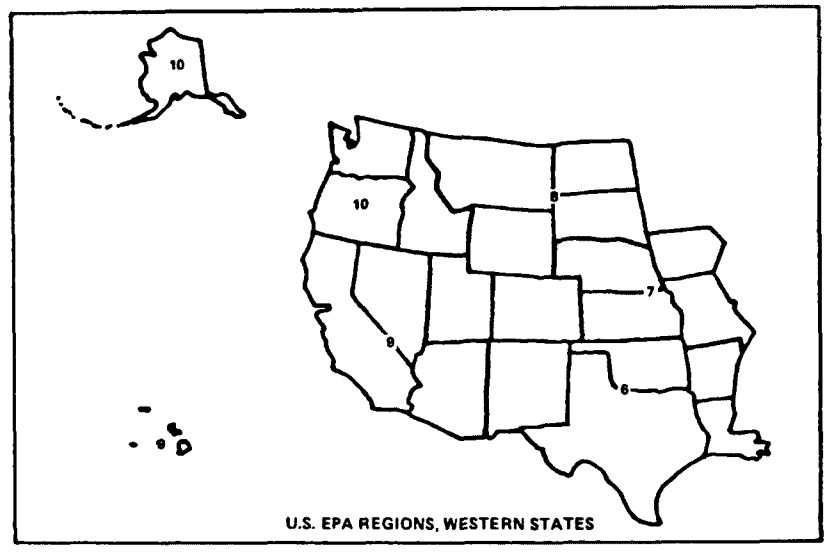


Figure 5-22. Regional trends of annual mean total suspended particulate concentrations, 1972-1977, Eastern states.



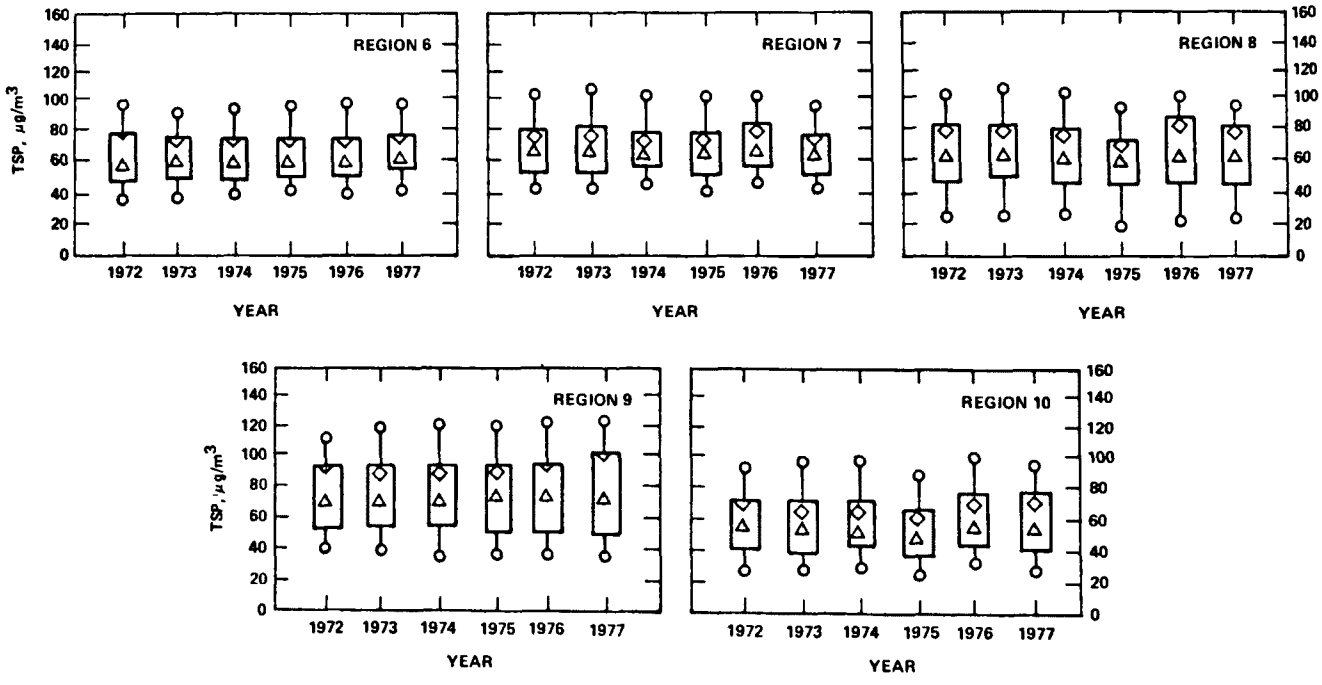


Figure 5-23. Regional trends of annual mean total suspended particulate concentrations, 1972-1977, Western states.

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In the Eastern United States, in EPA Regions I and II, the composite average across sites has decreased from 60 $\mu g/m^3$ to approximately 55 $\mu g/m^3$. The distribution of concentrations is much narrower in Regions I and II than it is in the more industrialized Regions III, IV, and V.

In Region III the composite average decreased from 78 to 60 $\mu g/m^3$, with the 90th percentile in the distribution of annual mean concentrations decreasing from slightly over 100 to about 95 $\mu g/m^3$. In Region IV the composite average decreased only slightly, from 65 to 60 $\mu g/m^3$, but has remained relatively stable or has even increased slightly since 1975. In Region V the composite average decreased from 80 to 70 $\mu g/m^3$, and the 90th percentile has decreased from 100 to 85 $\mu g/m^3$, reflecting the effectiveness of point source control.

The Western States make up Regions VI through X. In Region VI the composite average has remained at approximately 75 $\mu g/m^3$ and the 90th percentile has increased slightly since 1973, to about 100 $\mu g/m^3$. Industrial, utility, and related growth in this area as well as in Region IV is probably responsible for keeping TSP concentrations from decreasing. In region VII the composite average has been almost constant, varying only slightly between 80 and 75 $\mu g/m^3$. The 90th percentile has varied between 110 and 100 $\mu g/^3$. Region VIII shows wide distribution in the concentrations. The 10th percentile, at about 20 $\mu g/m^3$, is the lowest among all regions. The 90th percentile, approximately 100 $\mu g/m^3$, is equal to about the highest concentrations in any region. The composite average has varied over the 6-year record, but is essentially the same, approximately 80 $\mu g/m^3$, in 1977 as it was in 1972. The background air quality in the upper States of this region (Montana, North and South Dakota, Wyoming) is among the best in the country. Thus, some of the low levels (20 $\mu g/m^3$ and below) represent some of the lowest background concentrations measured in the United States. The high composite average and high 90th percentile levels reflect the impact of locating monitors near industrial sources such as smelters and the fugitive dust emissions from windblown soils. Region IX has a composite average of 100 $\mu g/m^3$, which is up from 90 $\mu g/m^3$ in the early 1970's. The 90th percentile is also high, at 120 $\mu g/m^3$. Thus, Region IX has some of the highest levels in the country. Region X has a composite average of approximately 70 $\mu g/m^3$, which is up slightly from a low of 60 $\mu g/m^3$ in 1975. The 90th percentile varies between 90 and 100 $\mu g/m^3$.

The overall trend in improvement from 1972 through 1975 was followed by a reversal in some regions in 1976. Despite this short-term reversal in 1976, 60 percent of the sites showed long-term improvement from 1972 to 1977. For those sites at which TSP concentrations violated the current annual standard, 77 percent showed long-term improvements. Approximately 25 percent of these sites reported their lowest annual values in 1977. Possibly, the short-term reversal in 1976 was due to unusually dry weather, resulting in windblown dust that may have contributed to elevated TSP levels throughout the Central Plains, Far West, Southwest, and Southeast.

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5.4 SIZE OF ATMOSPHERIC PARTICLES

5.4.1 Introduction

In Chapter 2, the general features of size distributions of atmospheric particles were discussed in some detail. In recapitulation, it should be recalled that atmospheric particles tend to be more prevalent in certain particle size bands or modes than in others. Particles which have grown from the gas phase, either because of condensation or atmospheric transformation or combustion, occur initially as very fine nuclei 0.05 micrometer or smaller. These tend to grow rapidly to accumulation mode particles around 0.5 micrometer in size which are relatively stable in the air. Because of their initially gaseous origin, this range of particle sizes includes inorganic ions such as sulfate, nitrate and ammonium ion, combustion-formed carbon, organic aerosols from photochemical conversions plus a variety of trace elements frequently associated with combustion sources.

Airborne particles of soil or dust mostly result from entrainment by the motion of the air or from other mechanical action and most of the mass of these materials is in particles larger than 5 micrometers. While the relative amounts of these two particle types are highly variable in both time and place, almost always there is a clearly observable minimum or gap in atmospheric mass distribution occurring in the particle size range of roughly 1 to 3 micrometers. In this range there are only minor percentages of the total mass and this material appears to be overlap from the two major categories. The larger particles frequently contain clay minerals, bits of local rocks, limestone aggregate from roadways, fly ash from power plants, and a wide variety of other substances ranging from insect parts, pollen and sawdust to liquid globules of acidic smut blown from boiler tubes (Draftz and Severin, 1980). The elemental analysis of these larger particles is usually dominated by silicon, aluminum, magnesium, calcium and iron, all components of soil and of flyash (See Chapter 4). Therefore, it can be difficult or impossible to assign particular sources for this component on the basis of elemental analysis alone and frequently this group of elements is called "crustal material." (Cahill, T. A., et. al., 1979).

In the last several years, a general perception has been growing that not all of the particulate mass is equally damaging to the environment (see Chapter 11). For this reason a body of information on the mass of particulate material in various size categories has been gradually accumulating and is here summarized. Furthermore, a national network of sampling stations equipped with size-selective sampling devices is being set up currently. While some tabulated data are already available from this network and are summarized here, no detailed interpretative analysis has been published as yet, nor is any chemical analytical data available. The analysis of monitoring results from the national inhalable particle (IP) network must then, wait for subsequent revisions of this document.

In the discussion which follows, the concentration of major chemical components of atmospheric aerosols are organized by the size mode or particle category in which they are

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most frequently observed. This is not to say that sulfate ion, for example, is exclusively a component of fine particles. Sometimes, say in the vincinity of a cement manufacturing facility, there can be substantial amounts of coarse calcium sulfate. However, the relationship between size and composition of particles is so general that more reason is saved by this organization than by any other.

Since the finer particles seem to have less diversity and since measurements of the major anion components of this fraction have been made for a long time, this group is discussed first. The more complicated coarse fraction has not been very well defined, indeed may not be definable by chemical analysis alone. There is considerable interest in this size range currently, though, and studies of these materials are cited in the second part.

5.4.2 Size Distribution of Particle Mass

Evidence from chemical analysis and physical theory (Chapter 2) strongly suggests that atmospheric aerosols commonly occur in two distinct modes. The fine or accumulation mode is attributed to growth of particles from the gas phase and subsequent agglomeration. The coarse mode is made up of mechanically abraded or ground particles. Therefore it is not surprising to find atmospheric particle mass distributed among fine and coarse particles with a rather clear interval of demarcation in between.

Unfortunately, gravimetric data by size fraction have been sparse until comparatively recently. Furthermore, most was obtained with impactors which are influenced by particle "bounce". (See Chapter 3) Several works suggested the existence of a distinct minimum in the mass-size distribution in the 1968-70 time period. Lee, et. al. (1968) observed only 14% of the aerosol mass between 2 and 4 μm in 3 samples from Fairfax, Ohio. Lundgren (1970) found only 10% of aerosol mass in this range in 10 Riverside, California aerosols samples ranging from 47 to 144 $\mu g/m^3$. O'Donnell et al. (1970) found only 10% in the 2-4 μm range in one Pittsburgh, Pa. sample. Lee and Garanson (1972) and Lee, et. al. (1972) have reported many impactor size distribution for six cities obtained in 1970, all indicating 12-15% of aerosol mass between 2-5 μm. However, many of these data are clouded by bounce and entry losses and probably are biased toward low coarse mode distributions.

More recently, evidence from electrostatic sizing equipment has confirmed this general trend. Figures 5-24 through 5-27 show the distribution of particle volume by size. These data differ from mass distributions because particle density (mass/volume) was not measured as a function of size. Figures 5-24 and 5-25 present distributions in and around St. Louis, Missouri, for a variety of conditions. Generally these distributions show distinct minimum values in the vicinity of 1-2 μm.

However, the combined influence of nearby sources and of aerosol aging can produce major shifts in volume and presumably mass distribution. For example, Figure 5-25 shows a third, very fine "nuclei" mode of particles centering around 0.05 μm. This mode can be attributed to the presence of nearby automotive traffic. Also shown in Figure 5-25 is the rather narrow

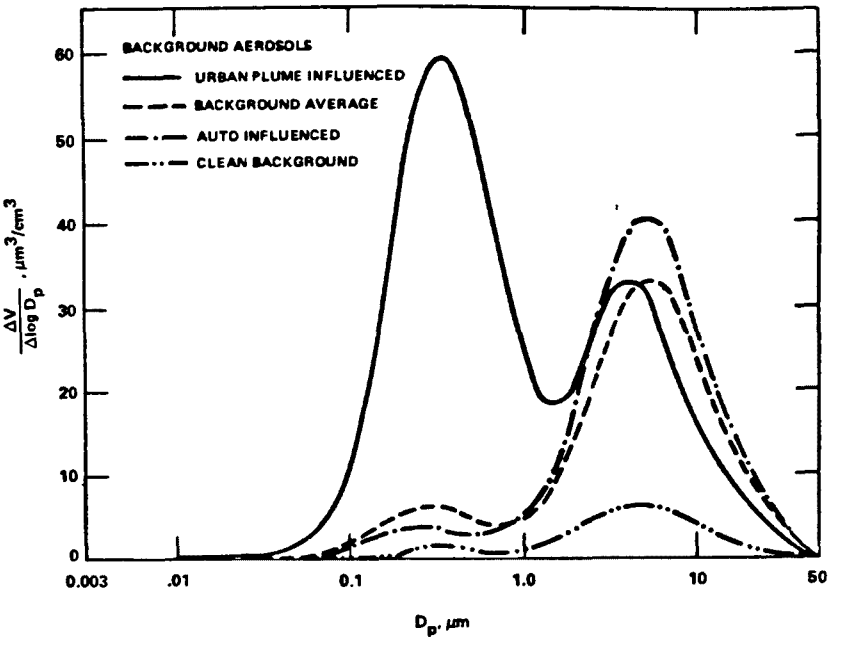

Figure 5-24. Linear-log plot of the volume distributions for the four background distributions. Notice how much the urban plume adds to the accumulation mode of the background.

Source: Whitby, 1978.

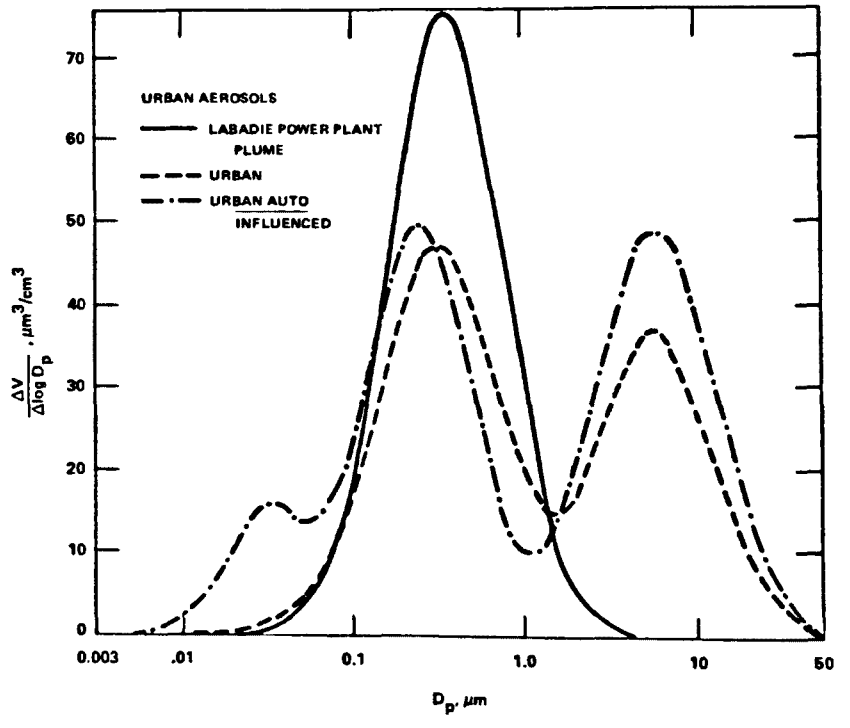

Figure 5-25. Linear-log plot of the volume distributions for two urban aerosols and a typical distribution measured in the Labadie coal-fired power plant plume near St. Louis. Size distributions measured above a few hundred meters above the ground generally have a rather small coarse particle mode.

Source: Whitby, 1978.

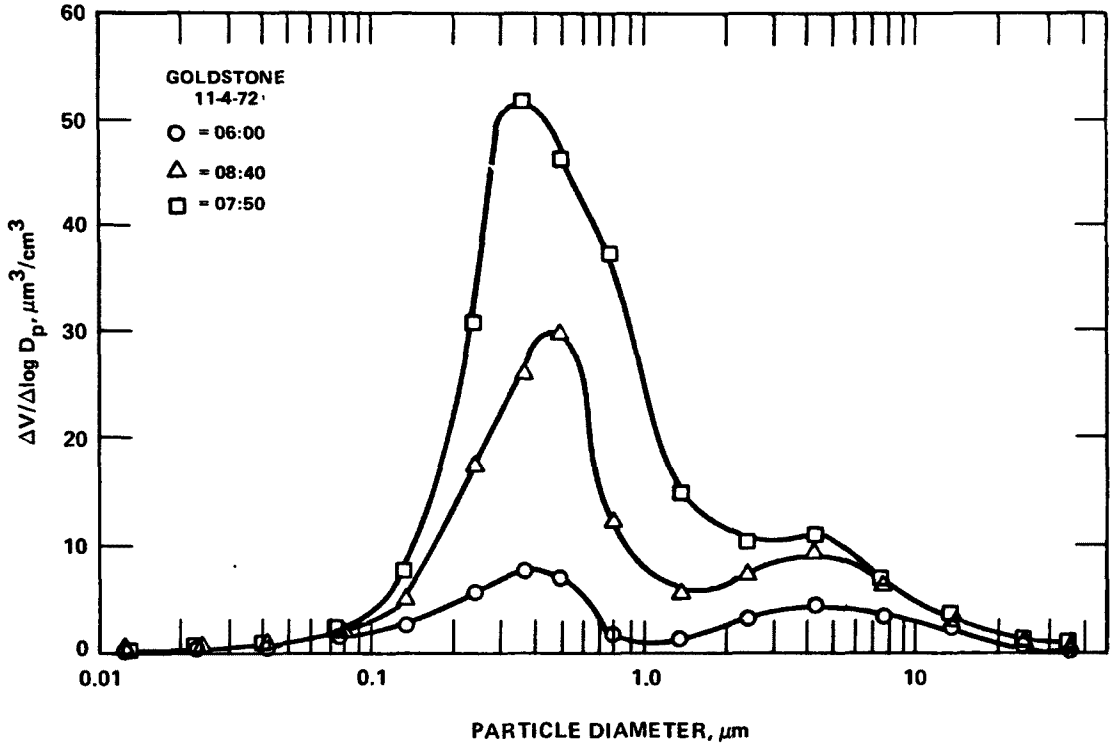

Figure 5-26. Incursion of aged smog from Los Angeles at the Goldstone tracking station in the Mojave Desert in California. Note the buildup in the accumulation mode.

Source: National Research Council (1979).

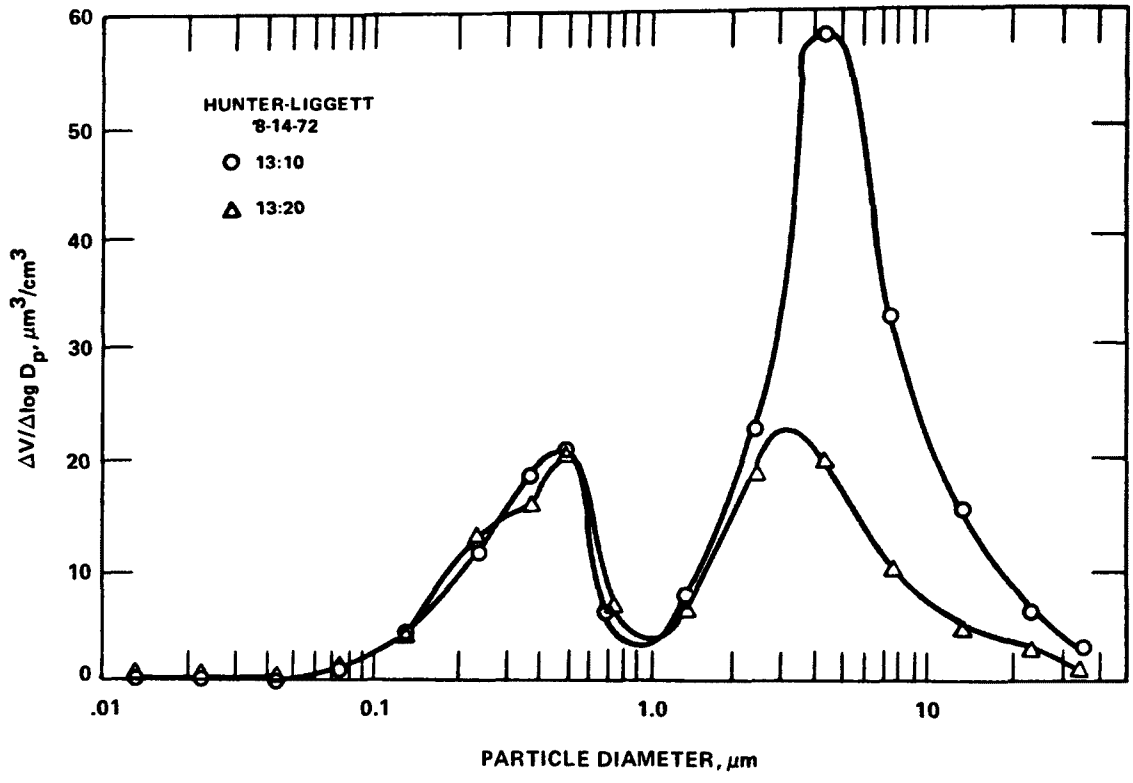

Figure 5-27. Sudden growth of the coarse particle mode due to local dust sources measured at the Hunter-Liggett Military Reservation in California. This shows the independence of the accumulation and coarse particle mode.

Source: National Research Council (1979).

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size distribution from a coal-fired power plant adding to the fine aerosol burden. However, the mass-size distribution from large sources can vary dramatically among sources depending on the type and efficiency of control equipment. (See Chapter 4)

There can be major shifts in the relative proportions of fine and coarse particle mass as an aerosol ages (i.e. moves with the wind). Figures 5-26 and 5-27 show dramatic examples of this phenomena obtained during the 1972 California ACHEX experiment. In the first case, aged aerosol is transported in the wind to the site from the Los Angeles area; during this process coarse particles settle out. In the second case, local winds stir up dust shifting the distribution toward larger sizes. (National Research Council, 1979).

A summary of mass data calculated from electrostatic size disbributions for several environments is shown in Table 5-7. Here, the dramatic variations in coarse and fine particle fractions found in practice are clear.

More recently, a number of studies have been done with virtual impactors designed to obtain mass samples of the 0-2.5 μm fine fraction and a 2.5-15 μm coarse fraction. Researchers from EPA's Environmental Science Research Labs have measured coarse and fine aerosol mass concentrations in several locations. Dzubay et al. (1977) report on 18 days of summer sampling in St. Louis, Stevens et al. (1979) report on two months of summer sampling in Houston, Texas and Stevens et al., (1980) discuss results of an extensive sampling for a week in the Smoky Mountains. Courtney et al. (1980), discuss the early results from winter sampling at two locations in Denver, Colorado. Table 5-8 below summarized their reported findings.

In another short term study, Lewis and Macias, (1980) sampled atmospheric aerosols for 21 days in Charleston, West Virginia. The fine fraction average was 33.4 $\mu g/m^3$ and the coarse fraction average was 27.1 $\mu g/m^3$.

Because of the influence of particle size on a variety of adverse effects including health, visibility, and soiling (see later effects chapters), EPA is establishing a network of size-selective particulate monitors. Ultimately this grid will include 250 stations to be established over a 3-year period. During the period April 1, 1979, to June 30, 1980, a total of 94 stations were established. A map showing current sampler location is shown in Fig. 5-28. (EPA, 1981) Since dichotomous samplers are used in this network, together with Hi-Vols, it is possible to obtain a general conception of the relationship between TSP (0 - ~ 60 μm), dichotomous total (D_{total}) or "inhalable" particles mass (0-15 μm) and the fine and coarse fractions defined above.

A total of 1960 dichotomous fine and coarse measurements and 2675 TSP measurements are now in this data base; Hi-Vol measurements with a size-selective inlet are now also being made. In this data base, daily TSP values range from 33.2 $\mu g/m^3$ in Litchfield, Connecticut to 474.4 $\mu g/m^3$ in Dallas, Texas. Maximum dichotomous sampler values ranged from 28.7 $\mu g/m^3$ in Pearl City, Hawaii to 267.5 $\mu g/m^3$ in Rubidoux, California. (EPA, 1981)

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TABLE 5-7. FINE AND COARSE AEROSOL CONCENTRATIONS FROM SOME URBAN MEASUREMENTS COMPARED TO CLEAN AREAS

Location	Condition	Concentration ($\mu g/m^3$)[a]	
		Fine particles	Coarse particles
St. Louis	Very polluted	296.0	94.0
Los Angeles	Grand Average	37.0	30.0
Los Angeles freeway	Wind from freeway	77.0	59.0
Denver	Grand average	16.6	232.0
Goldstone	Clean	1.5	3.0
Milford, Mich.	Very clean	1.03	0.82
Pt. Arguello (seaside)	Marine air	1.1	53.0

[a]Calculated from volume distribution using assumed particle density, Pp = 1 gm/cm^3

Source: National Research Council, 1979.

*

TABLE 5-8. FINE FRACTION AND COARSE FRACTION DICHOTOMOUS SAMPLING BY ENVIRONMENTAL SCIENCE RESEARCH LAB, USEPA IN 4 LOCATIONS

Location	Period	Days	Comments	Concentration Fine ($\mu g/m^3$)	Coarse ($\mu g/m^3$)
St. Louis	Summer	18	Urban	29	22
			Rural	26	15
Houston	Summer	28	Urban	52.2	39.8
Denver	Winter	19	Urban Site D	18.1	22.5
			Urban Site N	25.4	23.4
			Urban Site D	23.2	33.0
			Urban Site N	26.4	26.5
	Winter	19	Urban	26.5	27.1
	Spring	28	Urban	16.1	9.8
Smoky Mtns	Fall	7	Remote Day	26.4	6.2
			Remote Night	22.0	4.9

Figure 5-28. Inhalable particulate network sites established as of March 19, 1980.

*

Because of the limited time period available for analysis (April 1979 to June 1980), it would be unwise to consider analysis of this data as indicative of geographical on seasonal trends in particle size. But some additional general factors associated with particle size can be seen from inspection of the data summary in Table 5-9. (The ratios in the table are averages of individual sample pair's ratios, and thus will not equal ratios of the average concentrations given.)

On the average the dichotomous total (D_{total}) is a fraction of the TSP, but this ratio varies widely across the country, from about 0.4 to almost 1 in Portland, Oregon and Litchfield, Connecticut (5 samples). However, most Portland and all Litchfield samples were collected during the winter months where rainfall or snow cover could have materially reduced dust levels.

The fraction of fine and coarse components is even more variable. The coarse mass fraction of the total sub-15 μm mass ranges from about 1/5 to 2/3 in this selected set and even higher for individual days. Particularly striking are the average values for Dallas and El Paso, Texas. At both sites, the sub-15 μm mass was only about half the TSP mass. However, in Dallas only 27% of this was in the 2.5-15 μm range while in El Paso, 64% was "coarse". At this point, it appears that much remains to be learned about the coarse fraction and its contribution to aerosol mass.

5.5 CHEMICAL ANALYSIS OF FINE PARTICLES

It is widely recognized that sulfate, nitrate, and ammonium ions, organics, carbon, and combustion associated metals are the major components of fine particle mass. Unfortunately, few studies of aerosol composition have attempted material balance and fewer still have done so with size fractionation.

Nevertheless, a great deal has been learned about the chemical and elemental composition of airborne particulate since the early experiments in the 50s by Junge in Frankfurt, Germany, Roundhill, Massachusetts, Hawaii, and various sites in Florida (Junge 1952). The observation of Junge that sulfate, ammonium, and nitrate ions appear predominantly in the fine particulate fraction has been confirmed in independent field observations, both in urban and rural areas (Lewis and Macias, 1980; Dzubay and Stevens, 1975). In analyzing the St. Louis, Mo., dichotomous sampler data by x-ray fluorescence, Dzubay and Stevens found 75 percent of the zinc, sulfur, bromine, arsenic, silenium, and lead occurred in the fine particulates, and at least 75 percent of the silicon, calcium, titanium, and iron in the coarse fraction (Dzubay, 1980).

Studies of Charleston, W. Va. particles, Lewis and Macias report material balances of fine and coarse particles accounting for 69 percent and 60 percent of the mass respectively. Eighty-five percent of the sulfate and ammonium ions were in the fine particles where they accounted for 30 and 12.8 percent of the mass respectively. Carbon, both elemental and organic, was mainly in the fine aerosol (61 percent) where it accounted for 18.2 percent of the mass.

*

TABLE 5-9. RECENT DICHOTOMOUS SAMPLER AND TSP DATA FROM SELECTED SITES--ARITHMETIC AVERAGES

Location		No. of observations	TSP $\mu g/m^3$	D_{TOTAL}/TSP (# pairs)	Coarse $\mu g/m^3$	Fine $\mu g/m^3$	Coarse/ D_{TOTAL}
Northeast							
Buffalo, NY	TSP	28	93.7	0.70 (21)	25.2	25.9	0.50
	D_{Total}	40					
Erie Co., NY	TSP	41	32.8	0.64 (25)	5.1	16.2	0.24
	D_{Total}	44					
Litchfield, CN	TSP	5	18.9	0.86 (1)	6.6	13.3	0.33
	D_{Total}	5					
Philadelphia, PA	TSP	102	45.1	0.83 (40)	13.3	22. 5	0.38
	D_{Total}	109					
Southeast							
Birmingham, AL	TSP	38	60.8	0.68 (23)	15.0	24.4	0.38
	D_{Total}	40					
Midwest							
Minneapolis, MN	TSP	44	50.1	0.61 (26)	15.6	16.4	0.46
	D_{Total}	41					
Cincinnati, OH	TSP	51	53.6	0.77 (26)	14.4	25.2	0.35
	D_{Total}	48					
Southwest							
Dallas, TX	TSP	22	94.9	0.47 (21)	9.8	24.1	0.27
	D_{Total}	24					
El Paso, TX	TSP	29	86.5	0.51 (7)	46.3	11.7	0.64
	D_{Total}	26					
Far West							
Los Angeles, CA	TSP	43	68.4	0.53 (18)	21.3	24.6	0.47
	D_{Total}	50					
Portland, OR	TSP	37	66.7	0.90 (19)	42.3	22.0	0.60
	D_{Total}	36					
Pearl City, HA	TSP	27	33.0	0.43 (11)	7.9	8.4	0.47
	D_{Total}	25					

*

Stevens, et al. (1978) have reviewed size-fraction analysis for six sites including the St. Louis and Charleston data sets mentioned above, together with New York, Portland, Oregon, Philadelphia, and Glendora, California. They conclude that sulfate ion is predominantly a fine component (70 percent) which usually accounts for 40 percent of the mass of that fraction and occassionally up to 50%. The sulfate must be present as ammonium salts or as sulfuric acid since metallic sulfate could be only 10-30% of the total at maximum. (Stevens et al., 1978)

In one site in the Great Smoky Mountains, 89% of the fine particle mass was accounted for. (Stevens, et al., 1980) Sulfate accounted for 61% of the fine particle mass, ammonium ion 12%, elemental carbon 5%, and organic carbon 10% with a variety of trace elements, mainly lead, accounting for the balance. In this study only organic carbon was also a significant component of the coarse particles.

Studies in a number of sites in California have produced similar results. Flocchini, et al., 1978) and Cahill, et al., (1977) have reported size fraction distributions for sulfur (presumably sulfate) in three districts of California. In all areas sulfur was present almost exclusively in the sub 3.6 μm fraction. In dry weather, sulfur was found in sub-0.65 μm fractions, while under humid conditions the sulfate appeared in the 0.65 to 3.6 μm cut.

Since sulfate, nitrate, ammonium ion, elemental carbon and organics are the major components of the fine aerosol, analytical data for them, whether size fractionated or total, will be discussed together in this section.

5.5.1 Sulfates

The term "atmospheric sulfates" describes a variety of sulfur compounds, including ammonium sulfate, ammonium bisulfate, sulfuric acid, calcium sulfate, and a variety of metal salts. Most of the historic data on atmospheric concentrations of sulfates is based on the water-soluble extract of TSP filters and measurements of the sulfate ion. These measurements were subject to artifact formation on the glass fiber filters used in the early NASN measurements. For a complete discussion of these issues see Chapter 3. In general, it is now accepted that pre-1974 or -1975 TSP sulfate measurements using the traditional glass fiber filters may have overestimated sulfates by as much as 2 $\mu g/m^3$ in areas where ambient SO_2 concentrations were high.

The range of annual average TSP sulfate concentrations is from less than 1 $\mu g/m^3$ in some states to almost 20 $\mu g/m^3$ in urban industrial areas of the Northeast. For 24-hr average concentrations, sulfate concentrations have ranged from near zero to more than 80 $\mu g/m^3$.

Sulfate, particularly ammonium sulfate, appears to account for the majority of fine particle mass in many locations (Dzubay, 1980; Stevens et al., 1980; Watson, 1979; Flocchini et al., 1978; Stevens et al., 1978; Pierson et al., 1980). Although some of this material may be emitted directly from sources, the majority appears to be secondary, i.e., formed by chemical reactions in the atmosphere (Friedlander, 1973; Grosjean and Friedlander, 1975).

*

Spatial and temporal variations. The spatial distribution of sulfate concentration for 1974 is displayed in Figure 5-29. Figure 5-29(a) presents the annual average concentrations. An area having an annual average of more than 15 $\mu g/m^3$ extends from the lower Ohio Valley through the upper Ohio Valley, including major portions of Kentucky, West Virginia, Ohio, and western Pennsylvania. The areas with annual averages exceeding 10 $\mu g/m^3$ include almost all of the United States east of the Mississippi, except for the South Atlantic States and the upper New England areas.

Through the central Midwest area, values of 4 to 9 $\mu g/m^3$ are reported. The high values seen in the Rocky Mountain States may originate from local smelters and coal-fired power plants. The Far Western States and the Pacific Northwest experience annual sulfate levels below 2 to 3 $\mu g/m^3$, except for the Los Angeles area. The Los Angeles levels are not shown in this figure, but a 1975 National Academy of sciences report on air quality and stationary source emission controls indicates that they are between 7 and 13 $\mu g/m^3$ (National Academy of Sciences, 1975).

Seasonal variations in sulfate concentrations are shown in Figures 5-29(b) and 5-29(c) for the winter months and the summer months. The area of elevated sulfate greatly expands during the summer months. As demonstrated by several regional studies on atmospheric sulfate transport, sulfate concentrations can be elevated over large geographical regions under certain meteorological conditions (Eliassen, 1978; Lyons and et al., 1978; Perhak, 1978; Whelpdale, 1978). This is support for the transport and conversion beyond the source regions of sulfur dioxide emissions. It is clear from these contour maps of high sulfate levels that a large portion of the U.S. population is exposed to annual sulfate concentrations in the ambient air of more than 10 $\mu g/m^3$. In view of the increasing sulfur dioxide emissions from increased use of coal throughout the United States, particularly in the South Central States, the area of maximum sulfate levels might expand and shift to the lower Ohio Valley area and the Southeast.

In a large-scale study of atmospheric sulfate in eastern Canada, Whelpdale (1978) reports mean levels of 10 $\mu g/m^3$ over southern Ontario. The mean levels of sulfates dropped to less than 2.5 $\mu g/m^3$ above the 49th parallel. Figure 5-30 displays these values for the period of study. During episodic conditions that affect primarily and lower Great Lakes region, the 24-hr concentrations have been reported as high as 40 to 50 $\mu g/m^3$. These episodic conditions are associated with the position of a high-pressure cell over eastern Canada with southwest flow occuring on the back side of the high pressure. This synoptic situation favors transport of sulfur dioxide and sulfates from the high sulfur dioxide source regions of the industrialized Northeastern United States.

Recently new information on the interrelationship of sulfur dioxide, nitrogen dioxide, ozone, TSP, sulfates, and nitrates has become available from large-scale regional study. The Electric Power Research Institute (EPRI) Sulfate Regional Experiment (SURE) involves intensive monitoring from some 54 rural stations and an aircraft sampling program. The area being

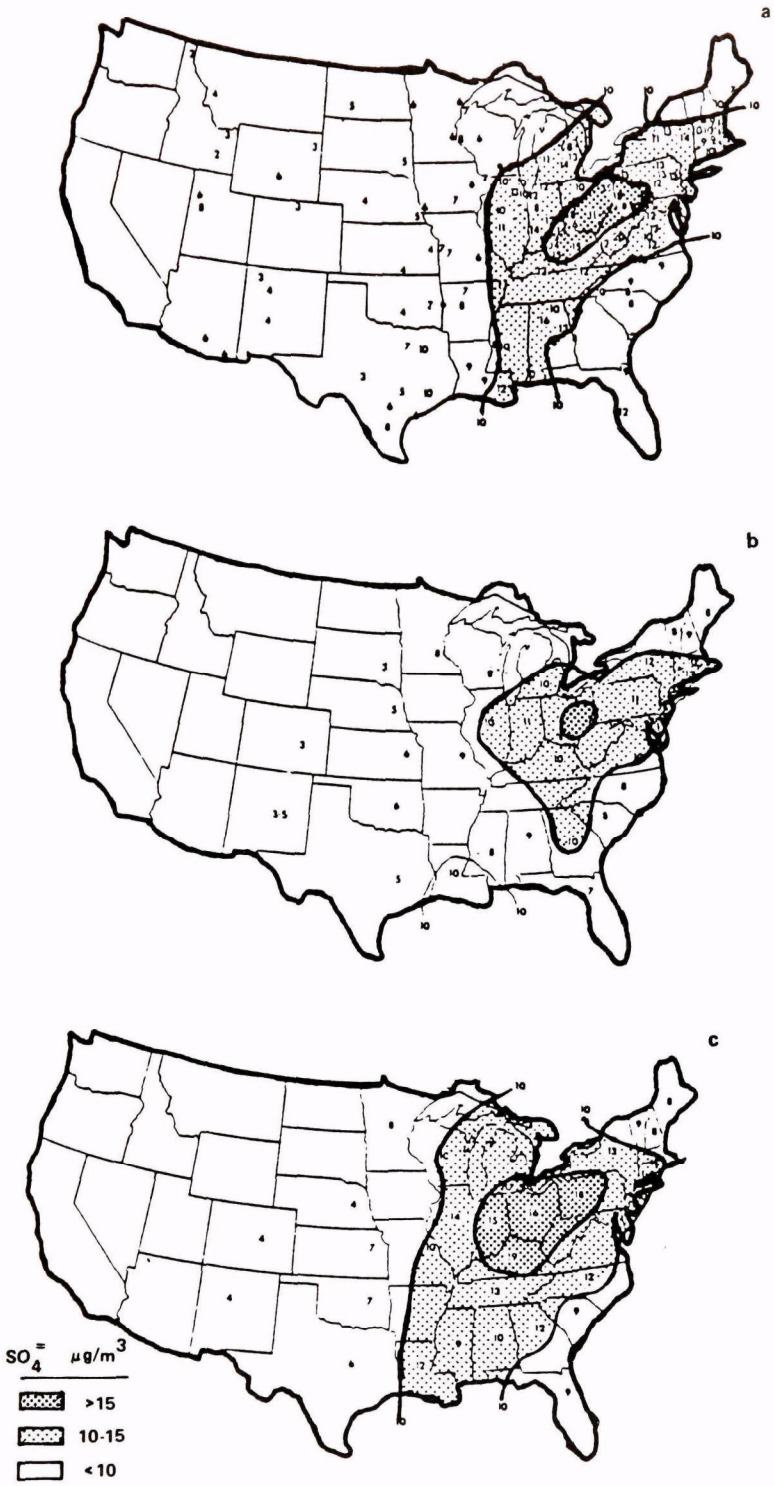

Figure 5-29. Contour maps of sulfate concentrations for 1974 are shown for: (a) annual average; (b) winter average; (c) summer average.

Source: National Research Council, (1978a).

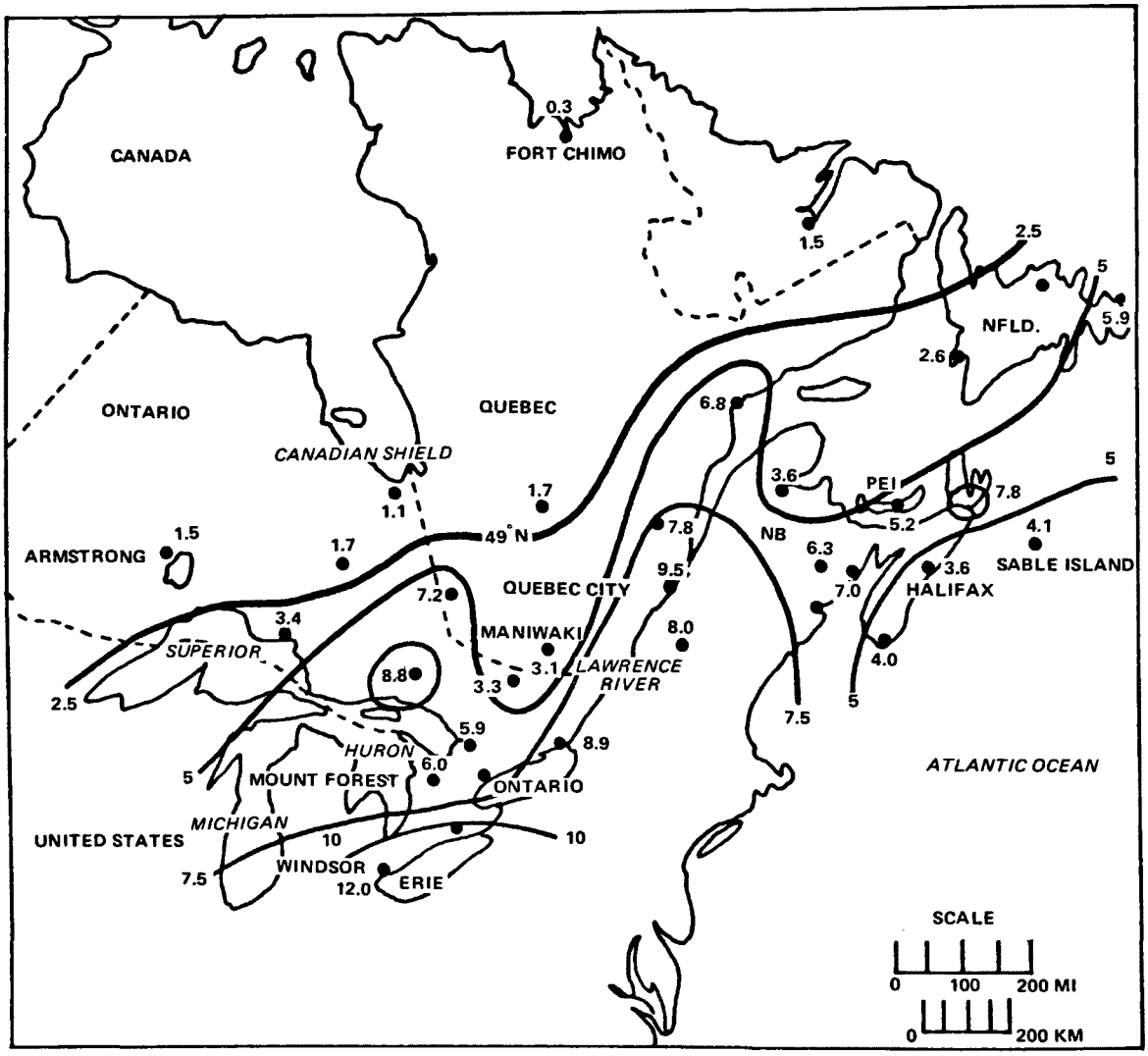

Figure 5-30. Intensive Sulfate Study area in Eastern Canada shows the geometric mean of the concentration of particulate soluble sulfate during the study period. Units are micrograms of sulfate per cubic meter.

Source: Whelpdale (1978).

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studied is 2400 x 1840 km; it extends from Kansas to the Atlantic coast and from mid-Alabama to southeastern Canada (see Figure 5-31) (Hidy et al., 1979).

Mueller et al. (1979) reported on the earlier SURE data collected in 1974 and 1975 and presented the preliminary results of an intensive field study made during July 1977 through February 1978. Using the limited historic data base, they indicate that the rural stations experience a frequency of occurrence of 24-hour average sulfate concentration similar to that observed around large metropolitan areas such as New York City. As seen in Figure 5-32, 24-hr values greater than 10 $\mu g/m^3$ occurred in approximately half the data, and the occurrence of 24-hr sulfate levels exceeding 20 $\mu g/m^3$ was about 10 to 12 percent.

Based on concentrations of 10 to 20 $\mu g/m^3$ as an indicator of elevated exposure, the average concentrations over the entire SURE network area were estimated by a linear interpolation procedure with a resolution of 80 x 80 km grids. Episodes of elevated sulfates are extensive; during an episode in early August 1977, the area where sulfate levels exceeded 20 $\mu g/m^3$ expanded to more than 500,000 km^2. Two regional episodes occurred in January and early February 1977. In August, 39 percent of the sulfate values exceeded 10 $\mu g/m^3$; in January the figure was 30 percent; five percent of the values exceeded 20 $\mu g/m^3$. In October, 20 percent of the values exceeded 10 $\mu g/m^3$, and less than 1 percent of the values exceeded 20 $\mu g/m^3$. Figure 5-33 shows the estimated number of days exceeding 10 $\mu g/m^3$, for August 1977 and January-February 1978. In August, almost the entire Northeast had at least 10 days with sulfate concentrations greater than 10 $\mu g/m^3$. The area having 20 or more days with more than 10 $\mu g/m^3$ involved Ohio, West Virginia, Maryland, Pennsylvania, and New York. By contrast, in the winter months the area of prolonged elevated sulfate concentrations shifts toward the West and Southeast. The upper Ohio Valley remains high, and an increase in the number of days with more than 10 $\mu g/m^3$ also occurs over Tennessee, Alabama, and Georgia.

Studies of seasonal variations have reported elevated concentrations in the summer months (Hitchcock, 1976; Hidy et al., 1978). The summer monthly mean concentrations of sulfate in some regions can be twice those for the winter months. The seasonal variation in sulfate concentrations in southeastern and midwestern cities is less distinct than the variation in New York City or Los Angeles (see Figures 5-34 and 5-35). Presently, it is generally reported that elevated summertime sulfate concentrations are the result of increased homogeneous and heterogeneous oxidation of anthropogenically produced SO_2. However, oxidation of biologically produced hydrogen sulfide has been offered as an explanation for some high sulfate concentrations in isolated areas.

Lavery et al. (1979) postulate the existence of two meteorological conditions that result in regional accumulation of particulate sulfate concentrations above 20 $\mu g/m^3$ in the Northeastern United States:

> The first regime consists of cases where widespread stagnation occurs with a large high pressure area slowly moving eastward over the midwestern and eastern United States. Zones of polluted air collect over areas within 100-300 kilometers of high sulfur dioxide emissions sources. These zones maintain themselves over periods of one to four days in warm,

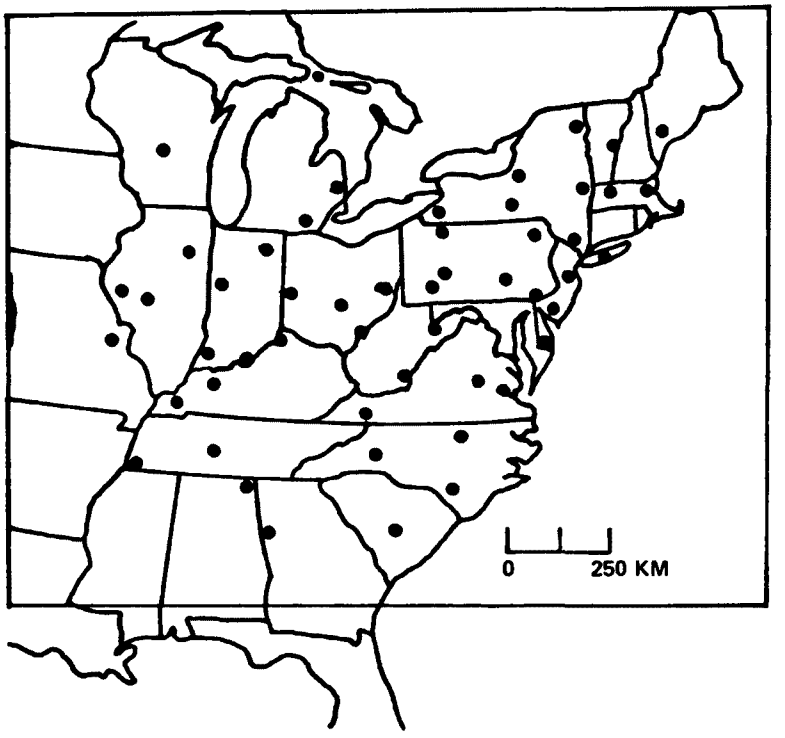

Figure 5-31. Map of SURE regions shows locations of ground measurement stations.

Source: Hidy et al. (1979).

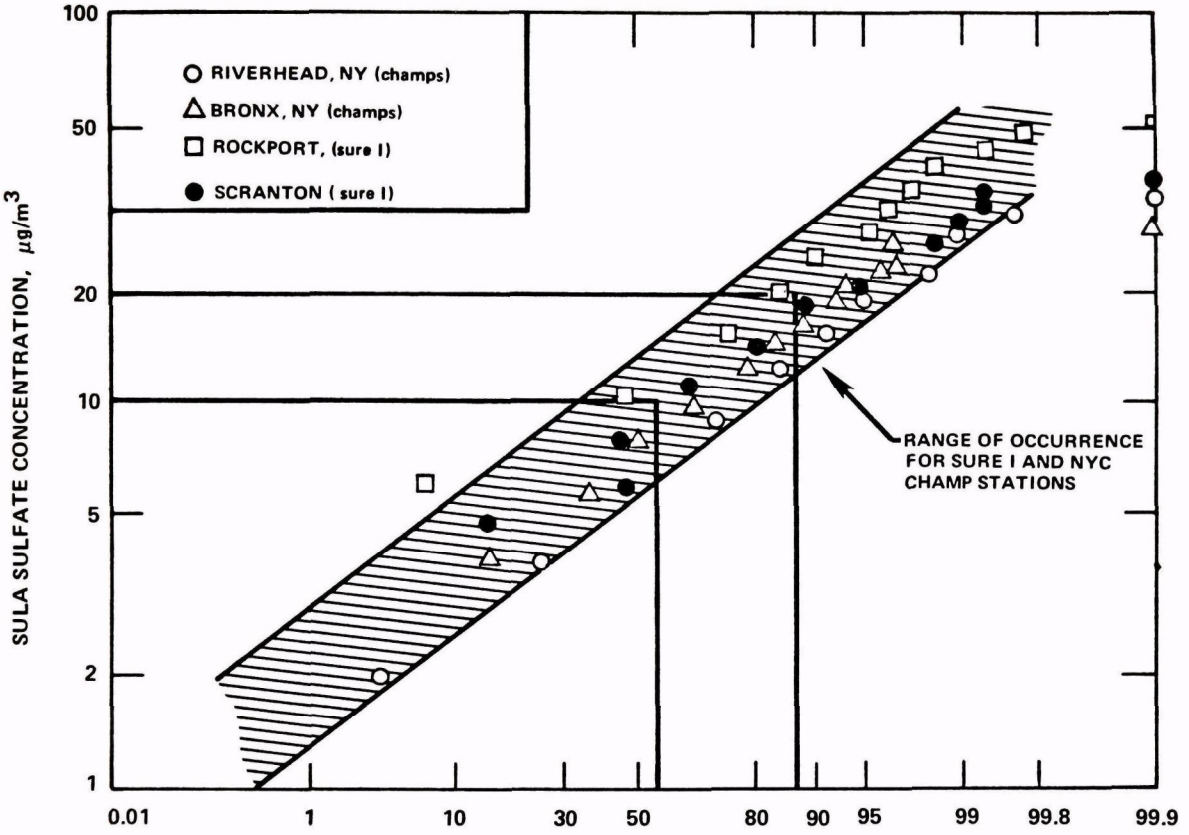

Figure 5-32. Cumulative plots show the frequency of sulfate concentrations in the SURE region on the basis of the 1974-75 historical data.

Source: Mueller et al. (1979).

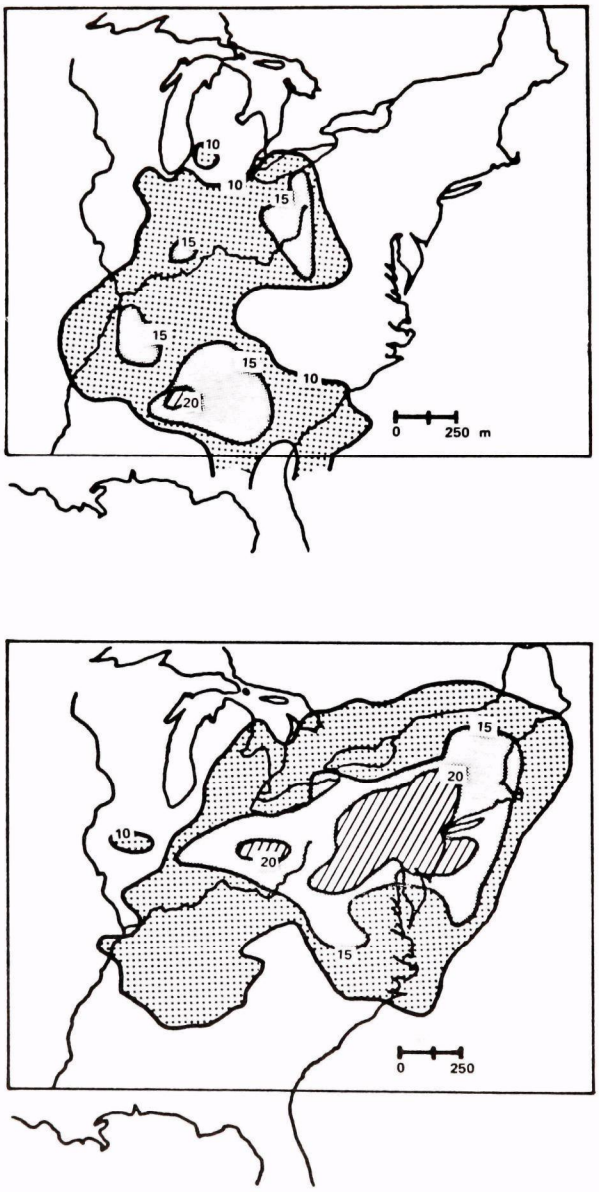

Figure 5-33. Map shows the spatial distribution of number of days per month that the sulfate concentration equaled or exceeded 10 $\mu g/m^3$. Station data were extrapolated according to r^{-2}. (A) January-February 1978 (31 days); (B) August 1977 (31 days).

Source: Mueller et al. (1979).

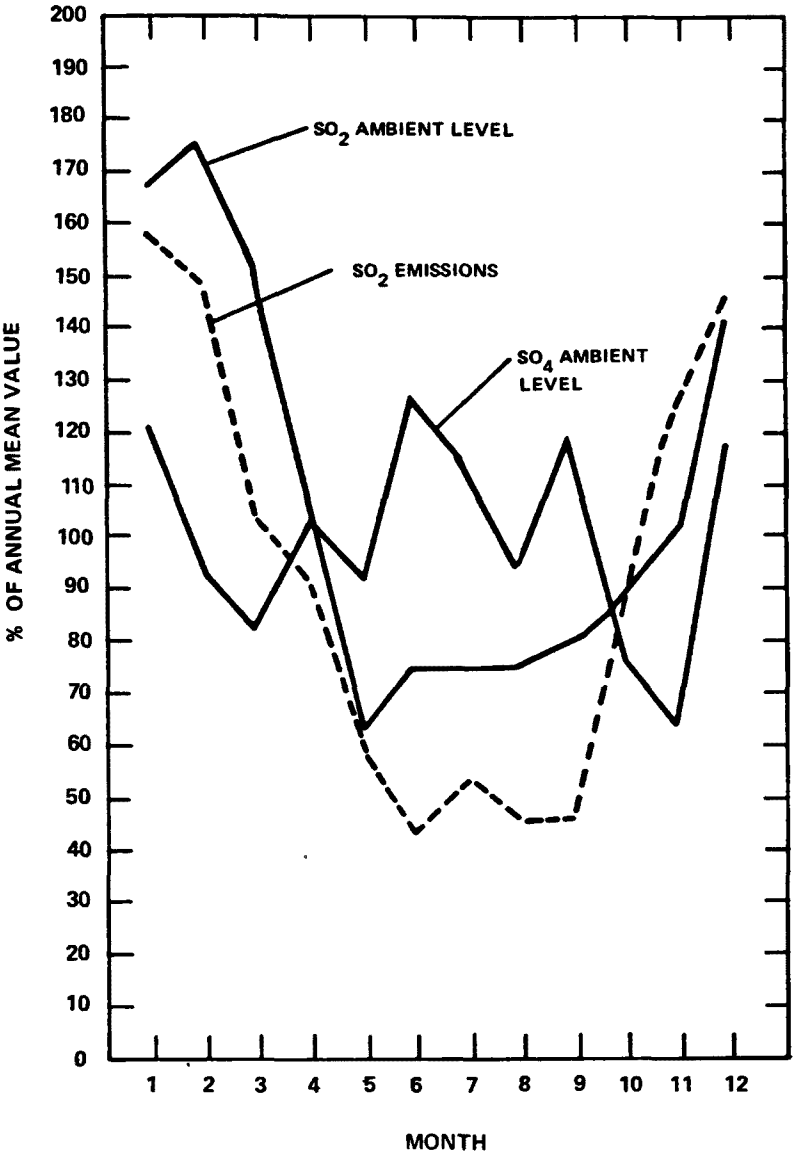

Figure 5-34. 1977 seasonal patterns of SO_2 emissions and 24-hr average SO_2 and SO_4 ambient levels in the New York area are normalized to the annual average values.

Source: Lynn et al. (1975).

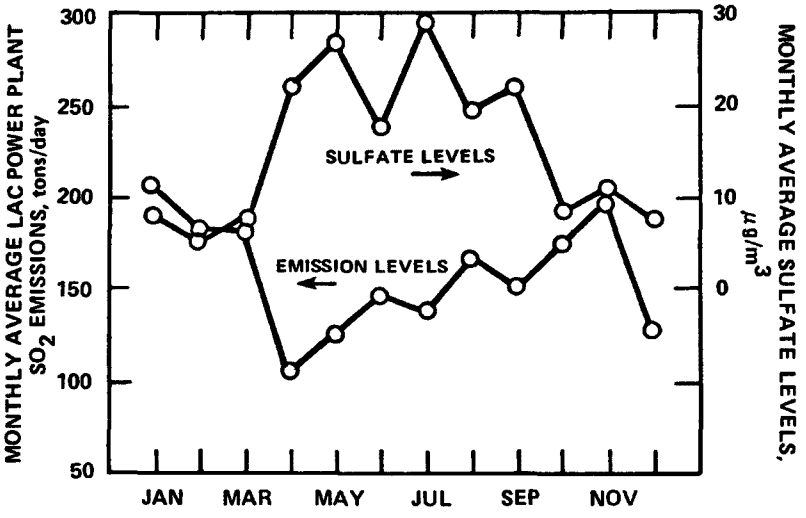

Figure 5-35. Monthly variation in monthly mean of 24-hr average sulfate concentration at downtown Los Angeles is compared with monthly mean 1973 Los Angeles County power plant SO_2 emissions.

Source: Hidy et al. (1978).

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moist air, with light winds, around the southern and western parts of the high pressure area. The second regime appears to be conducive to long-range (greater than 500 km) sulfate transport and involves a channeling of air flow between the west side of the Appalachian Mountains and weak cold fronts approximately oriented west-southwest to east-northeast and traveling south-eastward. The channeling appears to be combined with capped vertical mixing associated with subsidence around the frontal system. These episodes can last up to four days.

Urban variations. The preceding discussion of spatial and temporal variations of sulfate was derived for the most part from widely spaced rural monitoring stations. It is of interest to note spatial variations on the much smaller scale of a metropolitan area. The sulfate measured on this scale may consist of a natural background component, a long-distance transported component, a component formed locally in the atmosphere, and/or an artifact formed on the filter. Hidy et al. (1978) compare urban sulfate distributions from the previously reported works of Lynn et al. (1975) for the New York City area, and Kurosaka (1976) did the same of the Los Angeles area. These areas differ in meteorology and climate, but the population and total sulfur dioxide emissions are similar.

The population density of New York City is greater than that of Los Angeles (See Table 5-10). In addition, the emission patterns are dissimilar. As seen in Figure 5-36, there is a significant difference in sulfate concentrations across the New York urban area, with the highest values observed in a strip from Staten Island northeast into Brooklyn. This may be biased by the wintertime emissions; in summer, fairly uniform sulfate concentrations have been found in the New York metropolitan area. The highest concentrations of purely sulfur dioxide emissions are in eastern New Jersey, Staten Island, Brooklyn, and the high-density areas of Manhattan. Within a distance of 10 to 50 km from the sources of highest SO_2 concentration, the sulfate concentrations have decreased by 30 to 40 percent from their maximum values.

As shown in Figure 5-37, the mean annual average concentrations derived from 24-hr values in Los Angeles show a relatively uniform distribution across the Los Angeles basin area. A weak maximum is seen in the area near Burbank, and another maximum may occur in the San Bernardino area. The areas of major sulfur dioxide emissions are El Segundo and Long Beach areas and Fontana. A pattern similar to New York is found in the Los Angeles area; at distances exceeding 50 km from the areas of highest concentration, the sulfate levels drop off significantly.

Spengler and Dockery (1979) have measured sulfates in particles less than 3.5 μm is diameter using a network of 10 to 12 sites in each of six cities for periods of up to 2 years. Analysis of variance shows no significant variation among sites within the cities of Topeka, KS; Portage, WI; Kingston, TN; and Watertown, MA. Some slight variations occur among the sites in St. Louis, and significant variations occur among the sites in Steubenville, OH. Only the Corondolet area of southeast St. Louis was monitored, not the entire city. There is a coke plant and a lead pigment plant nearby, which causes large SO_2 gradients and perhaps also sulfate gradients. In Steubenville, the TSP and SO_2 values near the river are

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TABLE 5-10. SOME CHARACTERISTICS OF POLLUTION IN THE NEW YORK AND LOS ANGELES AREAS

Parameter	Los Angeles	New York
Surface area considered,[a] km^2	21,000	17,000
Population estimate (1970)	9,000,000	12,000,000
Population density, no./km^2	430	710
SO_2 emissions, tons/yr[b]	238,000	266,000
SO_2 emission density, kg/km^2/yr	10,300	14,200
Maximum temperature, °C[c]	22.8 (5.5)[d]	15.0 (7.4)
Minimum temperature, °C[c]	10.8 (4.6)	9.3 (8.4)
Relative humidity, %[e]	50.2 (17.0)	59.6 (16.5)
Normal precipitation, cm	36	106
Mean wind speed, m/sec[f]	3.3 (1.4)	5.8 (2.3)
Mixing height, m[g]	849 (472)	1290 (906)
Ventilation, m^2/sec	2690 (2160)	7460 (6200)
SO_2, μg/m^3 [h]	12.5 (19.9)	42.9 (45.0)
Water-soluble sulfate (SO_4^{2-}), μg/m^3 [h]	10.1 (7.9)	8.9 (5.7)
NO_2, μg/m^3 [h]	83.9 (44.3)	67.6 (36.0)
Water-soluble nitrate (NO_3^-), μg/m^3 [h]	9.1 (7.7)	2.6 (2.1)
O_3, μg/m^3 [h]	52 (34)	20 (22)
Total particulate mass concentration (TSP) less sulfate and nitrate, TSPM, μg/m^3	64.5 (27.4)	40.4 (19.9)

[a]Greater metropolitan areas; Los Angeles, South Coast Air Basin; New York, tri-state metropolitan area.
[b]Based on EPA Air Quality Control Regions.
[c]Annual mean of daily maximum or minimum hourly temperature.
[d]Numbers in parentheses are standard deviations.
[e]Annual mean of daily minimum humidity.
[f]Annual mean of noon wind speed at surface.
[g]Defined by annual mean of daily midday radiosonde sounding.
[h]Annual mean of 24-hr averaged values, 1974-75; Los Angeles, seven stations, New York, four stations (see Hidy et al., 1977b for details).

Source: Hidy et al. (1978).

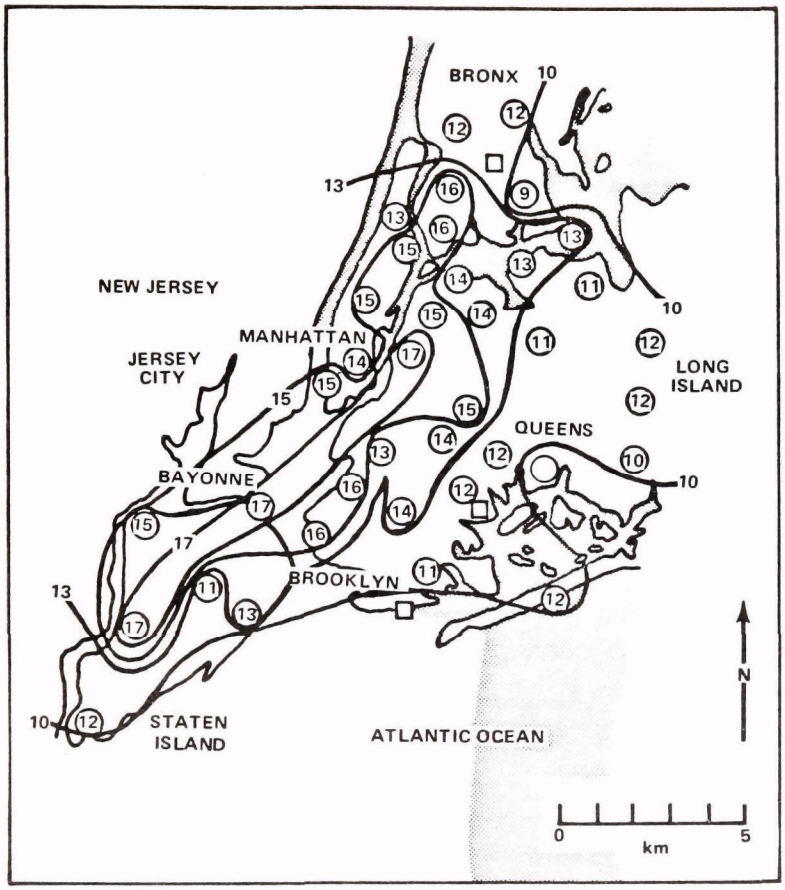

Figure 5-36. Map shows annual mean 24-hr average sulfate levels in micrograms per cubic meter in the New York area, based on 1972 data from Lynn et al. (1975). Squares are locations of three CHAMP site stations. The fourth station is at the tip of Long Island about 160 km from Manhattan.

Source: Hidy et al. (1978).

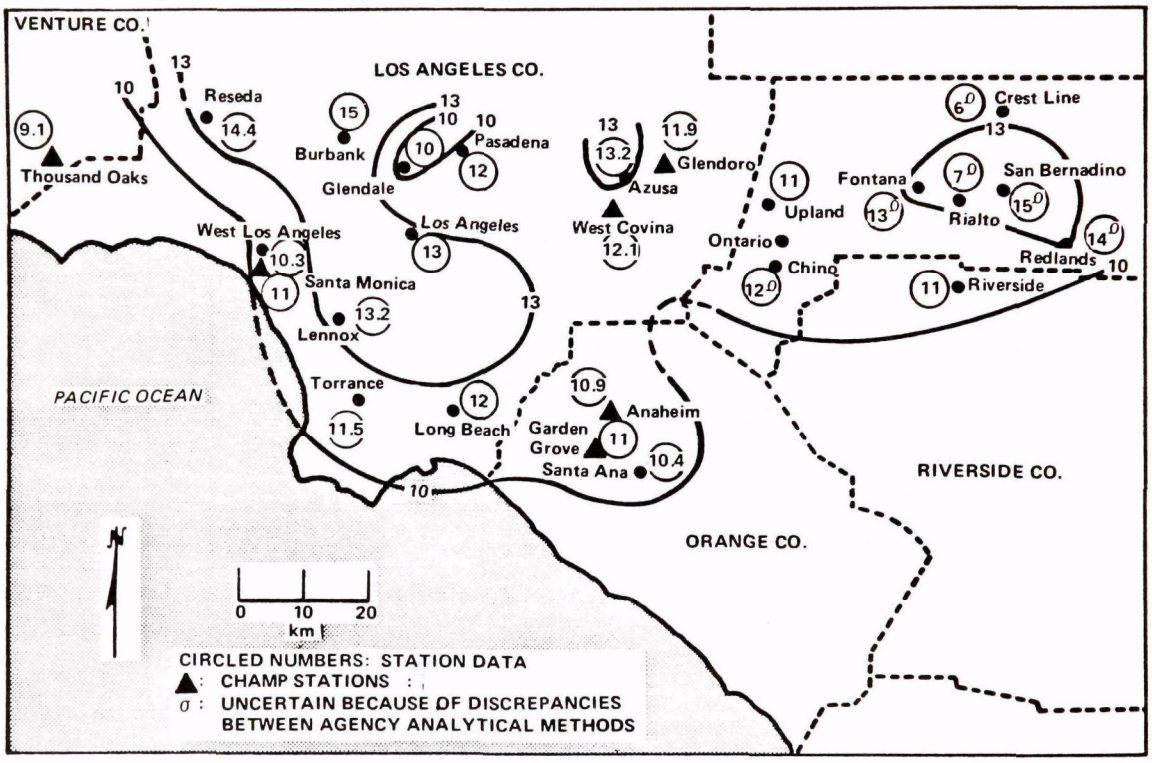

Figure 5-37. Distribution of annual average sulfate concentration in micrograms per cubic meter in the greater Los Angeles area is based on 1972-74 data.

Source: Kurosaka (1976).

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approximately twice the concentrations 5 km to the west of the river. For sulfates in this size range the pattern is similar and the gradient is not as pronounced, but the differences among sites are significant.

An attempt has been made to explain the variability in sulfate data for both the Los Angeles area and the New York City area by means of stepwise linear regression. Table 5-11 displays the three principal independent variables and the r values associated with them in explaining the variance of the daily sulfate concentrations. The results are very consistent in both areas except for Vista, CA, a community about 100 miles southeast of Los Angeles.

TABLE 5-11. PRIMARY RANKING OF VARIABLES FOR CORRELATING AIRBORNE SULFATE IN TWO CITIES BASED ON A STEPWISE LINEAR REGRESSION OF 15 VARIABLES FROM CHAMP AND RELATED MONITORING STATIONS

A. Los Angeles area

	Anaheim	Garden Grove	West Covina	Glendora	Santa Monica	Thousand Oaks	Vista[a]
Variable							
1	O_3	O_3	O_3	TSPM	O_3	TSPM	T_{min}
2	TSPM	TSPM	TSPM	RH	RH	RH	O_x
3	RH	RH	RH	O_3	TSPM	O_x	RH
Correlation coefficient (R)	0.71	0.77	0.79	0.79	0.79	0.72	0.56

B. New York

	Brooklyn	Queens	Bronx	Riverhead, L.I.
Variable				
1	TSPM	TSPM	TSPM	TSPM
2	RH	RH	O_3	RH
3	O_3	O_3	RH	O_3
Correlation coefficent (R)	0.60	0.63	0.54	0.62

[a]Located 50 km north of San Diego and 16 km inland from the coast.
[b]RH, Relative humidity.
[c]OX, 1-hr daily maximum ozone value.

Source: Hidy et al. (1978).

The results indicate that the most important variables are the 24-hr ozone level, the midday relative humidity, and the total mass concentration, minus the sulfate and nitrate fraction. Hidy et al. (1978) also suggest that these three factors are important in determining the daily variations of sulfate concentrations. The ozone or oxidant levels are an indication of photochemical oxidation, the relative humidity is an indication of water content of the air mass, and TSP is an indication of reactions involving particulate matter.

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The local sulfur dioxide concentrations did not enter into the correlation sequence as one of the three principal variables. The findings of Spengler et al. (1979) appear quite consistent with these findings since the only city with a significant spatial variation among sites for sulfates also had a variation among sites for the respirable particles and TSP.

5.5.2 Nitrates

Nitrate aerosols make up a varying amount of the total suspended particulate matter. Although widely reported to be significantly less than the sulfate fraction, nitrates nevertheless represent an important constituent. Most nitrates in the atmosphere are formed in gas-to-aerosol reactions, principally involving nitrogen dioxide and nitric oxide. These reactions may yield nitric acid (gas or aerosols), ammonium nitrate, sodium nitrate, and lesser amounts of other compounds. A minor fraction of the nitrate aerosols measured in the atmosphere can be attributed to wind erosion of soil and resuspension of fertilizers (National Research Council, 1978). These sources may be more important locally near fertilizer plants or transfer facilities, as well as munition factories.

Measurement of particulate nitrate has proven especially difficult (see Chapter 3). Analytical methods for aerosol nitrate analysis do not differentiate among particles containing neutral ammonium nitrate, sodium nitrate, and nitric acid. It is therefore impossible to estimate the relative quantities of neutral and acid nitrates in the aerosol. The reader is cautioned that most of the literature values cited below probably should be taken as total nitrate, gaseous HNO_3 + particulate nitrate. It would be incorrect to interpret the data as particulate nitrate.

Mean nitrate aerosol concentrations from urban and nonurban NASN sites are summarized in Figure 5-38 and 5-39, respectively. The annual average concentrations shown are in micrograms per cubic meter, as measured from high-volume samples. Concentrations in urban air are substantially higher than those in nonurban air. Although year-to-year variations are substantial, both urban and nonurban averages show upward trends. These trends are consistent with the increase in emissions of nitrogen dioxide. A zone of high urban concentrations exceeding 4 $\mu g/m^3$ extends eastward from Chicago through the industrialized Northeast through Pennsylvania to the Philadelphia area. Other zones of high nitrates are found in southern Louisiana, around Birmingham, AL, and near Little Rock, AR. In general, a zone of high urban nitrates 3 $\mu g/m^3$ and larger extends up from southeastern Texas through the Midwest and across through the Northeast. Of course, a major emission source may cause high nitrate gradients in the area surrounding. For example, a study in Chattanooga (Helms et al., 1970; National Academy of Sciences, 1977) showed an average nitrate concentration of 48.9 $\mu g/m^3$ for a site close to the Volunteer Army Ammunition Plant. This is more than three times the NASN maximum station average for 1965 (13.5 $\mu g/m^3$). This station average was 15 to 20 times higher than that of the four other Chattanooga sites presumably not influenced directly by the munitions plant. Their averages ranged from 2.4 to 3.8 $\mu g/m^3$. While the artifact phenomenon may discredit the absolute values, the ratios among sites have more credibility.

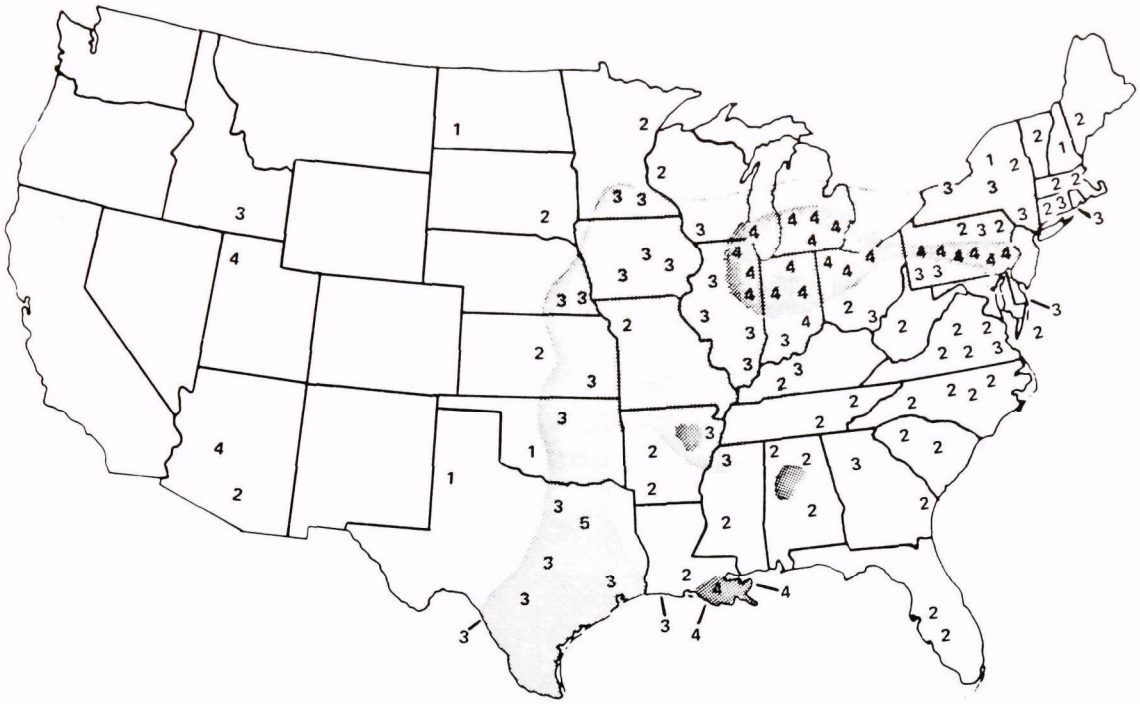

Figure 5-38. Map shows U.S. mean annual ambient nitrate levels in micrograms per cubic meter.

Source: Akland (1977).

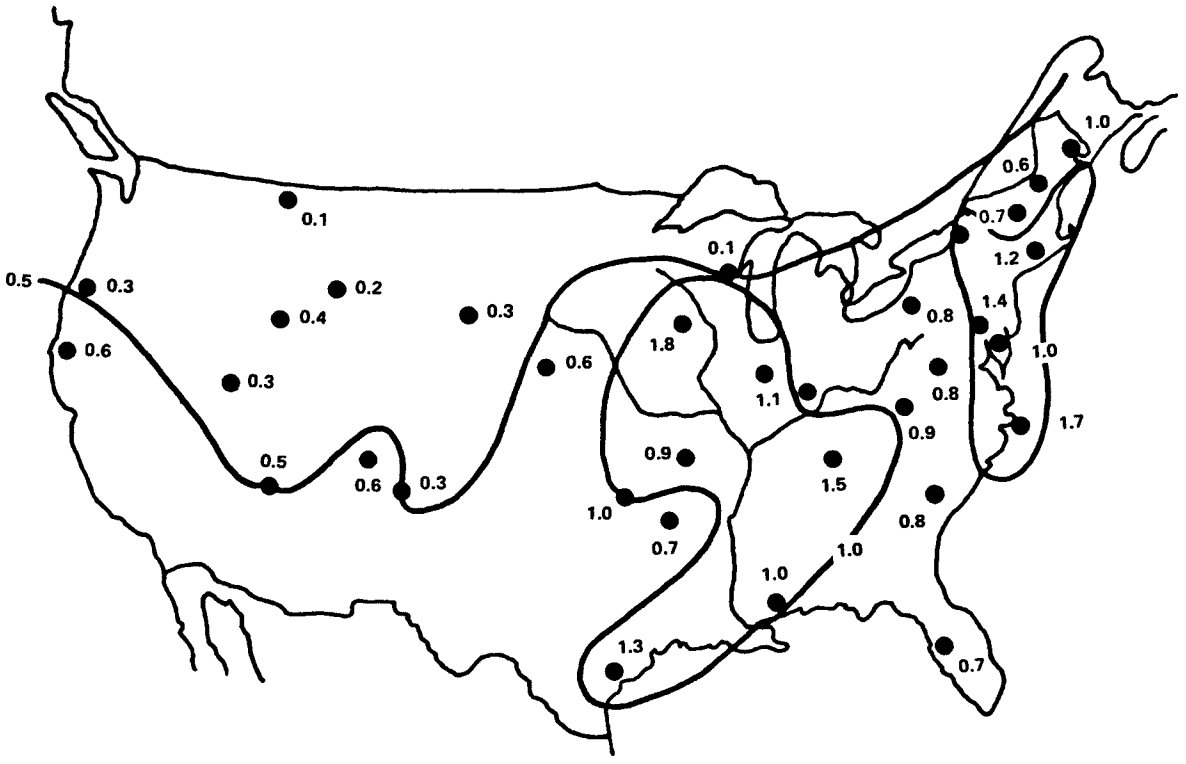

Figure 5-39. Mean nitrate concentrations in micrograms per cubic meter were measured at nonurban sites by the U.S. Environmental Protection Agency (unpublished data).

Source: National Research Council (1979).

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It is obvious from these figures that the data base is quite incomplete for the west coast. No data are reported for the Los Angeles area, nor for the large metropolitan areas of San Francisco, Seattle, and Portland.

A few studies have sought information on nitrate concentrations by composition and particle size. Orel and Seinfeld (1977) compared the formation, sizes, and concentrations of ambient sulfate and nitrate particles. Unlike sulfuric acid, the nitric acid that is formed tends to remain in the gaseous phase, although it may be an important component of acid precipitation. The EPRI SURE Project (Kneip et al., 1979) reports nitrate ion concentrations one-tenth the concentration of sulfate ions. The monthly mean values for August and October 1977 are less than 0.6 $\mu g/m^3$ ammonium nitrate at three locations acrcss the Northeast. On a few occasions the daily levels exceded 1.5 $\mu g/m^3$.

Data from the sulfate and nitrate data base of the California Aerosol Characterization Experiment are reported by Appel et al. (1978). Summer measurements for 1972 and 1973 from five fixed and one mobile site indicate that the mass median diameter for nitrates is between 0.3 and 1.6 μm. Twenty-four-hour averaged concentrations of nitrate ion varied across the Los Angeles basin, from a low of 4 $\mu g/m^3$ in Dominguez Hills to a high of 31 $\mu g/m^3$ in the eastern community of Rubidoux. In contrast to sulfate, the diurnal pattern for nitrate often has a maximum during the morning close to the maximum for gas-phase nitrogen oxides. The authors concluded that the ratios of ionic constituents and ambient ammonia levels suggested that ammonium salts were the principal form of sulfate and nitrate.

Until recently such high nitrate levels were not suspected in other regions of the United States. However, the Environmental Protection Agency has just completed the first analysis from a dichotomous particle sampling program in Denver, CO. The 24-hr nitrate levels, primarily in the fine fraction, often exceeded 10 $\mu g/m^3$ (Courtney et al., 1980).

Japanese workers have been investigating atmospheric nitrates for some time. Kadawaki (1977) has found a bimodal distribution of nitrates in the Nagoya area of Japan. Submicron particles (0.4 to 0.6 μm in diameter) are ammonium nitrate; whereas the coarse particles (3 to 5 μm in diameter) are sodium nitrate. Background nonurban levels as low as 0.8 to 0.9 $\mu g/m^3$ on the outer islands of Japan have been reported (Kito, 1977). Maximum average concentrations in the city of Kawasaki were reported to be as high as nearly 7 $\mu g/m^3$ (Terabe, 1977).

In summary, our knowledge of nitrates in the atmosphere is rather limited. No comprehensive data set exists. The NASN measures nitrate ion every 12th day at relatively few sites; spatial and short-term temporal variations cannot be discerned. In fact, there are many cities for which no measured values of nitrates have been reported. Furthermore, historic data before 1977 are in doubt because of the artifact formation on the filters. There is some evidence that ammonium nitrate is in the fine fraction, while the artifact is predominantly in the coarse fraction. There are spatial patterns in nitrate concentrations. Cities tend to have higher levels of nitrates than do rural regions. Some studies indicate

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that localized areas may have substantially higher nitrate levels. This raises the concern that available data on nitrate concentrations may underestimate the actual population exposure. In the near future, new sampling and analysis techniques should substantially expand our knowledge of nitrate aerosols, nitric acid, and other nitrogen compounds.

5.5.3 Carbon and Organics

A variety of carbon-containing compounds often account for a substantial, but highly variable, portion of fine particle mass. Elemental carbon, which is emitted from a variety of combustion sources, is a significant component also, usually accounting for 10-20% of urban aerosol mass.

Particles emitted from combustion sources frequently have fuel-derived organic substances sorbed on their surfaces (see chapter 4) and such components are commonly found in atmospheric particles. Very much greater concentrations are found associated with high ozone levels. It is now widely believed that this material is formed by chemical reactions in the atmosphere which produce compounds of lower volatility than their precursor molecules. These processes are discussed in more detail in Chapters 2 and 6.

In addition to the organic species accounting for aerosol mass, there are also present in the particles very much smaller amounts of polynuclear aromatic hydrocarbons, components of special interest because several are known to be carcinogenic. One of these compounds, benzo(a)pyrene is conventionally measured in NASN TSP samples. A complete discussion of these substances is contained in the Polycyclic Organic Matter document (Santodonato et al., 1979) to which the reader is referred.

Several comprehensive reviews of airborne-organic particulate matter can be found in the following references: (National Academy of Sciences, 1972; Duce, 1978; Daisey, 1980; Hahn, 1980; Lamb et al., 1980). Other related publications include National Academy of Sciences (1976), Perera and Ahmed (1978), and Grosjean (1977).

5.5.3.1 Physical Properties of Particulate Organics--Many atmospheric organic compounds are distributed between the vapor and particulate phases of the aerosol (De Wiest and Rondia, 1976; Krstulovic et al., 1977; Cautreels and Van Cauwenberghe, 1978) and presumably, this distribution can vary with temperature. Because of this volatility, there can be substantial losses of low molecular weight compounds during sampling (Cautreels and Van Cauwenberghe, 1978; Krstulovic et al., 1977; De Wiest and Rondia, 1976; Katz and Chan, 1980; Schwartz et al., 1981). At the high temperatures found in combustion sources, larger proportions of the emitted organic compounds will be present in the vapor phase. These compounds will condense on the surface of particulate matter as the emissions cool and, thus, be enriched at the surface. Natusch and co-workers (1976) have found that this occurs when PAH is emitted from power plant stacks. Such surface enrichment can affect the biological impact of POM. While there is the possibility that POM may exist as particles formed by self-condensation, most POM is probably absorbed on the surface of other particles, much of it presumably with soot

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particles (Thomas et al., 1968). The effect of the substrate upon which POM is adsorbed upon the chemical and biological reactivity of these compounds is almost entirely unknown. Korfmacher and co-workers (1980) have recently reported that photodegradation of some PAH compounds proceeds much more slowly when the compounds are adsorbed on coal fly ash than when adsorbed on other substrates such as silica gel.

The distribution of organics between vapor and particulate phases is also profoundly influenced by chemical reactions in the atmosphere. Grosjean and Friedlander (1975) found that during photochemical oxidant incidents organic substances are converted from volatile to relatively non-volatile species. In this process the fraction of organic mass in the particle phase (relative to the gas) can grow from very low values, 1 percent or so, to about 6 percent of the vapor and particle total.

While both mass and size distribution of organic substances in particles is clouded by their volatility, there have been some attempts to establish the fine/ coarse ratios. Some of the heavier polycyclic components are known to be predominantly fine particle components (Mueller et al., 1964; De Maio and Corn, 1966; Kertesy-Saringer et al., 1971; Pierce and Katz, 1975; De Wiest, 1978; Van Vaeck and Van Cauwenberghe, 1978, 1980). In Los Angeles oxidants incidents, virtually all the organic particles are smaller than 2.5 μm (Schuetzle et al., 1975; Mueller et al., Hidy et al., 1975). Van Vaeck and Van Cauwenberghe (1978) report that aliphatic hydrocarbons and carboxylic acids are predominantly (90 percent) in fine particles in European samples. Since in general, organic compounds are distributed disproportionately in the fine fraction aerosols, it is not surprising to see that they represent an important fraction of the mass. Organic substances are estimated to be between 25 and 47% of the fine particulate fraction in the U.S. (Steigerwald, 1975). However, there are also reports of significant fractions of organic substances in coarse particles in both urban and rural samples (Stephens et al., 1980; Hidy et al., 1980). It appears there is much to be learned about the size distribution of organic particles.

5.5.3.2 Carbon and Total Organic Mass--There are limited historical data on the mass fraction of elemental carbon in atmospheric aerosols in history but very recent work is contributing information in this area (Rosen et al., 1980; Novakov, 1980; Wolff et al., 1980; Huntzicker et al., 1980; Stephens and McClenny, 1980; Lewis and Macias, 1980; Stevens et al., 1980). Techniques currently employed detect both organics and carbon by optical absorption and selective combustion techniques.

Novakov (1980) reports elemental and organic carbon in over 1000 samples collected from a variety of urban sites. In New York City, the principle species present was elemental carbon, accounting for two thirds or more of the carbon mass; the balance was organic. In Denver about 60 percent was elemental carbon, while in Los Angeles about 70 percent was organic and the balance elemental carbon.

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Wolff et al. (1980), using a somewhat different technique, reported carbon concentrations in 10 U.S. locations. "Apparent" elemental carbon was reported to range from 1.1 $\mu g/m^3$ in a remote South Dakota location to 13.3 $\mu g/m^3$ in New York City. These values covered a range of 4 to 11 percent of the TSP.

Stevens et al. (1980), Stevens and McClenny (1980) and Lewis and Macias (1980) have reported total carbon values of 8.4 $\mu g/m^3$ (14 percent of D_{TOTAL}) in Charleston, West Virginia, while in the Great Smoky Mountains only 1.1 $\mu g/m^3$ (3 percent of D_{TOTAL}) was elemental carbon and 3.4 $\mu g/m^3$ (12 percent of D_{TOTAL}) was organic carbon.

The mass of organic substances present in atmospheric aerosols was at one time approximated by solvent-extraction with benzene in routine NASN hi-vol samples. Other solvents have also been used in such determinations. Unfortunately, such determinations were terminated in 1970 and except for a few intensive studies (Daisey, 1980; Grojean and Friedlander, 1975); Wesolowski et al., 1980) there has been no extensive data base on organic extractables covering the past ten years.

Some typical values for particle number and mass concentrations of organics are listed in Table 5-12. The organic fraction of the mass concentration as measured by the benzene-soluble component is also listed, with the benzo(a)pyrene fraction for comparison.* In the organic fraction, a variety of organic compounds have been identified, including some materials classified as PAH (Corn, 1968). However, the identified fraction represents only 10% of the organic components of the urban aerosol. Although the total aerosol number concentration is often very large in cities, the mass concentration varies less and rarely exceeds about 200 $\mu g/m^3$ in the United States. The benzene-soluble fraction of this is about 10-20 percent of the total mass, and the concentration of benzo(a)pyrene is far lower. Even in remote areas, there is a contribution of organic material.

A limited number of samples have been collected in unpolluted atmospheres. Levels in remote areas and in marine air for the ether-soluble fraction of organic particulate matter have been as low as 0.51 (0.18-0.84) $\mu g/m^3$ STP. Marine air with a continental influence had averages of 0.93 (0.48-1.38) $\mu g/m^3$ STP and continental air 1.2 (0.69-1.71) $\mu g/m^3$ STP. Similar concentrations have been observed at Barrow, Alaska, a remote site in the Arctic, for cyclohexane- and dichloromethane-soluble POM (Daisey et al., 1981).

Variations in the concentration of organic particulate matter by location, meteorological conditions, season and by time of day have been observed repeatedly (Hidy et al., 1975; Gordon, 1976; Calvert, 1976). By way of illustration, Figure 5-40 shows the differing contributions of the organic fraction in samples obtained in two cities in southern California (National Academy of Sciences, 1972). In both instances, however, the organic fraction represents a sizeable portion of total suspended particulate material.

*The benzene-soluble extract is not necessarily equivalent to the total amount of organic material in the sample, but it is taken to be representative of such a fraction.

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TABLE 5-12. TYPICAL VALUES OF AEROSOL CONCENTRATION FOR DIFFERENT GEOGRAPHIC AREAS (ANNUAL AVERAGES)[a]

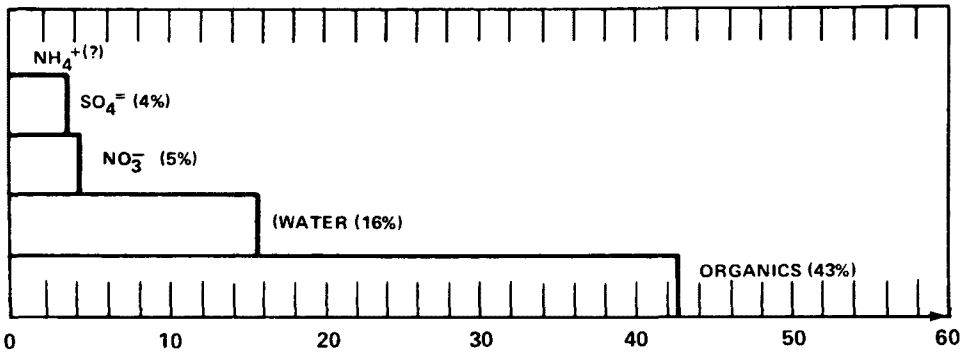
Location	Number of particles/cm^3[b]	Mass concentration (m), $\mu g/m^3$[c]	Benzene soluble fraction of m, $\mu g/m^3$	Benzo[a]pyrene fraction of m, $\mu g/m^3$
Nonurban				
Continental				
General	10^3 - 10^4	20 - 80	1.1 - 2.2	-
California	10^3 - 10^4	39	2.8	0.48
Oregon	-	47	0.9	0.09
Colorado	10^3 - 10^4	14	1.1	0.11
Indiana	-	39	2.1	0.25
Maine	-	18	1.2	0.12
New York	-	29	1.8	0.25
So. Carolina	-	40	2.7	0.43
Maritime				
General	10^3 - 10^4	-	-	-
Pacific offshore	10^3 - 10^4	19 - 146	1.5 - 6.1[d]	-
Oahu, Hawaii	10^3 - 10^4	10 - 49[d]	0.7 - 6.3[d]	-
Urban				
Continental				
General	10^3 - 10^4	>100	7	-
Los Angeles	10^3 - 10^4	93	12.5	1.87
Portland	-	72	6.6	2.60
Denver	10^3 - 10^3	110	9.0	2.52
Minneapolis	10^3 - 10^3	70	6.1	1.18
Chattanooga	-	105	6.9	4.18
New York	-	105	3.9	3.63
Greenville, S.C.	-	76	7.4	7.49
Maritime				
Honolulu, Hawaii	10^3 - 10^4	40	2.3	0.59
San Juan, Puerto Rico	-	77	6.9	1.42

[a]Data based on 1969 National Air Surveillance Network observations, except for maritime data.

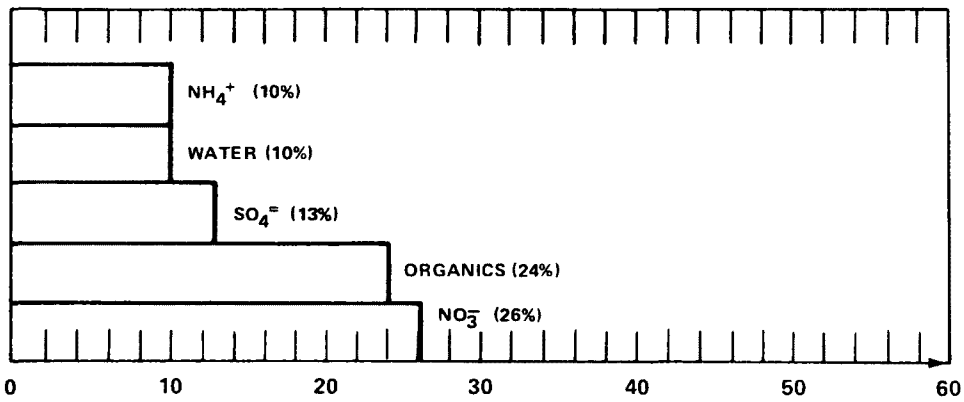
[b]Aitken nuclei

[c]Geometric means.

[d]Short-term data.



PASADENA, 9/20/72; TWO HOUR SAMPLE OVER 1200-1400 PST; LOW OXIDANT, TOTAL MASS CONCENTRATION, 79 $\mu g/m^3$.



POMONA, 10/24/72; SAMPLES FROM 1200-1400 PST; MODERATE OXIDANT, TOTAL MASS CONCENTRATION, 178 $\mu g/m^3$.

Figure 5-40. Calculated distribution of aerosol constituents for two aerosol samples taken in the Los Angeles basin.

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A pattern of elevated wintertime concentrations of particulate organics has been observed in NYC and in Mainz, West Germany. Winter samples in Mainz of ether-extractable organic material averaged 27 $\mu g/m^3$ for TSP concentrations averaging 150 $\mu g/m^3$. Winter samples collected in February, 1977 in NYC had a total extractable organic fraction of 22 $\mu g/m^3$ for a TSP average of 96 $\mu g/m^3$. The August, 1976 levels were 13.3 $\mu g/m^3$ for a TSP average of 86 $\mu g/m^3$ (Kneip et al., 1979).

A 1971 study of Colucci and Begeman is an example of a more detailed short-term urban survey of PAH than is available for NASN. From 1964 to 1965, these investigators found that the concentrations of benzo(a)pyrene and benz(a)anthracene were 4 1/2 times greater in central Los Angeles than at two suburban sites. However, the suburban site downwind of the downtown area (on the average) appeared to have systematically higher benzo(a)pyrene concentrations than the upwind site. Daily concentrations reported in the Los Angeles area ranged from 0.1 $\mu g/m^3$ to over 10 $\mu g/m^3$, depending on the season. Benz(a)anthracene concentrations were 1 1/2 times larger than the benzo(a)pyrene concentrations. Annual average benzo(a)pyrene concentrations were similar to the NASN data for downtown Los Angeles. The PAH concentrations increased substantially in winter. Benzo(a)pyrene concentrations were higher at night, in contrast with those of other pollutants. All pollutants were higher on weekdays than on weekends. Benzo(a)pyrene concentration was found to be correlated with carbon monoxide and lead concentrations, with coefficients ranging from 0.6 to 0.9. Benzo(a)pyrene concentration was also related significantly to that of hydrocarbon vapors, oxides of nitrogen, and vanadium (a nonautomotive pollutant). Despite the strong relation to lead, the statistics in the study failed to reveal a clear identification of benzo(a)pyrene emissions with automotive or stationary combustion sources.

Trends of BaP concentrations as measured at 34 NASN urban sites are displayed in Figure 5-41. It is indeed encouraging to see the steady decline in BaP concentrations that has occurred since the mid-60's. The 90th percentile of quarterly measurements has been reduced dramatically from near 7 ng/m^3 to less than 2 ng/m^3. These changes reflect both controls and shifting of sources. Incomplete combustion of fossil fuels., especially coal, is a primary source of BaP. Major point and area sources include residential coal-fired furnances, coal-fired utilities and industrial boilers, coke ovens, petroleum refineries, and incinerators (see Chapter 4). Shifts away from coal for residential, commercial, and light industrial use have made a substantial contribution to the reduction of urban BaP concentrations. To a lesser extent the control of particulate emissions has also helped to lower concentrations.

The national trends in benzene-soluble particulates and BaP as reported by Faoro (1975) may not be true everywhere. Indeed, specific organic fractions may show opposite trends. Daisey (1980) discusses BSO trends for NYC; annual averages for the NY University station, normalized to account for year-to-year meteorological variations, are reported in Table 5-13.

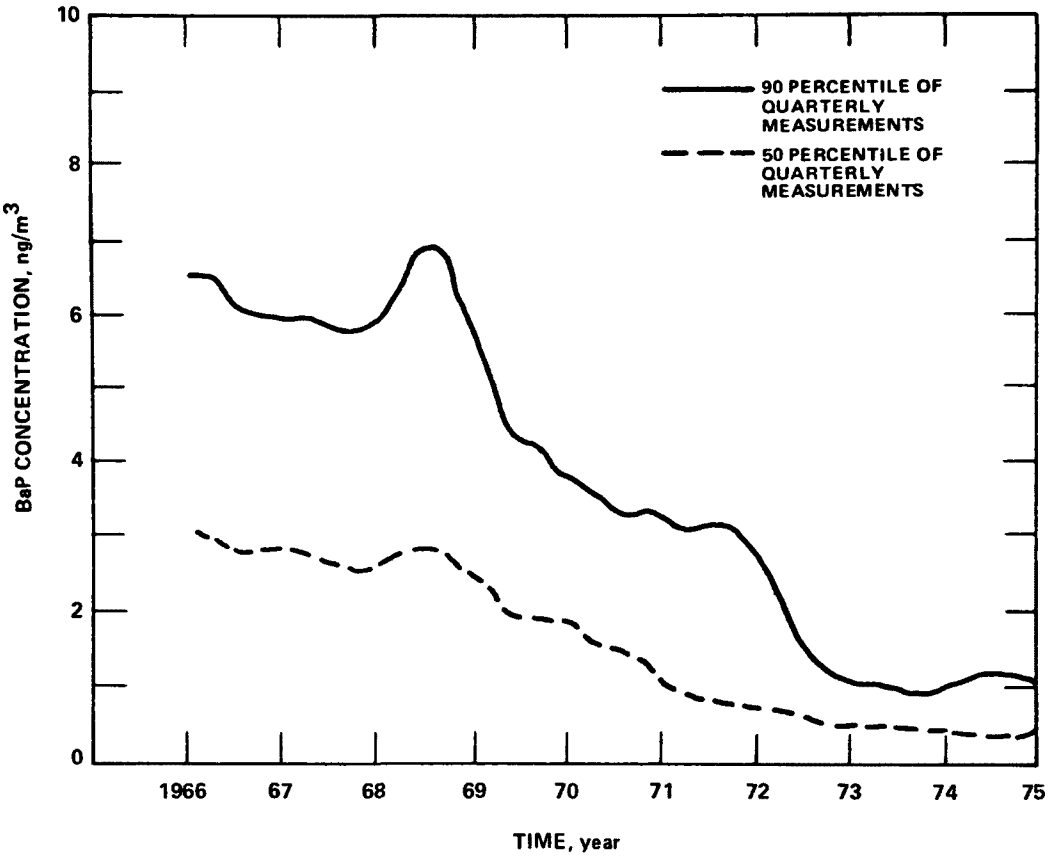

Figure 5-41. Benzo(a)pyrene seasonality and trends (1966 to 1975) in the 50th and 90th percentiles for 34 NASN urban sites.

Source: U.S. Environmental Protection Agency, 1979.

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TABLE 5-13. ANNUAL AVERAGES OF ORGANIC FRACTIONS IN TOTAL SUSPENDED PARTICULATE MATTER, NEW YORK CITY[a], DISPERSION NORMALIZED

Year	TSP, $\mu g/m^3$	Organic fraction[b] $\mu g/m^3$	Persent organics in TSP
1968	95.7	10.2	10.6
1969	129	10.8	8.4
1977 - 1978	59.8	8.8[c]	14.7

[a]NYU Medical Center Station

[b]Total of non-polar (benzene-soluble) and polar (acetone-soluble) organics

[c]Respirable (<_3.5 μ) organics only

Daisey, 1980.

Although TSP had decreased by 40% between 1968 and 1978, the POM fraction had not decreased proportionately.

5.5.3.3 Chemical Composition of Particle Organics. Particulate organic matter has often been fractionated by means of acid-base extractions followed by colume chromatography (Hueper, et al., 1962; Tabor, et al., 1958; Hoffmann and Wynder, 1977; Asahina, et al., 1972). The composition data reported by Hoffmann and Wynder (1977), Table 5-14, for Detroit particulate matter is fairly typical and presents a view of the general proportions of various broad classes of compounds which are present. Hoffmann and Wynder (1977) found that the PAH containing fraction was principally responsible for the tumorigenic properties of POM in mice.

Specific classes of compounds which have been identified to date in the organic fraction of airborne particulate matter include polyclic aromatic hydrocarbons, aromatic and aliphatic hydrocarbons, aza-arenes, aliphatic and aromatic aldehydes and ketones, quinones, phenols, polyols, phthalic acid esters, sulfur heterocyclics, aryl and alkyl halides, chlorophenols, nitro compounds and alkylating agents (Hoffmann and Wynder, 1977; Daisey, 1980; Lamb et al., 1980). Of all the airborne organic compounds the most information exists for the classes of polycyclic organic matter (POM). The greatest attention has been focused on the subclasses of polycyclic aromatic hydrocarbons (PAH) and the polycyclic heterocyclic compounds such as the aza-arenes, because many of the compounds in this class are potent carcinogens on animals. Some of the compounds identified in POM are pyrene, benzo(a)pyrene, benzo(e)pyrene, benz(a)anthracene, perylene, chrylene, chrysene, coronene, fluorathane, benzo(ghi)perylene and alkyl derivations of these compounds (Sawicki et al., 1962; Sawicki et al., 1965).

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TABLE 5-14. COMPOSITION OF THE ORGANIC FRACTION OF AIRBORNE PARTICULATE MATTER COLLECTED IN DETROIT[a,c]

Fraction	Percent of Total Extractable Organic Matter
Aliphatic Hydrocarbons	48.3
Aromatic Hydrocarbons[b]	3.6
Neutral Oxidized Hydrocarbons	20.8
Acidic Compounds	14.8
Basic Compounds	0.55
Insolubles	10.8

[a]From Hoffman and Wynder, 1977.

[b]Included polycyclic aromatic hydrocarbons.

[c]3/μg/m^3 annual average Benzene-soluble organics.
TSP not reported.

Benzo(a)pyrene was one of the earliest compounds in this mixture of organic matter than was identified and then routinely measured. Some measurements for benzo(a)pyrene in the U.S. date to the early fifties. Sawicki and co-workers in the sixties extracted the identified many organic compounds. Today there is a renewed effort, using more sophisticated tecnhiques, and attempting to answer the many questions still remaining on the biological significance, variations and concentrations, specific source contributions, and the reactivity of airborne organic matter.

In 1972, the National Academy of Science published an extensive report on the biologic effects of airborne matter, entitled, Biologic Effects of Atmospheric Pollutants: Particulate Polycyclic Organic Matter. According to the report, emission source data for airborne organic substances are generally expressed in terms of estimated BaP emissions. Benzo(a)pyrene is used as a surrogate for detecting the presence of airborne organic pollutants because it appears to be a prominent constituent of POM. BaP is also a known animal carcinogen, and the best documented of all the polycyclic organic compounds (National Academy of Sciences, 1972). BaP cannot be regarded as a perfect indicator of polycyclic aromatic hydrocarbons in the air, nor of their carcinogenic properties; however, because better data are generally not

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available, BaP is presently used as an indicator of the potential carcinogenicity of general air pollution (Bridbord, et al., 1976).

Despite much work on certain subfractions of POM, such as the polycyclic organic fraction, other compound classes such as the oxidized hydrocarbons remain relatively unexplored. Sawicki (1976) has estimated that "over 99% of the organic pollutants in the air have never been determined."

Classes of biologically active compounds other than PAH and related polycyclic organics have been identified in airborne particulate matter. This includes alkylating agents Kneip et al., 1979; Agarwal et al., 1980) N-nitrosamines (Kneip et al., 1979) nitro derivatives of PAH (Jäger, 1978) and the compounds responsible for the mutagenic activity of POM in the Ames assay (Kneip, et al., 1979; Talcott and Wei, 1977; Pitts et al., 1977; Daisey et al., 1979). In addition, there may also be unstable compounds present in the aerosol, such as epoxides and lactones (Van Duuren, 1972) which are of significance to human health but which decompose upon collection by conventional sampling techniques. There is a need to identify specific compounds such as these, to evaluate their significance to human health and to determine their sources and concentrations in the ambient atmosphere. There is also a need to identify sampling artifacts and develop improved sampling techniques for organic compounds in the aerosol.

In photochemical incidents, volatile hydrocarbons are converted to very large quantities of 5-7 carbon bifunctional carboxylic acids. (Schuetzle, et al., 1975; Grosjean and Friedlander, 1975; Cronn, et al., 1977). Schuetzle, et al. (1975) in a 1972 ACHEX incident report that alkanes and alkyl naphthalenes account for 1.5-3 percent of the fine particle mass, and bifunctional compounds amounted to about 11 percent. In addition to glutoric, adipic and pimelic acids, the corresponding hydroxy carboxylic acids and a variety of their nitrate and nitrite ester derivatives were reported.

Cronn, et al. (1977), confirmed those findings in a series of sub 3.5 μm samples taken during the 1973 California Air Characterization Experiment. These authors found levels of organics up to 65 $\mu g/m^3$ out of a fine particle loading of 230 $\mu g/m^3$. These substances included small amounts of alkanes, alkyl naphthalenes and piperidines (up to 12 $\mu g/m^3$) and much larger quantities of C_5-C_7 dicarboxylic acids, hydroxy-acids and amides.

Grosjean and Friedlander (1975) have found organic extractables up to 141 $\mu g/m^3$ during an incident in 1973 and 1/2 to 1/3 of this mass was polar organics. These organics together with ammonium sulfate and nitrate accounted for 95 percent of the secondary aerosol during photochemical incidents. Therefore, there is substantial evidence that organic particles can be influenced in a very major way by photochemistry.

5.5.4 Metallic Components of Fine Particles

It is useful to study not only the chemical but also the elemental composition of the particles. Many trace elements are known to be toxic and can act as catalysts in atmospheric reactions. Table 5-15 indicates the mean and maximum concentrations of several elements found

TABLE 5-15 COMPARISON OF URBAN AND NONURBAN ANNUAL AVERAGE CONCENTRATIONS FOR SELECTED METALS, 1970-1974

	Be[a]		Cd		Cr		Co		Fe		Pb		Mn		Ni		Ti		V	
	U[b]	NU[b]	U	NU	U	NU	U	NU	U	NU	U	NU	U	NU	U	NU	U	NU	U	NU
1970																				
Maximum	2.9	.24	.099	.0001	.130	.075	014	LD	14.2	1.62	5.83	1.471	2.10	068	.277	.097	.26	.093	1.222	112
Arithmetic mean	LD[c]	LD	.003	.0001	.008	.003	LD	LD	1.7	.38	1.19	.088	.07	.015	.015	.005	.05	.013	.052	.008
Std. deviation	0.2	.03	.007	--	.011	.009	.001	--	1.3	.27	.80	.190	.12	.013	.028	.014	.03	.011	.116	.019
1971																				
Maximum	0.7	.24	.295	.0001	.171	.061	.085	LD	16.0	2.80	6.31	1.134	1.95	.102	.347	.083	.51	.069	1.325	.209
Arithmetic mean	0.1	.01	.004	.0001	.009	.004	.001	LD	2.1	.51	1.23	.047	.08	.018	.015	.003	.04	.017	.041	.007
Std. deviation	0.1	.03	.016	--	.014	.007	.003	--	1.6	.38	.87	.155	.11	.015	.028	.011	.05	.020	.108	.024
1972																				
Maximum	LD	LD	.112	.0001	.143	.039	.042	LD	6.4	1.15	6.88	1.048	.86	.046	.268	.082	48	.092	.858	.205
Arithmetic mean	--	LD	.002	.0001	.006	.002	LD	LD	1.2	.25	1.13	139	.04	.007	.011	.004	.04	.027	.022	.004
Std. deviation	--	--	.007	--	.010	.004	.002	--	.8	.22	.78	.169	.06	.009	.023	.012	.03	.022	.056	.019
1973																				
Maximum	LD	LD	.032	.0001	.228	.066	.027	LD	6.9	1.19	5.83	.939	.56	.030	.439	.280	.23	.084	.393	.035
Arithmetic mean	LD	LD	.001	.0001	.007	.003	.001	LD	1.1	.19	.92	.110	.04	.004	.014	.011	.04	.028	.016	.002
Std. deviation	--	--	.003	--	.015	.009	.002	--	.8	.18	.64	.149	.05	.005	.037	.037	.03	.021	.034	.005
1974																				
Maximum	0.2	LD	.077	.0002	.073	.009	.029	LD	6.2	.69	4.09	.534	.35	.033	.639	.026	.22	.066	.248	.023
Arithmetic mean	LD	LD	.002	.0002	.006	.002	LD	LD	1.1	.24	.89	.111	.04	.006	.009	.002	.04	.020	.019	.002
Std. deviation	--	--	.005	--	.006	.002	.001	--	.7	17	.57	.111	.04	.007	.029	.004	.03	.017	.037	.004

[a]expressed in ng/m^3
[b]U=urban
NU=nonurban
[c]LD=less than detectable

Source: G. Akland, 1976.

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in urban and nonurban areas in the U.S. from 1970 to 1974. In general the trace elements tend to be enriched in urban aerosols (Table 5-16) because of the concentrations of industrial sources and greater fuel combustion. As Table 5-17 indicates, they are not homogeneously distributed among the various particle size fractions. There is also spatial variability in the composition of the aerosol, as indicated by Table 5-18. These intercity differences reflect the difference in industries and types of fuel used in these urban areas.

Hi-vol filter samples from the NASN have been routinely analyzed for certain metals going back to the early 1960s. The data for certain metals for the year 1965-1974 have been summarized in an E.P.A. report (Faoro and McMullen, 1977). This report presents the composite national and regional trends for nine trace metals. These are the fuel-related metals--lead, vanadium, nickel, and titanium--and the industry-related metals--cadmium, chromium, copper, iron, and manganese. These trends were derived from samples collected from 92 urban and 16 nonurban NASN hi-vol stations.

The instrumental techniques for detecting metals changed in 1970, significantly improving the lower sensitivity of the detection. This report, in addition to two others (EPA, 1976) and (Akland, 1976) describes the methods used and the implications to trends analysis. In general, the data presented here serves as an indication of the changes in atmospheric concentrations of various metals occurring in different regions of the country. For the most part the trends are consistent with changes in emission patterns due to industrial source control and changes in fuel use.

Similar to trends in urban TSP concentrations, metals concentrations have declined in most urban areas, with the exceptions of copper, titanium, and possibly chromium. Table 5-19 summarizes metal trends and possible causes for these trends. Both beryllium and cobalt have such very low concentrations that trends cannot be identified with any certainty. Trends in other metals, such as vanadium and nickel, parallel air pollution control regulations mandating the use of low sulfur fuels. There has been a drop in vanadium and nickel, particularly in the Northeast, because the desulfurization process of petroleum also removes these impurities. Titanium, on the other hand, may have increased due to the rise in coal use by utilities. Decrease in iron, manganese, and cadmium concentrations are probably related to reduced particulate emissions from steel plants and related industries and from improved incineration or the practice of sanitary landfill instead of incineration. No trends were apparent for copper, but it is felt that the high concentrations are a result of contamination from the commutators of the high volume samplers.

5.5.4.1 Lead--The seasonal patterns and trends in the quarterly-averaged urban lead concentrations are displayed in Figure 5-42. The national composite 50th percentile of lead concentrations has decreased from about 1.1 $\mu g/m^3$ in 1971 to 0.84 $\mu g/m^3$ in 1974. This is about a 24 percent decrease. This decrease is attributed to the decrease in lead content in gasoline and particularly the decrease in premium gas sales since 1970. The premium gas has a higher lead content than regular gas. Lead content of gasoline will continue to decrease in

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TABLE 5-16. RATIOS OF URBAN (U) TO SUBURBAN (S) CONCENTRATIONS IN AIR, CLEVELAND, OHIO, AREA

Element	U/S	Element	U/S	Element	U/S
Antimony	6.9	Mercury	3.0	Silicon, tin	1.8
Chloride	6.5	Iron	2.8	Copper, vanadium	1.8
Beryllium	6.1	Cadmium	2.5	Aluminum	1.7
Chromium	5.6	Sodium	2.4	Zinc	1.6
Cobalt	3.4	Magnesium	2.4	Arsenic	1.4
Bismuth	3.3	Manganese	2.2	Selenium	1.3
		Calcium	2.0	Bromine	1.2

$\bar{X} = 2.8$

Source: Report of the ECE Task Force on Fine Particulate Pollution. Task Force of the Economic Commission for Europe's Working Party on Air Pollution Problems. Geneva, World Health Organization, December 1977.

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TABLE 5-17. CORRELATIONS OF CHEMICAL CONTENT WITH PARTICLE SIZE

a) Predominant Particle Size for Various Substances

Normally fine	Normally coarse	Normally bimodel	Variable
Sulfates	Iron, calcium	Chloride	Nickel
Organic (condensed vapors)	Titanium	Nitrate	Tin
Lead	Magnesium		Vanadium
Arsenic	Potassium		Antimony
Selenium	Phosphate		Manganese
Hydrogen ion	Silicon		Zinc
Ammonium salts	Aluminum		Copper
Soot			

b) Ratios of Element Distribution Between Fine and Coarse Particles

(St. Louis Urban Aerosol, 18-day average, Aug.-Sept., 1975)

Predominantly fine		Predominantly coarse	
Element	Fine/coarse	Element	Fine/Coarse
Sulfur	8.90	Calcium	0.09
Lead	3.67	Silicon	0.13
		Iron	0.29
		Potassium	0.33
		Titanium	0.55

Source: Miller, F. J. et al., 1979.
Dzubay, T. G. et al., 1977.

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TABLE 5-18. PARTICULATE ANALYSES FROM SELECTED URBAN LOCATIONS

	Atlanta, Georgia	Birmingham, Alabama	Baltimore, Maryland	Albuquerque, New Mexico
Suspended particulates	97.	142.	146.	120.
Antimony	0.000	0.000	0.000	0.000
Beryllium	0.000	0.000	0.000	0.000
Bismuth	0.000	0.000	0.000	0.000
Cadmium	0.017	0.008	0.003	0.000
Chromium	0.002	0.005	0.018	0.001
Cobolt	0.000	0.000	0.000	0.000
Copper	0.04	0.06	0.06	0.07
Iron	1.2	1.7	0.8	a
Manganese	0.06	0.15	0.08	0.03
Nickel	0.007	0.004	0.034	0.000
Tin	0.02	0.01	0.01	0.01
Titanium	0.03	0.03	0.01	0.01
Vanadium	0.001	0.003	0.071	0.001
Zinc	0.52	1.09	0.34	0.00

[a]Not analyzed.

Arithmetic mean values for 1966 expressed as micrograms per cubic meter.

Copyright by the American Association for the Advancement of Science, 1970.

Source: Corn, M. 1976.

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TABLE 5-19. TRENDS IN REPORTED URBAN METAL CONCENTRATIONS AND THEIR POSSIBLE CAUSES

Metal	Observed trends	Possible causes
Fuel combustion-related metals:		
Beryllium	Unknown	
Lead	Down last 5 years	Lower lead content in gasolines after 1969
Nickel	Down	Reduction of Ni in residual oils
Titanium	Up	Increasing use of coal in electric utilities
Vanadium	Down	Reduction of V in residual oils
Industry-related metals:		
Cadmium	Down	Controls in metal industry and improved incineration practices
Chromium	No trend	Unknown
Cobalt	Unknown	
Copper	No trend	Contamination from hi-vol commutator
Iron	Down	Improved incineration or waste burning practices, fuel switching, controls in steel industry
Manganese	Down	Controls in metals industry

Source: Faoro and McMullen, 1977.

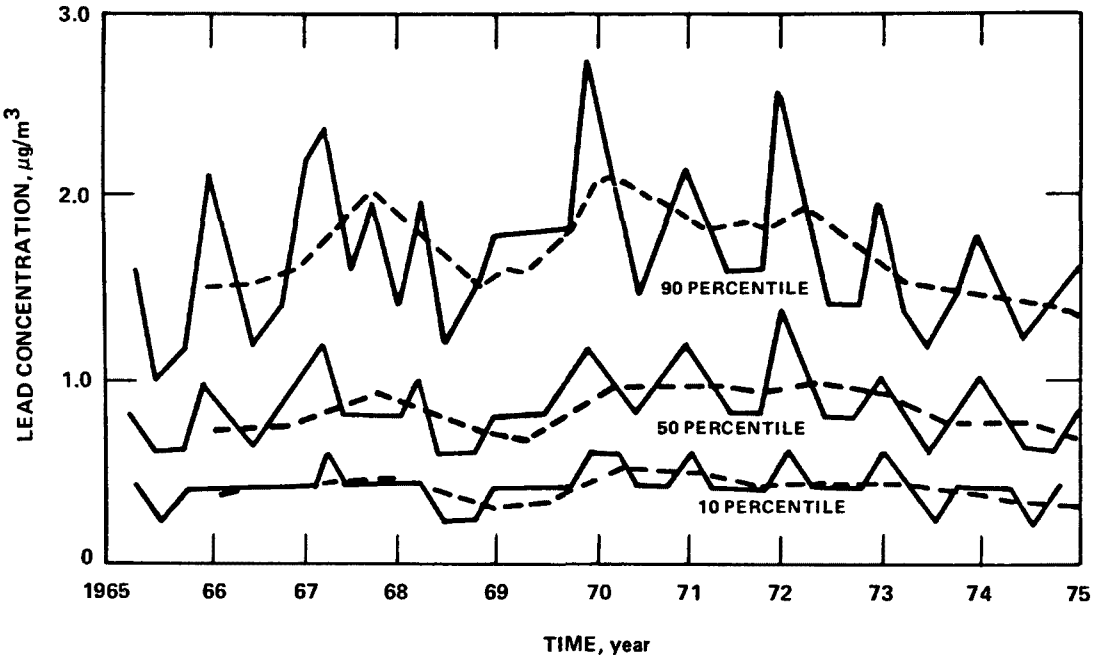

Figure 5-42. Seasonal patterns and trends in quarterly average urban lead concentrations.

Source: Faoro, R.B. and T.B. McMullen, 1977.

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the future because of increased use of unleaded gasolines in the new cars equipped with catalytic converters. This national decrease is not experienced equally in various regions of the country, due to differences in growth rate and vehicle miles travelled. These results, however, should be used with caution because of the relatively small number of stations used in determining the trends. A NASN location in downtown Los Angeles experienced the highest lead concentrations, averaging between 4 and 5 $\mu g/m^3$ until 1971; the concentrations decreased to about 2 $\mu g/m^3$ in 1974. Again the reduction of lead content in gasoline and the increased use of lead-free gasoline may have contributed to this decline, but also the decrease in vehicle miles travelled in downtown urban areas has contributed to this downward trend. There is some evidence that the rural sites have shown either stable or slightly increasing patterns in ambient air lead content.

5.5.4.2 Vanadium and Nickel--Figure 5-43 shows, for the five broad geographical areas of the United States, the 90th percentiles of the annually averaged vanadium concentration. It can be seen that the Northeast has substantially higher vanadium concentrations than any other area of the United States. Over this 10-year record the concentrations of vanadium decreased 74 percent, from 0.35 $\mu g/m^3$ in 1969 to 0.09 $\mu g/m^3$ in 1974, most of this drop occurring between 1971 and 1972. The slight increase apparent in the South is caused mainly by two or three stations showing relatively high readings in 1972-74; this is not characteristic of other sites in the region. For both vanadium and nickel, pronounced and regular high winter and low summer seasonal variations in both the 50th and 90th percentiles occur in the Northeast. This is shown in Figure 5-44. These variations are attributed to the metal contents in the fuels used for space heating. The decrease in the 50th and 90th percentiles of these two metals reflects the decrease in the sulfur content in petroleum used in this area. This decrease is exemplified by the approximately 70 percent decrease in the sulfur content of residual oil in the New York City/Westchester County area since 1979. The vanadium concentrations are shown to decrease between 70 and 80 percent over the same time period at the New York City NASN site.

Trends in the 50th percentile of the annual averages for metals associated with industrial sources in urban areas are shown in Figure 5-45. Chromium and copper concentrations remained fairly steady over the ten-year period, but, as noted before, the copper concentrations are suspect because of contamination. Iron and manganese show declines, especially during the 1970-74 period. Beryllium, cadmium, and cobalt levels were below the level of detectability for the methods used, and hence cannot be reliably reported.

5.5.5 Acidity of Atmospheric Aerosols

Along with size and chemical composition, the acidity of fine atmospheric aerosols is an important property. Measurement of acidity by titration is preferred to pH measurements (June and Scheich, 1971). Measurements to date of the strong acid content of atmospheric aerosols have indicated that it is quite variable. Around certain sources such as cement and lime kilns, the airborne particles may be basic whereas around other sources such as sulfuric acid plants and coke plants the particulate emissions may be very acid.

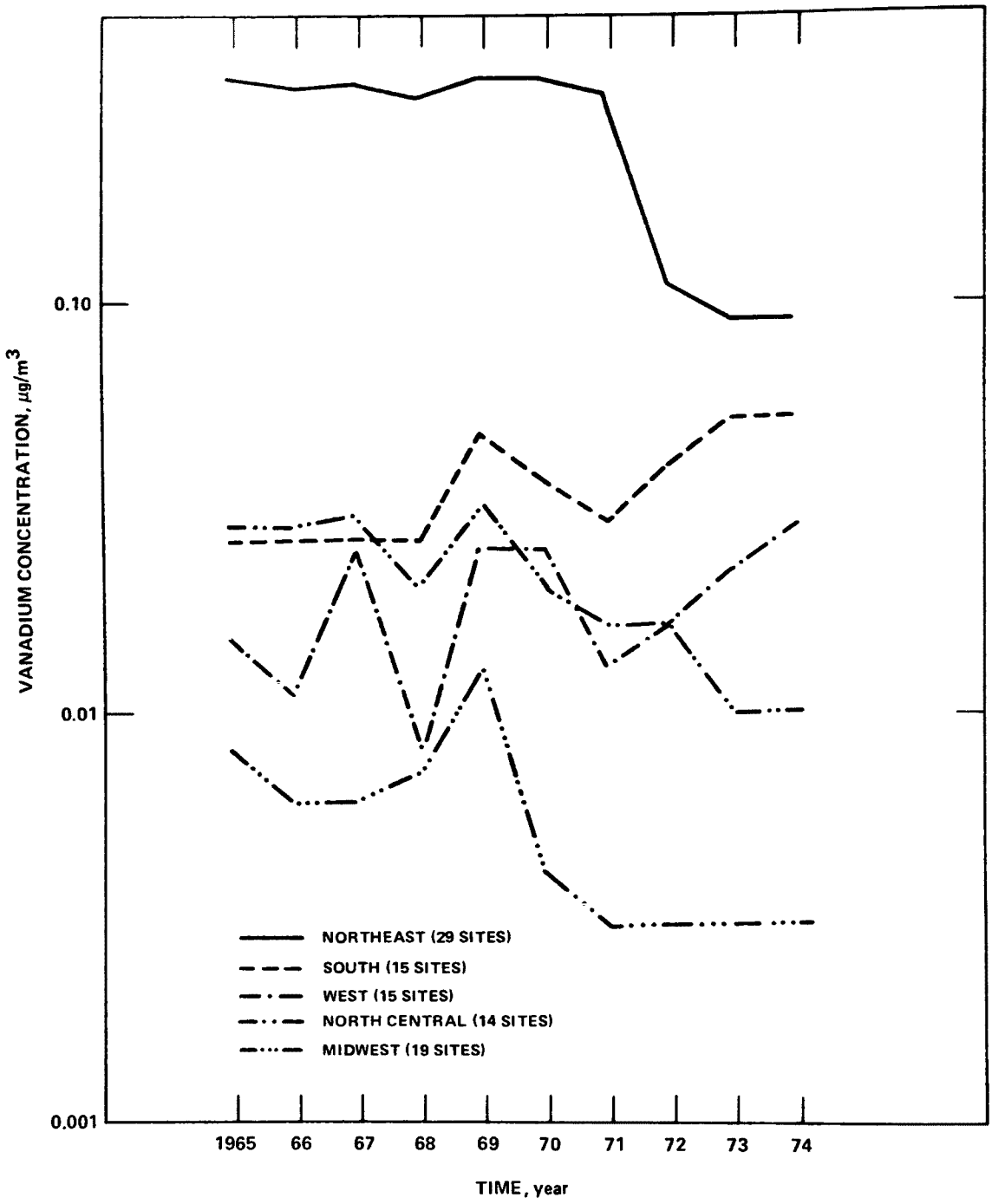

Figure 5-43. Regional trends in the 90th percentile of the annual averages for vanadium. (Δ indicates value below lower discrimination limit.)

Note: 1971-1974 90th percentile below lower discrimination limit - 0.003 = $\mu g/m^3$.

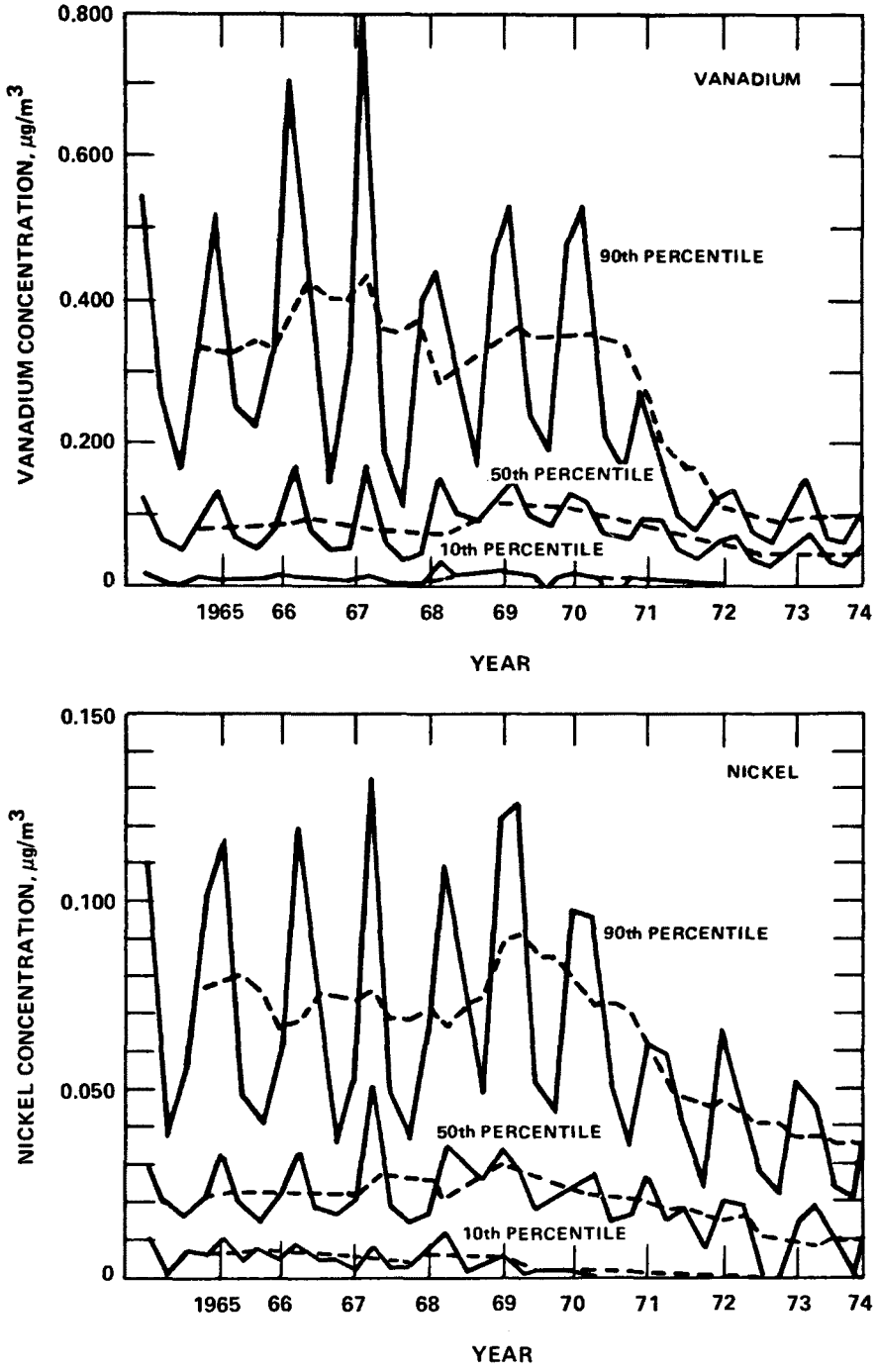

Figure 5-44. Seasonal variation in quarterly averages for nickel and vanadium at urban sites in the northeast.

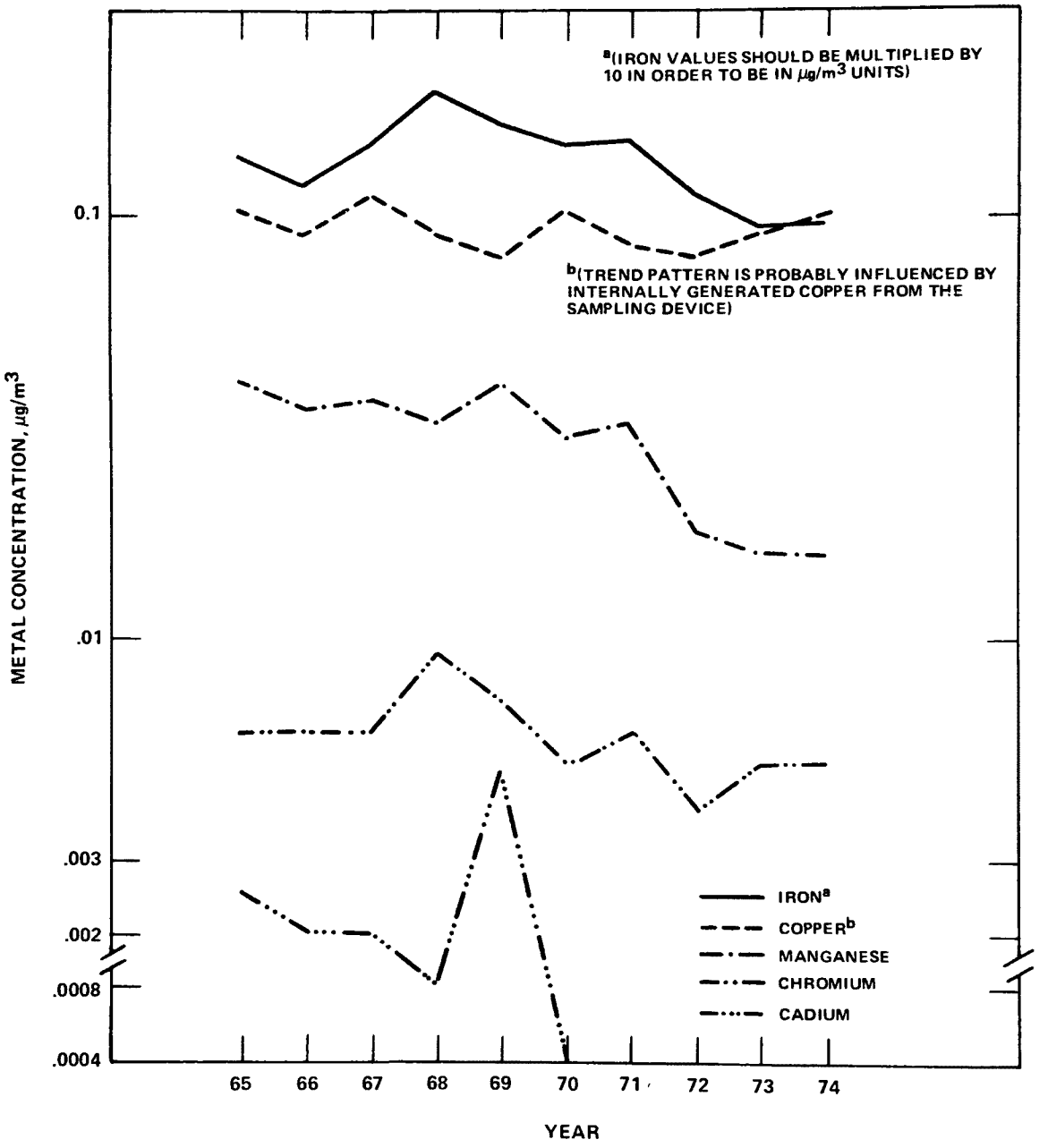

Figure 5-45. Trends in 50th percentile of annual averages for metals associated with metal industry sources at urban sites. (Δ indicates value below lower discrimination limit.)

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Weak and strong acids exist in the atmosphere in both gaseous and particulate form. Organic acids have been reported by Ketseridis et al. (1976), in rural and urban and marine atmospheres ranging between 0.3 $\mu g/m^3$ to 10 $\mu g/m^3$. Nitric acid is present in the atmosphere in concentrations ranging from < 1 to nearly 40 ppb (Spicer, 1977). Vapor-phase HCl may be present (Rahn et al., 1979) although quantitative data are sparse. These organic and inorganic gases can condense or be absorbed on particles either *in situ* or during filter sampling.

Most of the strong acid found in aerosol particles is chemically associated with the fine particulate sulfate aerosol mass. Charlson et al. (1978) and others cite numerous measurements of approximate chemical balance between ammonium cations and sulfate anions. Thus the major form of sulfate is ammonium sulfate (that is, sulfuric acid fully neutralized by ambient anmonia. However, on occasion urban and rural aerosols can be acid. Brosset et al. (1976), Brosset (1978), Hitchcock et al. (1980), Cobourn et al. (1978), Pierson et al. (1980), Lioy et al. (1980), Leaderer and Tanner (1980), Stevens et al. (1979), and Tanner et al. (1977, 1979) have all demonstrated that strong acid in the form of ammonium bisulfate and, less frequently H_2SO_4, may exist at significant levels in the ambient atmosphere. Strong acid levels equivalent to > 15 $\mu g/m^3$ of sulfuric acid have been observed for periods $\geq$ 6 hr.

In urban atmospheres sulfate anion usually appears primarily in the form of ammonium sulfate or ammonium bisulfate (NH_4^+/SO_4^{2-} molar ratios between 1 and 2) as reported by Lioy et al. (1980) for New York City, Leaderer and Tanner (1980) for New Haven and New York City, and Cobourn et al. (1978) for St. Louis. Presumably this greater extent of neutralization of urban sulfate aerosols is due to additional ammonia sources in urban areas, although it may be due in part to analytical interferences from coarse, basic particles such as resuspended cement dust present in large amounts in urban aerosols.

On the basis of recent experimental and theoretical work, Huntzicker et al. (1980) indicate that sulfate aerosol more acidic than $(NH_4)HSO_4$ should occur only when SO_2 is being oxidized rapidly and where the ratios of $[SO_2]$ to $[NH_3]$ are high or when the equilibrium vapor pressure of NH_3 over the partially-neutralized H_2SO_4 droplet exceeds the ambient NH_3 partial pressure. The situation is more complicated in ambient aerosols in which partially-ammoniated sulfate is present in mixtures with nitrate, carbonaceous and other aerosol components in solid or liquid form which may affect its neutralization rate. In particular, some data (Tanner, 1980a) suggest that the degree of mixing in the "well-mixed" boundary layer is inadequate to prevent vertical stratification of strong acid levels since ammonia is largely emitted (and nitric acid largely removed by dry deposition) at the earth's surface. Further information on the vertical distribution of strong acid and related species is needed before emission and neutralization rates may be used to predict acid levels in urban areas.

Cobourn et al. (1978) demonstrated that acid aerosol episodes could occur in urban areas as suggested by Tanner et al. (1977, 1979) and Brosset (1978). Cobourn et al. (1978), using a

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continuous sulfate monitor to distinguish sulfuric acid species from ammonium sulfate, recorded two acid aerosol episodes of three days or more duration in St. Louis, Mo. Both episodes were reported to have occurred simultaneously with a regional haze, one in July 1977, the other in February 1978. They ascribe the city occurrence of H_2SO_4 to conditions where atmospheric ammonia concentrations are exceptionally low (ammonia is temporarily depleted from the atmosphere).

The temporal variations of the acid fraction of the sulfate aerosol in St. Louis displayed patterns similar to those reported by Cunningham and Johnson (1976) in Chicago and Tanner (1980b) for the New York area. The aerosol acidity often changed drastically within a few hours. Cobourn et al. (1978) noted a diurnal pattern with highest acid levels in mid-afternoon and lowest at night. Leaderer and Tanner (1980), taking 6-hour samples, reported increased aerosol acidity in the 12 noon to 6 p.m. samples taken at High Point, New Jersey and Upton, Long Island (west and east of New York City, respectively), compared to other sampling times. At this time the relative contribution of SO_2 oxidation chemistry, temporal variations in NH_3 and SO_2 emission rates, diurnal variations in turbulent mixing rates, and varying height of the mixing layer to the diurnal patterns are not known. Dzubay (1980) observed that while sulfur and lead dominated the fine particles they were insignificant in the coarse particles. The similar composition of the rural and urban aerosols indicated that the urban was transported to the rural.

Measurements of acidity in Eastern U.S. aerosol samples indicate that strong acids are present more frequently and in larger amounts in rural and semi-rural samples than in the urban samples. Pierson et al. (1980) report 12-hour concentrations of hydrogen ions expressed as H_2SO_4 as high as 17 $\mu g/m^3$ in the Allegheny mountains of Pennsylvania in July and August 1977. It is likely that strong acid concentrations were substantially higher for periods less than 12 hours.

Lioy et al. (1980) and Leaderer et al. (1980) characterized the aerosol acidity in the region surrounding New York City during the summer of 1977. The samples taken at High Point, N.J. (west - northwest of NYC) were more acidic (17.8 $\mu g/m^3$, 6-hr average max. hydrogen ions expressed as H_2SO_4) than samples taken in New Haven, Conn. and Brookhaven, N. Y. on Long Island east of New York City.

Part of the period studied by Lioy et al. (1980) was coincident with the research of Pierson et al. (1980). Using the combined data set in conjunction with air parcel trajectories and haze analyses Lioy et al. (1980) suggested the presence of a regional acidic aerosol distribution which encompassed an area at least 200 miles in diameter during the period August 3-9, 1977.

5.6 COARSE PARTICLES IN AIR

5.6.1 Introduction

In Chapter 2 and in earlier sections of this chapter it was shown that air in cities usually contains large amounts of particles larger than 1-3 μm in size. Particles larger than

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10-20 μm tend to settle out of air suspension under the force of gravity. Yet in many areas these very large dust particles are also present in substantial quantity. The material we are describing is the dust on window ledges, the stuff which makes things dirty. In Chapter 11 you will see that that at least the smaller sizes of these coarse particles can be deposited in human airways where they might contribute to adverse effects on health. So coarse particle mass contributions are substantial and important in the context of air pollution effects.

The composition and sources of coarse particles are not as thoroughly studied as those of fine particles. One reason is they are more complex. For example, it is possible to recognize dozens of particle types in ambient air samples; these range from soil particles, limestone road aggregate, flyash and oil soot to cooking oil droplets, pollen, wood ashes and even instant coffee (McCrone, 1968; Draftz and Severin, 1980). Man's industry and activity stirs up dust, quite a lot of dust in arid climates. Unfortunately, the chemical composition of many kinds of coarse particles can be very similar, at least as determined by elemental analysis. Consequently, much of the evidence on large particle composition has been attained from deductions based on microscopical examination.

5.6.2 Elemental Analysis of Coarse Particles

Measurable elements which constitute the major portion of coarse particle mass in cities are silicon, aluminum, calcium, and iron (Akselsson et al., 1975; Lewis and Macias, 1980; Camp et al., 1978; Stevens et al., 1980; Dzubay, 1980; Stevens et al., 1978; Cahill et al., 1977; Hardy, 1979; Trijonis et al., 1980). Although these elements do exist in the fine fraction to a minor degree, they are everywhere substantially enriched in the coarse fraction.

Occurrence of some elements in coarse particles is very much time and place dependent, though, and Table 5-20 shows some data illustrative of this point. There appear to be substantial differences across the country in the fraction of these elements occurring in the coarse particles. The presence of local sources dominates both the mass and composition of coarse particles. However, Cooper and Watson (1980) have graphically demonstrated the similarity in elemental distribution for a variety of coarse particle sources as Figure 5-46 shows. Here, the most that can be said is that rock grinding operations produce remarkable similar coarse particle elemental compositions, whether the mechanical action is intentional or incidental to other activities. Cement dust and limestones (not surprisingly) also have similar elemental composition (Draftz, 1979).

Even greater evidence of localized influence on coarse particle concentrations can be seen with other elements. In the Smoky Mountains, titanium and chlorine are greatly enriched in the coarse particles (Stevens et al., 1980) while in St. Louis, titanium is mainly a fine particle component and chlorine is about evenly distributed between coarse and fine particles (Stevens et al., 1978; Akselsson et al., 1975). In the case of titanium the presence of a large coal-burning power plant plume over the city greatly influenced the fine particle titanium (Winchester et al., 1980). Chlorine appears to have its origins in fine automotive

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TABLE 5-20. COARSE PARTICLE SILICON, ALUMINUM, CALCIUM, AND IRON

Location	Dates	μg/m^3					coarse/fine mass ratios				Reference
		Coarse Mass	Si	Al	Ca	Fe	Si	Al	Ca	Fe	
Charleston, WV	08/25 - 9/14/76	27.1	2.8	1.1	0.96	0.59	6.8	15	9.7	4	Lewis and Macias, 1980
	05/11 - 05/19/77	43	7.7	NA	2.2	1.4	7	NA	7.4	4	Camp et al., 1978
Smoky Mountains, TN	09/21 - 09/26/78	5.6	0.50	0.20	0.32	0.12	15	10	20	4	Stevens et al., 1980
New York, NY	02/77	42.6	2.0	0.84	1.15	0.96	5.6	6.5	3.2	2.5	Stevens et al., 1978
Philadelphia, PA	03/77	17.5	1.8	0.64	0.94	0.69	7	13	6	3.2	Stevens et al., 1978
St Louis, MO	12/75	NA	4.3	8.7	1.9	1.0	10	4.4	16	3	Stevens et al., 1978
Portland, OR	02/77	27.6	2.8	1.2	0.76	0.95	31	5.6	11	5.0	Stevens et al., 1978
Glendora, CA	03/77	NA	1.0	0.3	0.44	0.36	5.3	>6	4.5	3	Stevens et al., 1978
St. Louis, MO	08/- 09/76	28.0	4.5	1.2	2.8	1.2	10	6	21	4.4	Dzubay, 1980

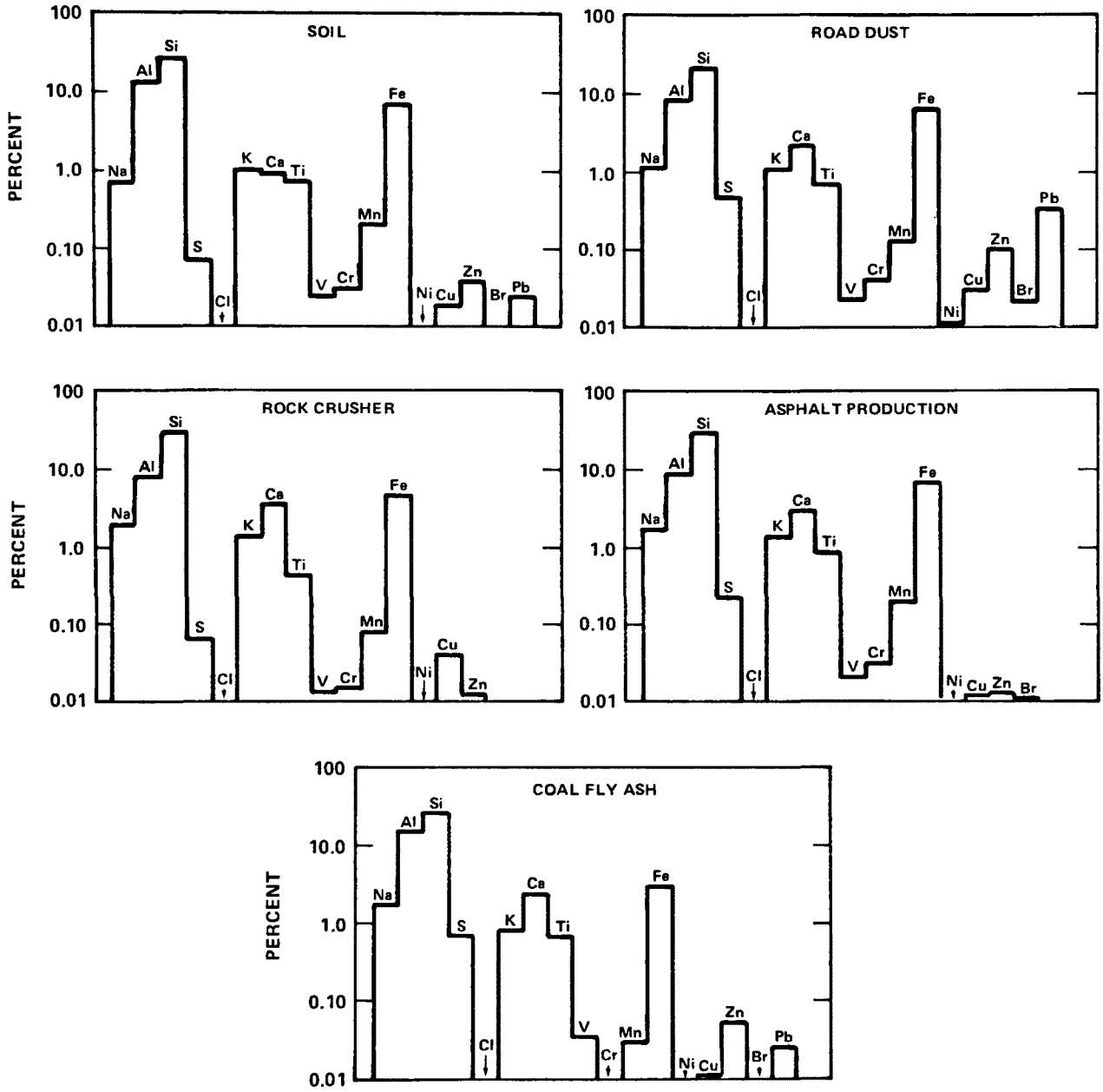

Figure 5-46. Elemental composition of some coarse particle components.

Source: Cooper and Watson (1980).

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particles at inland sites (Winchester et al., 1980) but in coarse sea-salt particles near the coast (Hardy, 1979; Draftz, 1979).

Organics and carbonates sometimes can be found in substantial quantities in coarse aerosols. For example, De Wiest (1978) found 30-50 percent of extractable organics in 2-10 μm particles. Lewis and Macias (1980) found 40 percent of the carbon (presumable mostly organ ics) in dichotomous coarse fractions in Charleston, WV, while Stevens et al. (1980) found about one third of the organics in the coarse fraction in the Smokey Mountains. Mueller et al. (1970) was able to differentiate between carbonates and elemental carbon by acid evolution of CO_2 but this technique, unfortunately, has not been applied to coarse particle analysis. Considering that calcium carbonate has often been found as a major component of urban coarse particle samples (Graf et al., 1977; Draftz, 1979), it is surprising that direct analysis for carbonate has not been reported.

As mentioned previously, most water-soluble inorganic ions are found in fine fractions.

5.6.3 Evidence from Microscopical Evaluation of Coarse Particles

Efforts to understand the importance of coarse particles in air have been hampered by the inability of simple chemical analyses (so very successful with fine particles) to reveal much of their nature. However, estimates of mass balances have suggested for a long time that these locally-generated coarse particles must constitute a substantial part of the suspended particle burden.

As an example, the most recent data from the Environmental Protection Agency network of dichotomous samplers and hi-vols could be interpreted as demonstrating significant amounts of particles greater than 15 μm in the air if the difference between D_{total} and TSP is taken as representing super-coarse particles. Table 5-21 displays some of these data for selected sites for illustrative purposes. It is clear that most sites have two thirds or more of the TSP in coarse and super-coarse particles. For the more arid and dusty parts of the country, rough estimates of this kind and common sense have suggested to pollution control officials that TSP must be dominated by locally generated coarse particles.

Since these larger objects can be readily inspected with an optical microscope, a substantial body of information has been accumulated by visually inspecting particle samples, such as hi-vol filters or impactor stages. The largest of these studies involved evaluation of 300 filters from 14 U.S. cities (Bradway and Record, 1976). Table 5-22 presents composite analyses for all filters from each of the cities. A wide variation was found in these filters ranging from virtually all dust in Denver and Oklahoma City to mostly dust with considerable fly ash and soot in most of the industrialized cities. Chattanooga was anomolous in that extremely large amounts of plant materials were found, including pollen, fibers, fragments of leaves and other tissues.

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TABLE 5-21. RELATIVE AMOUNTS OF FINE, COARSE, AND SUPER-COARSE PARTICLES AT SELECTED SITES

	Weight percent		
	Fine <2.5 μm	Coarse 2.5<cut>15	Super-coarse >15μm
Phoenix, AZ	34	6	60
El Paso, TX	16	51	33
Dallas, TX	26	10	64
Portland, OR	32	64	4
Los Angeles, CA	36	31	33
Akron OH	49	26	25
Philadelphia, PA	51	32	17
Hartford, CN	34	32	34

Note: The term 'super-coarse' refers to the difference between the total dichotomous sample concentration and the Hi-Vol TSP concentration.

Similar investigations were combined with emissions inventory, modelling, and control studies in Phoenix, Arizona, in 1977 (Richard et al., 1977, 1977a,b,c; Graf et al., 1977). In that city 90 percent of the TSP was found to be mineral dust apparently entrained in air by automotive traffic over 1100 miles of unpaved roads in the area and by intense construction activities in that rapidly growing desert city. Suck et al. (1978, 1979) found through meteorological modeling that very little motion of this coarse particulate matter occurs in the wind. Since wind velocities are characteristically low, agricultural influences are minor and coarse particles stay more or less where they are generated.

Microscopic evaluations of Miami and St. Louis particles have been conducted both on total filter samples and on impactor plates (Draftz, 1978, 1979; Draftz and Severin, 1980). In Miami calcite (calcium carbonate) was the principle component of the coarse particles. There was evidence that a small part of the calcite was recrystallized from ocean spray. However, most of the calcite appeared to be roadway aggregate suspended in the air. There were also significant quantities of halite (NaCl) and of other trace elements characteristic of sea salt.

The general picture from these studies is that coarse particles are contributed from numerous local sources and vary dramatically from place to place. It is likely that dust and

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TABLE 5-22. 14-CITY STUDY - MICROSCOPICAL IDENTIFICATION OF COARSE PARTICLES

Location	Wt. % of Component			
	Minerals	Combustion products	Biological material	Miscellaneous (rubber tire debris)
Oklahoma City	88	8	1	4
Denver	81	7	1	11
Miami	79	9	1	12
St. Louis	75	21	>1	4
Washington, DC	70	23	5	2
Baltimore	69	25	3	3
Birmingham	66	22	2	10
Philadelphia	64	33	1	2
Providence	64	22	1	13
Seattle	60	27	3	10
San Francisco	52	29	3	16
Cincinnati	51	44	1	4
Cleveland	51	40	1	8
Chattanooga	36	35	16	13

*
roadway aggregate suspended by traffic is a substantial source of coarse particles. But in some areas, industrialized cities especially, there is still some evidence of combustion source contributions.

5.6.4 Fugitive Dust

A variety of terms have been applied to the coarse particles suspended in the air by the action of machinery or traffic. The most common of these is fugitive dust and the actions which produce these particle emissions are frequently called "non-traditional" sources. This terminology refers to the fact that no one readily identifiable and controllable source produces stirred-up dust. Essentially all of man's motions, amplified many-fold by machinery, are responsible for the manmade component of this material.

The wind alone can be a major source when velocities are high and the soil aggregates are small. For example, Gillette (1978) has estimated soil fluxes for six test soils in a wind tunnel. He concluded that windspeed and crust play major roles in wind entrainment. A surface crust effectively eliminated fine particle entrainment and greatly reduced coarse particle entrainment.

In those areas where unpaved roads are common (e.g., the mountain states, the Southwest and the Northern Great Plains), it is clear that car and truck traffic can be a major source (See Chapter 4 and Carpenter and Weant, 1978). In large industrial plants, truck traffic over access roads can be a major source (Cowherd et al., 1979).

Wilson et al. (1979) found that car and truck traffic produced large amounts of dust on unpaved mining roads in Northeastern Minnesota. Particle sizes were mainly in the 6-30 μm range near the roadway, but large particles were found at about 1/5 the roadside level 400-500 meters downwind. There was visual evidence of dust coating roadside foliage and gusts of wind caused major short-term pulses in particle concentrations downwind of the road. Davidson and Friedlander (1978) have quantified deposition of coarse particles on Avena, the common wild-oat grass of the far west. Dry deposition on the stems of such plants was reported to be a significant removal mechanism for particles larger than about 7 μm.

Reentrainment of road dust has been found a major source of coarse particles in central business districts (CBD). In a study of several sites in Philadelphia, Record and Bradway (1978) concluded that entrainment of dust from roadways contributed the majority of street-level coarse particles and very significant levels at rooftops, 11 meters above the street. Rainfall, if there was enough of it, reduced the dust levels significantly, e.g. about 20 percent. However, attempts to flush the street with water redistributed the fine particles and increased the observed coarse particle level.

In a study of one site in Massachusetts, Record et al. (1979) found coarse particle levels highly correlated with traffic volume as shown in Figure 5-47. In this study very large contributions of roadway salt, used for winter snow control, were found in the coarse particles.

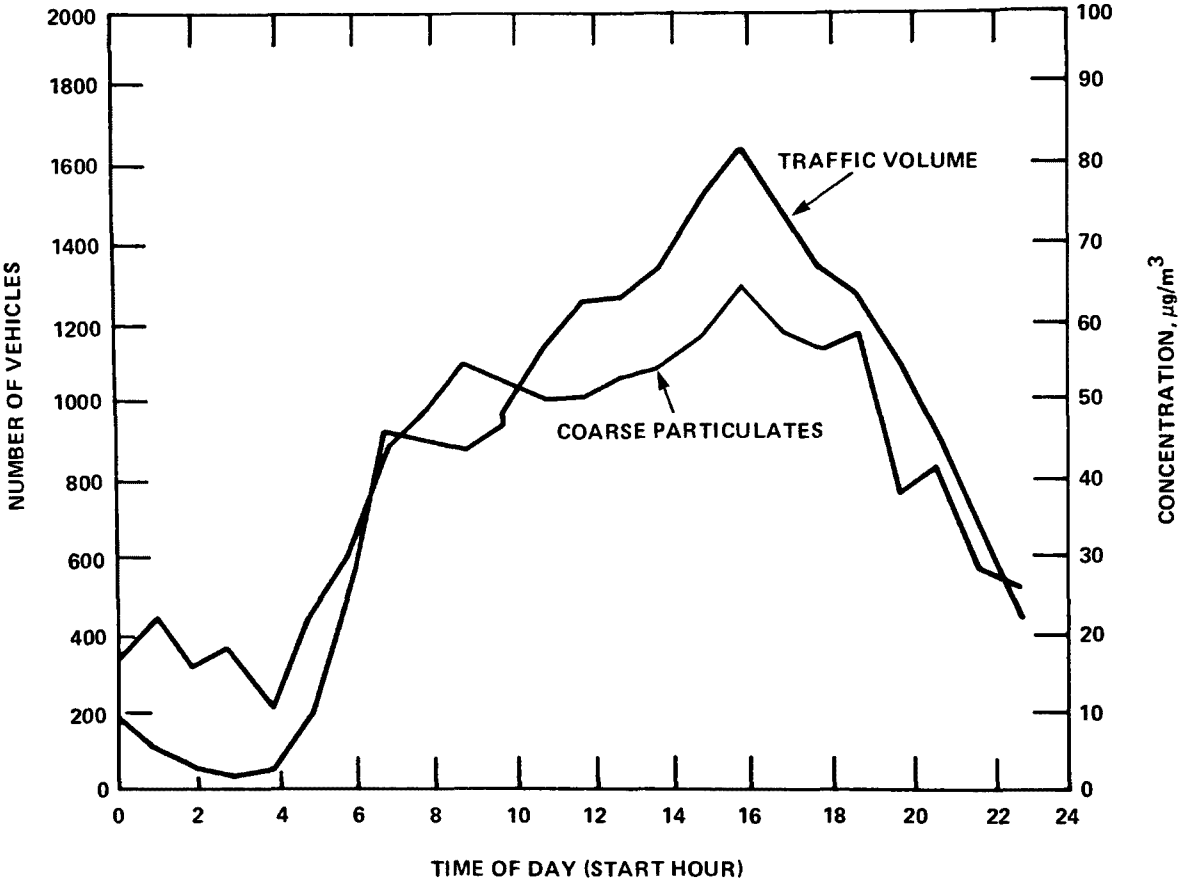

Figure 5-47. Diurnal variation of particulate concentrations and Plymouth Avenue traffic volume at Fall River, Mass., during March through June (weekdays only), shows contribution from reentrained particles.

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Yocom et al. (1981) estimated by analysis of a variety of records, the contribution of fugitive dust to area-wide particle burdens in Allegheny County, Pennsylvania. He found both industrial sources and roadways to be significant contributions, though in widely varying proportions. In the 12 study sites, roadway dust contributed from a low of 4 percent to a high of 45 percent of annual geometric mean TSP. In most sites 15 to 20 percent of these particles came from traffic. Industrial fugitive particle emissions were much more significant in this area, although the general range was similar, 5 to 40 percent of the annual level. In most sites, industrial fugitive dust contributed 20 to 30 percent of the TSP, outrunning roadway dust by about 30 percent. These two sources together with the general area background accounted for 80 to 90 percent of the TSP burden in Allegheny county.

5.6.5 Summary

The wind, traffic, construction, mining, and general industrial activity are the major causes of coarse particles suspended in the air. Dry climates, intense construction activity, lack of paving, salt from icy streets or the sea can all be contributing factors. The quantitative assignment of particular kinds of sources to the coarse and fine particle burdens has been addressed in a cursory and introductory fashion in this section. In the next part, more formal systems for this source apportionment will be addressed.

5.7 SOURCE-APPORTIONMENT OR SOURCE-RECEPTOR MODELS

For quite a long time, the goal of quantitatively assigning the contributions of particle sources to levels breathed by people or otherwise causing ill effects has been pursued. Recently, Cooper and Watson (1980) and Gordon (1980) have reviewed the current status of calculational systems or models to estimate source contributions to exposure. Cooper and Watson have described a number of these methods in a hierarchical sense and Figure 5-48 shows their analysis of related types of models capable of yielding at least semi-quantitative information. Several of the microscope-based conclusions were discussed in the previous section and the work of Yocom (1981) is basically an example of series analysis. However, the chemical mass balance and multivariate models have been used quite effectively recently and a few examples of these approaches are cited below. The results from 3 cities will be presented: St. Louis, MO; Denver, CO; and Portland, OR. These examples will help to show the contrast the fractional contribution of particular matter from different sources.

In analyzing the St. Louis Regional Air Pollution Study (RAPS) dichotomous sampler data by x-ray fluorescence, Dzubay and Stevens (1975) found 75 percent of the zinc, sulfur, bromine, arsenic, silenium, and lead occurred in the fine particulates, and at least 75 percent of the silicon, calcium, titanium, and iron in the coarse fraction (Dzubay, 1980). Using groupings of elements to represent sources, Dzubay has postulated the sources making fractional contributions to two-month summer mean concentrations at several dichotomous locations in St. Louis. Approximately 50 to 70 percent of the concentration of fine particles is made up of ammonium sulfates. The next largest identifiable source is motor vehicle

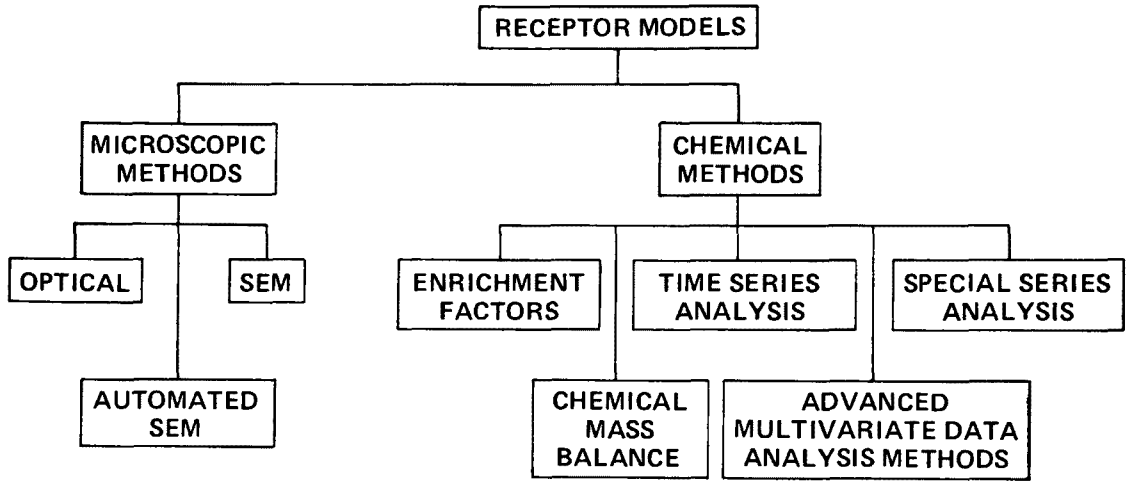

Figure 5-48. Types of receptor source apportionment models.

Source: Cooper and Watson (1980).

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emissions, followed by shale and other sources. The overwhelming majority of the ammonium sulfate is associated with the fine fraction. Similarly, in the urban core where a number of the monitors were located, the automobile component was strongly associated with the fine fraction.

Pace and Meyer (1979) separated the fractional constituents of the St.Louis dichotomous data to demonstrate the relative contributions of sources to the urban and non-urban concentrations (see Figure 5-49). As might be expected, the vehicle emission component is much smaller in the rural samples than it is in the urban samples. The sulfate fraction in the non-urban sites makes up a larger proportion of the toal fine particulate mass than does the sulfate fraction in the urban samples. The crustal component and the nondescribed components remain about the same in both sets of data. Looking at the coarse fraction, it is interesting to note that the crustal component is much larger in the urban sites than it is in the non-urban sites.

The monthly averages of size fractionated Denver aerosol mass are compared for two months, January and May, 1979 by Dzubay (1980). The sulfate component is smaller than in St. Louis and the motor vehicle component is larger (see Figure 5-50). The winter concentrations were higher for both the fine and coarse fraction. Much of this difference appears to be in the excess carbon and nitrate component. The coarse fraction contained road salt particles in the winter. In Denver samples, unlike eastern aerosol samples, the summer sulfate concentrations appear to be lower than in winter. The asterisks (*) indicate that some or all of the component could be due to excess carbon. In this case "excess carbon" is determined by the amount of carbon observed less the amount predicted. In the winter, the carbon concentration in the fine fraction was 17 $\mu g/m^3$. It was not determined for the coarse fraction. In May, the unfractionated carbon was 7.2 $\mu g/m^3$. Wood burning and auto exhaust are believed to be the important carbon sources in Denver.

Chemical-element balance techniques were applied to TSP and fine fraction aerosols collected in Portland, Oregon, in a year long study. Cooper et al. (1979) describe the experiment and results. Figure 5-51 summarized the resulting source allocation. As in several other findings, soils and road dust are important components of TSP. What the study did reveal was that burning vegetation was the second most important source, contributing almost 15 percent of the TSP mass and 20 percent of the fine particle mass. Sulfate is not the most abundant component of the fine particle mass. In fact, it is measured to be only 8 percent of the mass, fourth after auto exhaust, volatilizable carbon and aerosols from vegetation burning. The study points to the importance of residential wood burning as contributing to ambient aerosol concentrations.

Studies resolving the source components are great benefits to resolving the fractional contribution of local versus distant sources. Resolution of this question may await the application of receptor modeling to other cities and other regions of the country.

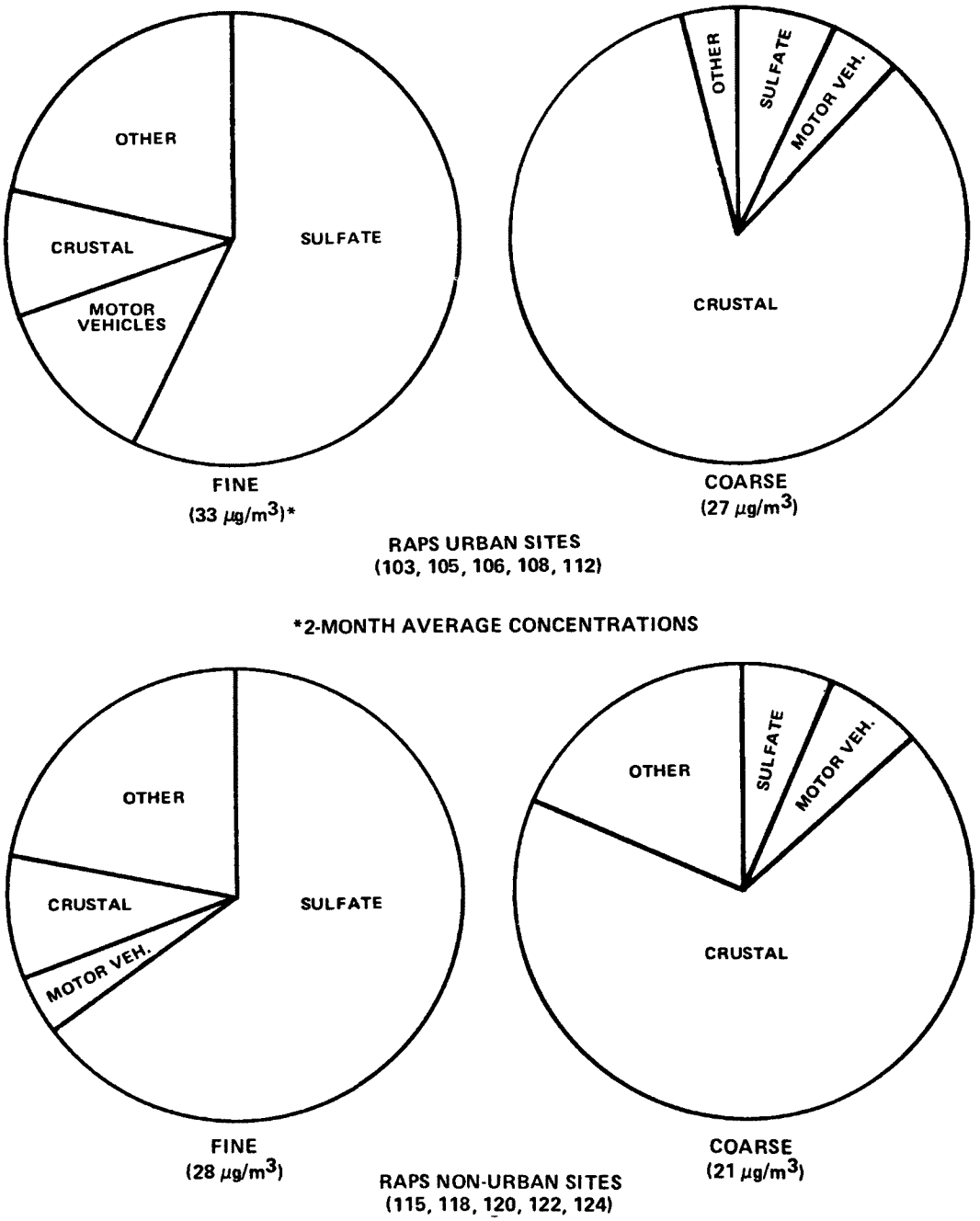

Figure 5-49. Source contributions at RAPS sites estimated by chemical element balance.

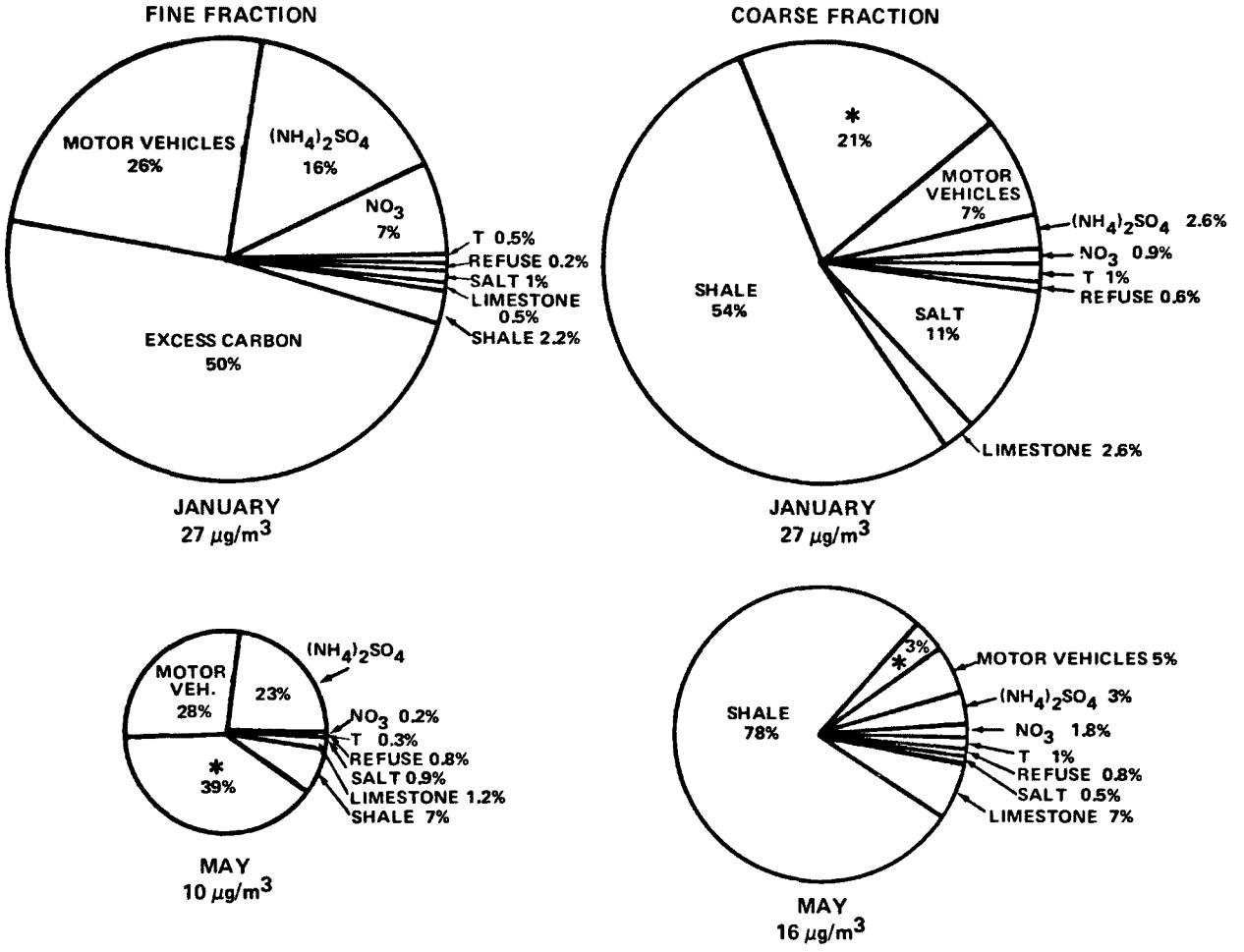

Figure 5-50. Monthly averages of size fractionated Denver aerosol mass and composition for January and May, 1979. The components labeled by (*) and by (T) are discussed in the text.

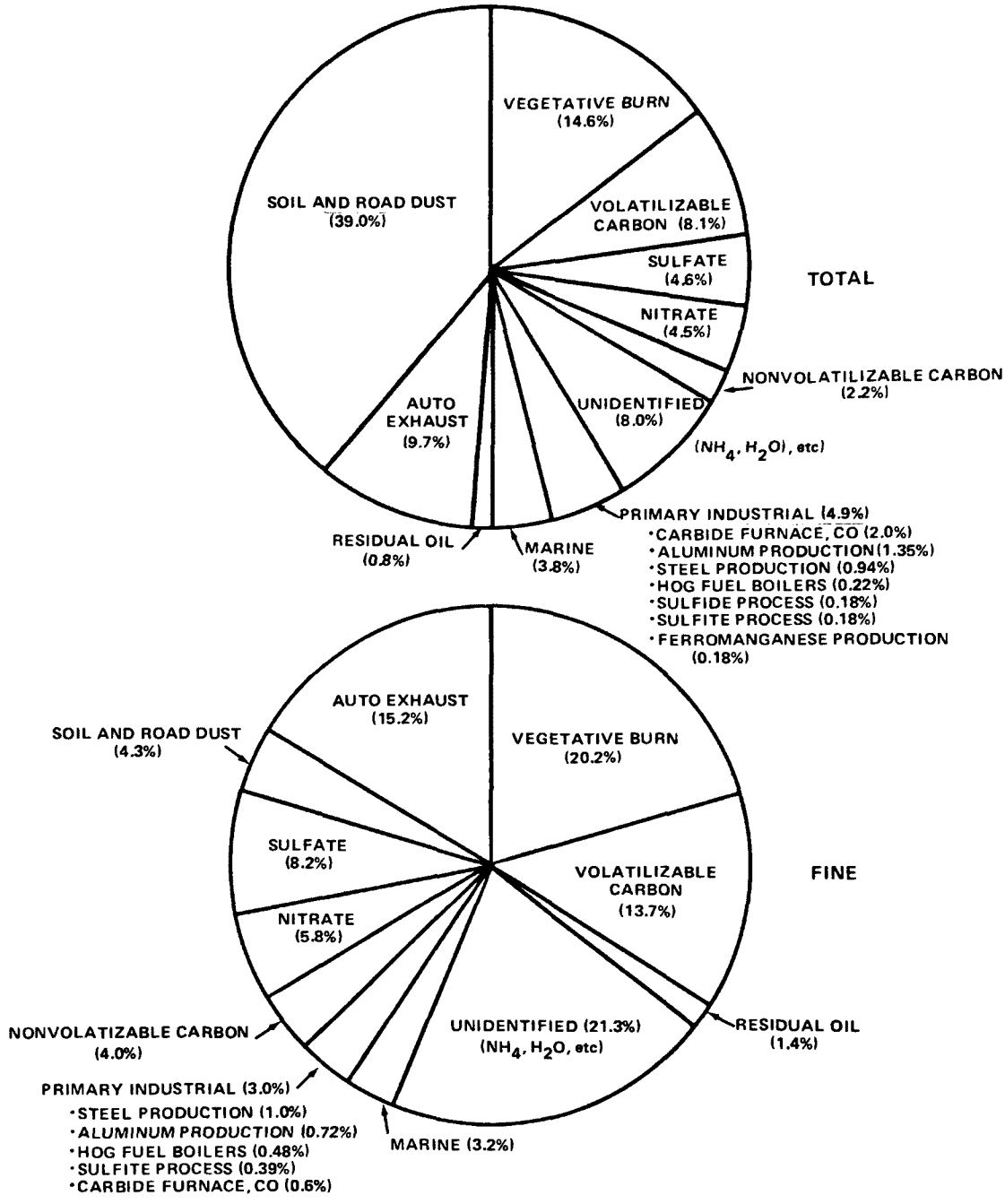

Figure 5-51. Aerosol source in downtown Portland, annual stratified arithmetic average. Does not include the 17%, on the average, of material collected with the standard hi-vol sampler which was not collected and characterized with the ERT-TSP sampler. Volatilizable and non-volatilizable carbon are operational definitions which approximately correspond to organic and elemental carbon, respectively.

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5.8 FACTORS INFLUENCING EXPOSURE

5.8.1 Introduction

To this point only outdoor concentrations of SO_2 and particles have been considered in the discussion. Outdoor concentrations are of major concern in estimating air pollution effects on visibility, ecological and materials damage. However, people spend the majority of their time inside buildings or other enclosures; they breathe mostly indoor air and, therefore, indoor concentrations dominate average exposure. To the extent that indoor concentrations are different from the outdoors, population exposures are different from those estimated by outdoor monitors.

In the United States our population is highly mobile. Many persons in their daily travel pass through areas of both high and low pollution levels within a city. Others work or play outdoors to a greater degree than the general population. Therefore, individual exposures to SO_2 and particles vary more widely than measurements from stationary outdoor monitors suggest. (Spengler, et al., 1978).

Furthermore, individual variations in respiratory anatomy, illness or smoking habits can exert important influences on the dose of a pollutant retained by individuals receiving the same exposure. For example, Cohen, et al. (1979) found that smokers retain test particles longer than non-smokers. Figure 5-52 presents the results of a study of 12 subjects, 3 of whom were smokers. Ten months following exposures to a known quantity of metallic dust, the non-smokers had cleared 85 to 95 percent of the dust from their lungs. At the same time smokers had retained about half of their original dose. Unfortunately, there are few other studies which can help in understanding these individual variations.

In this section the two major factors which influence human exposure to SO_2 and particles, indoor exposures and activity variations, are presented because they are important in understanding health effects. First the systematic differences between indoor and outdoor concentrations of SO_2, fine and coarse particles are discussed. Then the limited evidence for varying exposures of individuals depending on their activities is presented.

5.8.2 Indoor Concentrations of SO_2

Indoor concentrations of SO_2 are invariably lower than outdoors, usually by a factor of 2. (Spengler et al., 1978; Spengler et al., 1979). Since indoor sources of SO_2 are usually negligible, virtually all SO_2 indoors originated outdoors. Lower indoor concentrations are commonly attributed to SO_2 removal by contact with wall coatings, furniture, flooring and carpets, air conditioning filters and the like.

SO_2 removal inside chambers and rooms has been shown to be a function of the material present and the relative humidity. Cox and Penkett (1972) measured the decay rate of SO_2 inside containers. Reaction rates were found to be first order in SO_2, and irreversible absorption occurred on the walls. The removal rates were very sensitive to the relative humidity. As relative humidity increased, so did SO_2 removal, approaching a maximum value

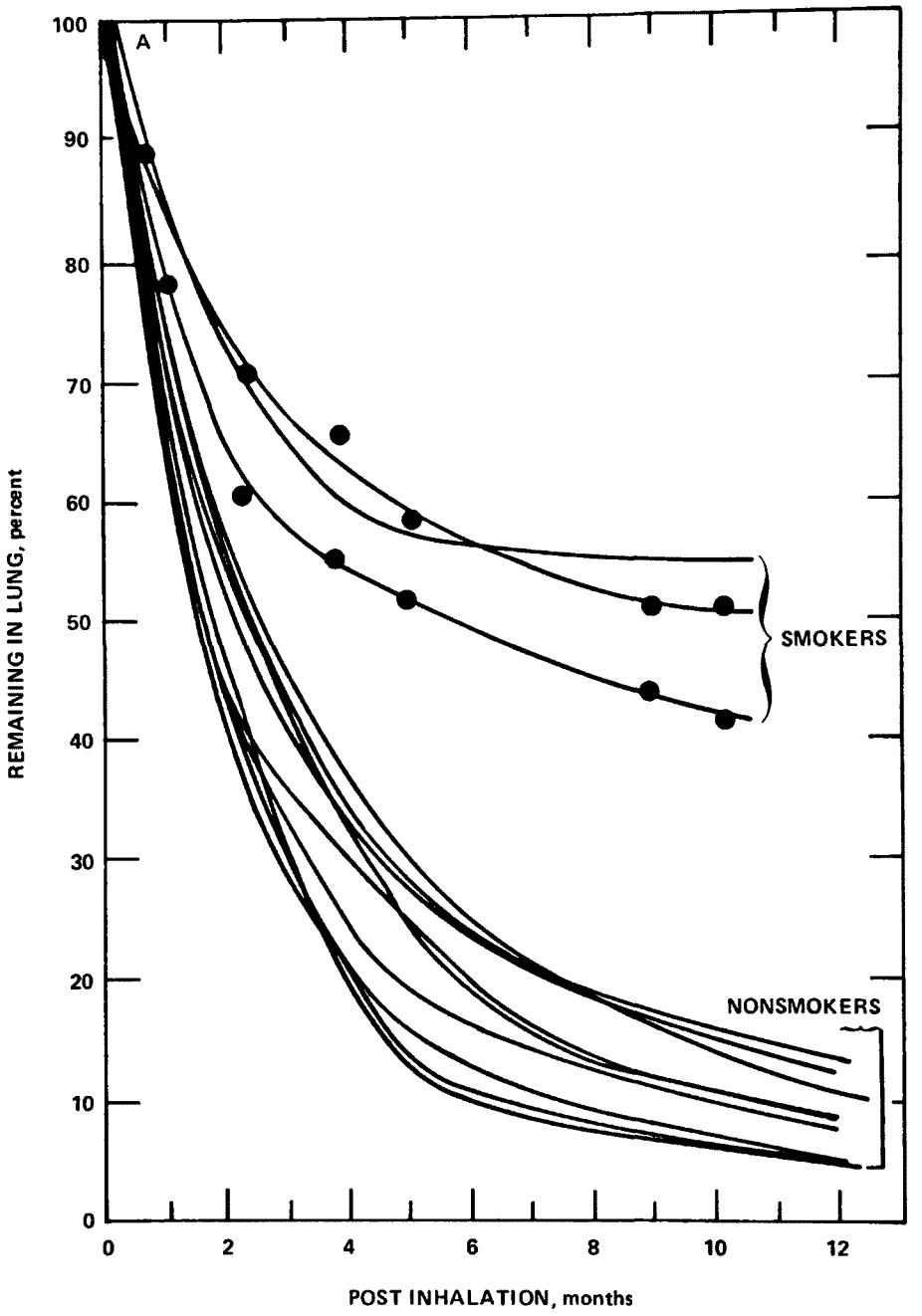

Figure 5-52. Smoking impairs long-term dust clearance from the lungs.

Source: Cohen, et al. (1979).

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slightly above 80 percent RH. (Cox and Penkett, 1972). Spedding studied SO_2 sorption by indoor surfaces (Spedding and Rowlands, 1970; Spedding, 1970; Spedding et al., 1971). The surface finish on wallpaper affected sorption rates of SO_2. Conventional wallpaper showed better uptake than PVC wallpaper. Hard woods sorbed SO_2 better and to a greater depth than did softer woods. SO_2 sorption was also measured for leather surfaces. The rate of absorption seemed to be influenced by the tanning process and the dyes used.

Walsh et al. (1977) measured sorption of SO_2 by typical indoor surfaces including wool carpets, wallpaper, and paint. Absorption rates, as measured by deposition velocities, were lower for carpets with an acidic pH than those which were either neutral or alkaline. Sorption of SO_2 appeared to be irreversible. When carpets were preexposed to an SO_2 concentration equivalent to 27 years of exposure at 30 $\mu g/m^3$, the amount of SO_2 uptake was reduced by a factor of three. Fresh emulsion paints had the highest deposition velocity or SO_2 absorption rates, and vinyl wallpaper had the lowest. It was concluded that the most effective sorbing materials likely to be present inside homes are cellulose wallpaper, furniture fabrics, and wool carpets.

Therefore, most studies report lower levels of SO_2 indoors than outdoors.

Anderson (1971) reports that indoor SO_2 concentrations average 51 percent of the outdoor concentrations over a 7.5-month period of paired 24-hr sampling inside and outside a single room. The correlation coefficient was only 0.52 (Anderson, 1971). Biersteker et al. (1965) analyzed over 800 paired samples from the living rooms and exteriors of 60 Rotterdam homes. Indoor SO_2 levels averaged 20 percent of the outdoor levels, and were lower for newer homes than older homes. This may imply longer air turnover times in the newer homes or a "fresher" surface area for SO_2 absorption (Biersteker et al., 1965). Weatherly (1966) measured SO_2 and smoke levels inside and outside a building in central London in early 1960. Indoor SO_2 levels were always lower than the corresponding ambient conditions, averaging 40 percent. Spengler et al. (1978, 1979) reported on paired SO_2 monitoring inside and outside some 75 homes in six cities. Figure 5-53 displays the annual SO_2 concentration in $\mu g/m^3$ averaged across each community's indoor/outdoor network of monitors (May 1977-April 1978). The cities are: Portage, WI; Topeka, KS; Kingston and Harriman, TN; Watertown, MA; St. Louis, MO; and Steubenville, OH. Where ambient levels were high, the indoor concentrations were 30-50 percent of the ambient levels. In Kingston, many of the indoor levels were less than the minimal detectable level and were averaged in as zeros. This was not done for Portage and Topeka, where ambient levels were very low; hence the indoor SO_2 levels in these cities appear to be reduced by only 20 percent of the outdoor concentrations.

The seasonal indoor/outdoor pattern for each city depends on the SO_2 sources in each city and the use of air conditioning. These differences can be seen by comparing the monthly mean indoor and outdoor SO_2 concentrations for Watertown and Steubenville, as shown in Figures 5-54 and 5-55. In Watertown, SO_2 is primarily derived from sulfur-laden fuels. The ambient levels

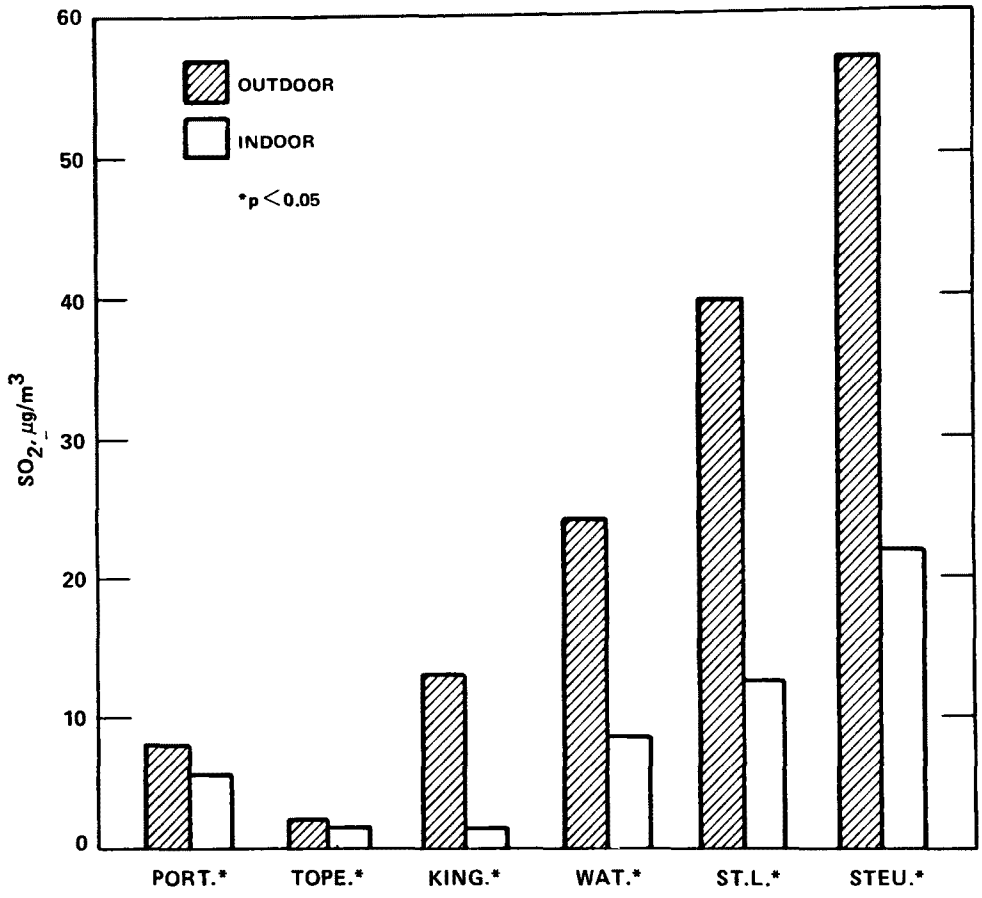

Figure 5-53. Annual sulfur dioxide concentrations averaged across each community's indoor and outdoor network (May 1977 – April 1978).

Source: Spengler et al., 1979.

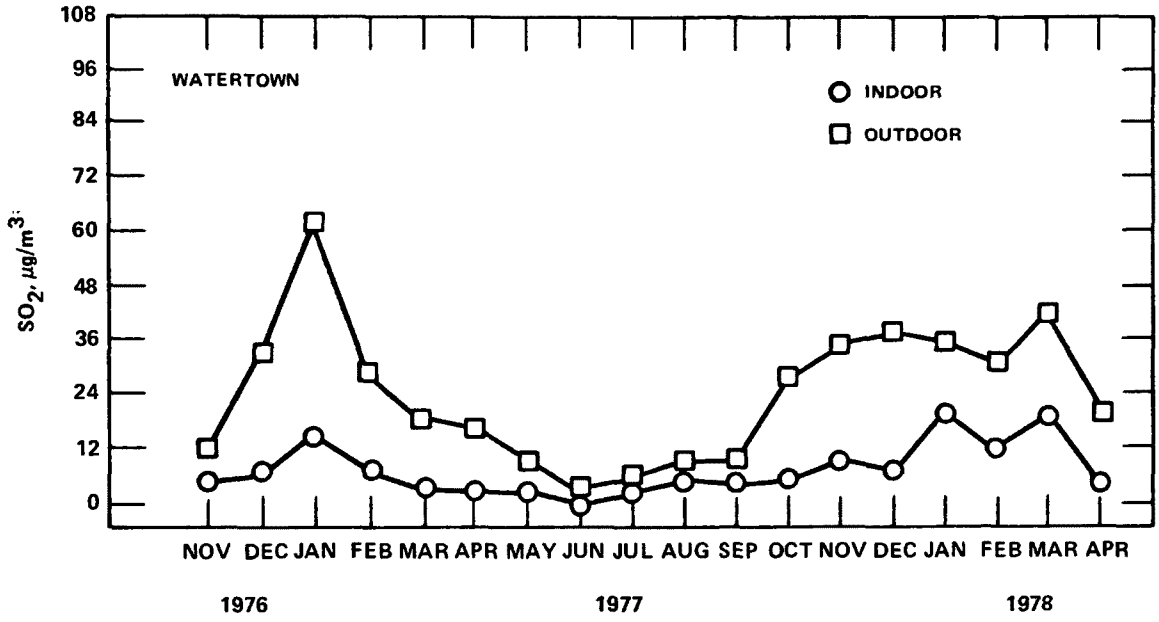

Figure 5-54. Monthly mean SO_2 concentrations averaged across Watertown's indoor and outdoor network (November 1976 – April 1978).

Source: Spengler et al. (1980).

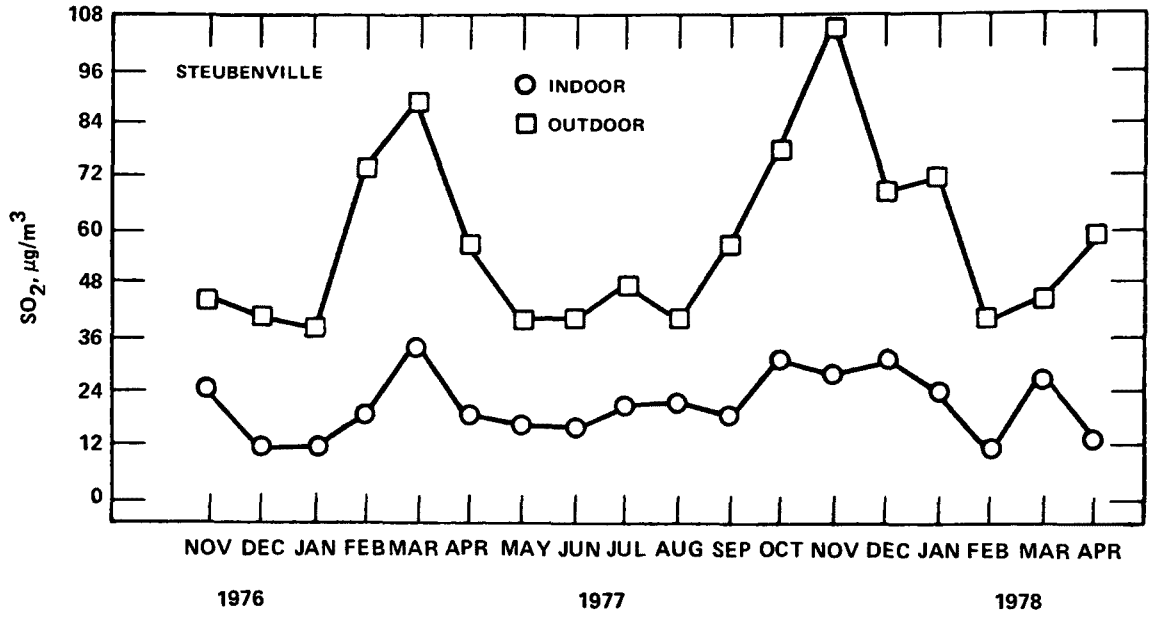

Figure 5-55. Monthly mean SO_2 concentrations averaged across Steubenville's indoor and outdoor network (November 1976 – April 1978).

Source: Spengler (1980).

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rise in the winter as more residual and distillate oil is used for space heating. The indoor/outdoor ratios become small because homes are sealed more tightly. In the summer, ambient levels decrease, but the indoor/outdoor ratio approaches unity because of increased ventilation. In Steubenville, the summer SO_2 levels are not substantially reduced from winter values, since residential and commercial space heating is not the primary source of SO_2 in this area. Yet the reduced indoor levels continue since more air conditioning is used in Steubenville (50 percent of homes samples). Even in the non-air-conditioned homes, summer levels are reduced by 30 to 40 percent.

While most information supports the idea of lower indoor SO_2 concentrations, exceptions are known. Yocom et al. (1971) found one home, heated by a leaky coal furnace, in which the indoor SO_2 level was periodically ten times the outdoor level. Bierstecker et al. (1965) have also found leaking flue gas contributions indoors.

However, the principal body of evidence suggests that indoor exposures are about half that found outdoors. Consequently, highest exposure levels are likely to be incurred by people who spend time outdoors near local SO_2 sources.

5.8.3 Particle Exposures Indoors

5.8.3.1 Introduction--Available data on indoor particle levels were collected by a wide variety of measurement procedures ranging from dustfall to condensation nuclei counting. Earlier in this chapter and in chapter 3 it was noted that the various particle measurement procedures have definite particle size biases. For example, dustfall and TSP mass measurements are dominated by coarse particles while light scattering and nuclei counting, on the one hand, and smokeshade and coefficient of haze on the other are better measures of fine particles and particulate carbon mass (one fine particle component), respectively.

Evidence from this variety of techniques has produced a consistent view of indoor and outdoor particle concentrations and sources, and this view is presented below by separate consideration of coarse and fine particle studies. Table 5-23 summarizes available studies by particle measurement technique.

5.8.3.2 Coarse Particle Concentrations Indoors--Particles larger than 5 or 10 μm tend to settle from the air and two studies using dustfall collection techniques suggest these particles are greatly reduced indoors. Whitby et al. (1957) studied dustfall in offices, laboratories and homes. Average indoor dustfall was only 15 to 20 percent of the outdoor level. No significant differences were found among residential or business locations. Schoffer et al. (1972) found indoor dustfall about 1/8 outdoor values in a study of 30 residential sites in four cities. There was little correlation between indoor and outdoor levels. Dustfall was higher in homes where windows were open.

Yocom et al. (1971) studied TSP in public buildings, offices and homes using a scaled-down version of the high-volume sampler. As mentioned previously the mass of such filter samples contains both coarse and fine particle fractions. Indoor levels were about

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TABLE 5-23. SUMMARY OF INDOOR/OUTDOOR (I/O) PARTICULATE MATTER MONITORING STUDIES BY METHOD

Method	Author	Location	Building type	Number of sites	Month or season	Sampling period	Mean Indoor	Mean Outdoor	Number of samples	I/O ratio
Dustfall[a]	Whitby et al. (1957)	Minneapolis	Residential	12	Annual		0.54	2.86		0.19
			Lab & office	30			0.47	2.86		0.16
	Schaefer et al. (1972)	Chicago, Washington, Atlanta, Austin-San Antonio	Residential		Mar.-Aug.		0.44	3.48	26	0.12
Total suspended particulate mass[b]	Yocom et al. (1971)	Hartford, CT	Public	2	Summer	12 hr	59	111		0.53
					Fall	12 hr	58	119		0.49
					Winter	12 hr	63	277		0.23
			Office	2	Summer	12 hr	53	108		0.49
					Fall	12 hr	31	50		0.60
					Winter	12 hr	42	122		0.35
			Residential	2	Summer	12 hr	62	67		0.94
					Fall	12 hr	53	77		0.69
					Winter	12 hr	43	97		0.44
Smoke[b]	Whitby et al. (1957)	Minneapolis	Lab & office				42	74		0.57
			Residential				46	74		0.62
		Louisville	Lab & office				101	124		0.81
			Residential				121	124		0.98
	Goldwater et al. (1961)	New York	Lab & office	12	Feb.-Mar.		149	263	12	0.57
			Residential	18	Feb.-Mar.		164	179	18	0.91

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TABLE 5-23 (continued).

Method	Author	Location	Building type	Number of sites	Month or season	Sampling period	Mean Indoor	Mean Outdoor	Number of samples	I/O ratio
	Jacobs et al. (1962)	New York	Residential	17	Apr.-May		239	226	17	1.06
	Weatherly (1960)	London	Office	1	Jan.-Mar.	1 hr	195	205		0.95
	Biersteker et al. (1965)	Rotterdam	Residential	60	Winter	24 hr	153	184	800	0.84
	Berdyev et al. (1967)	Dushambee	Residential 1st floor	1	Summer		1270	960	8	1.32
		U.S.S.R.	Residential 2nd floor	1	Summer		660	960	9	0.60
	Anderson (1972)	Arhus, Denmark	Classroom	1	Sept.-Apr.	24 hr	27	34	150	0.81
Respirable particulates[b]	Binder et al. (1976)	Ansonia, CT	Smoking homes	11	Sept.-Dec.	24 hr	132	58	11	2.28
			Non-smoking homes	9	Sept.-Dec.	24 hr	93	58	9	1.60
Particle counts[c]	Parvis (1952)	Italy	Residential	5			45.7 1000	97.6 1036		0.47 CN 0.97 PC
	Ishido et al. (1956)	Osaka	Apartment	1	March May June Nov.	24 hr 24 hr 24 hr 24 hr	1287 978 738 --	1528 1047 752 1897		0.84 0.91 0.98 --

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TABLE 5-23 (continued).

Method	Author	Location	Building type	Number of sites	Month or season	Sampling period	Mean Indoor	Mean Outdoor	Number of samples	I/O ratio
	Ishido (1959)	Osaka	Apartment	1			706	619		1.14
			Residential	1			662	678		0.98
			Hospital	1			1611	1595		1.01
			School	1			2382	2346		1.02
	Jacobs et al. (1962)	New York	Office & lab	12			424	481		0.88
			Homes	18			705	472		1.49
	Megaw (1962)	England	Test building	1					5	0.66
	Lefcoe and Inculet (1975)		Homes (AC & ESP)	2	Annual		510[d]	227[d]		1.46
							156[e]	59[e]		2.60
Coefficient of haze[g]	Whitby et al. (1957)	Minneapolis	Residential				0.6	1.05		0.57
			Lab & office				1.0	1.05		0.95
		Louisville	Residential				2.4	2.6		0.92
			Lab & office				2.8	2.6		1.06
	Carey et al. (1958)	Cincinnati	Residential		Oct.-Dec.		2.1	3.8		0.55
	Shephard (1959)	Cincinnati	Residential	9	Jan.		2.2	2.7		0.86
				9	Feb.		2.0	2.3		0.89
				9	Mar.		1.6	1.8		0.85
				9	Apr.		1.6	1.7		0.94
					May		--	1.0		--
					June		0.8	0.9		0.88
					July		0.8	0.8		1.00
					Aug.		1.3	0.8		1.63
				9	Sept.		0.8	0.5		0.80
				9	Oct.		1.5	0.9		1.15
				9	Nov.		1.7	1.1		0.89
				9	Dec.		1.8	1.5		1.06

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TABLE 5-23 (continued).

Method	Author	Location	Building type	Number of sites	Month or season	Sampling period	Mean Indoor	Mean Outdoor	Number of samples	I/O ratio
	Yocom et al. (1971)	Hartford, CT	Public	2	Summer		0.32	0.36		0.90
					Fall		0.33	0.34		0.97
					Winter		0.36	0.51		0.69
			Office	2	Summer		0.29	0.41		0.70
					Fall		0.20	0.26		0.78
					Winter		0.37	0.54		0.88
			Homes	2	Summer		0.41	0.42		0.98
					Fall		0.28	0.30		0.93
					Winter		0.32	0.39		0.82

[a]Measured as g/m^2/month.
[b]Measured as $\mu g/m^3$.
[c]Measured as number/cm^3.
[d]Particles >0.3 μm.
[e]Particles >0.5 μm.
[f]Particles >1.0 μm.
[g]Measured as COH/000 linear ft.

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half outdoor levels on the average. In summer and fall, private homes had almost the same interior daytime TSP values as those found outside although night interior levels were much lower than outside. In the same study it was shown that indoor/outdoor ratios in air conditioned office buildings differed seasonlly. In summer and winter indoor TSP was about half the outdoor values, but in fall when increased volumes of outdoor make up air were used in air conditioning, indoor and outdoor TSP values were about equal.

Yocom et al. (1970) also obtained some cascade impactor size distributions of indoor and outdoor particles in six structures in the Hartford, Connecticut area in the fall and winter. The mass of particles larger than 2.5 μm was always greater outdoors than indoors. However, the mass of sub-2.5 μm particles was mostly greater indoors than outdoors and the indoor/outdoor ratio varied from 0.63 to 2.6. In a subsequent report, Yocom et al. (1971) reported substantially increased organic particle levels indoors, confirming similar findings by Goldwater et al. (1961). This result was attributed to smoking and cooking, indoor activities which could also increase fine particle mass.

Alzona et al. (1979) have reported elemental analyses for calcium and iron, normally coarse particle components, and for zinc, lead and bromine, components of fine particles. In these studies, an experimental room was cleared of airborne particulate matter and then allowed to come to equilibrium under controlled penetration of outdoor ambient air. Experiments were carried out with windows "cracked" open and wide open, and with windows and/or room surfaces covered with plastic sheets. Filter samples drawn throughout the experiment were analyzed by x-ray excitation for elements of known outdoor origin (Fe, Zn, Pb, Br, Ca). Within several hours, equilibrium was reached in which the indoor/outdoor ratio was typically 0.3 (see Tables 5-24 and 5-25). On the basis of the indoor/outdoor element ratios, they conclude that remaining indoors with doors and windows partially closed reduces outdoor dust exposure by two-thirds. The indoor/outdoor ratios for coarse particle components calcium and iron were lower than for the fine particle components, zinc, lead and bromine. Therefore, it appears that tracer components of coarse particles do not penetrate any of these structures as readily as the fine components.

5.8.3.3 Fine Particles Indoors--In addition to the cascade impactor studies mentioned earlier in conjunction with the coarse particle discussion, there have been several recent reports of sub-3.5 μm particle mass measurements indoors and outdoors.

Binder et al. (1976) used high volume air samplers outdoors and personal samplers equipped with a 3.5 μm cut-off device. The personal monitors were carried by school children who spent 60 to 80 percent of their time indoors. In homes where there were smokers, the indoor fine particle mass was almost twice the outdoor TSP.

Spengler and Dockery have measured indoor and outdoor levels of sub-3.5 μm particulate mass using cyclone-equipped membrane filter samplers. Six cities were studied each with 10 to 15 monitoring sites (Spengler, 1979b; Dockery and Spengler, 1979b; and Dockery, 1979). Figure

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TABLE 5-24. MEASUREMENTS IN PRINCIPAL ROOM OF STUDY

Case	Number of runs	Conditions	I/O Ca	Fe	Zn	Pb	Br
J	3	Normal	0.10	0.17	0.52	0.49	0.33
K	2	Plastic over windows	0.10	0.15	0.71	0.17	0.17
L	1	Window wide open	0.52	0.81	0.93	1.2	1.0
M	2	Window cracked open	0.20	0.16	0.69	0.55	0.53
N	6	All surfaces plastic covered	0.02	0.12	0.24	0.15	0.20
P	3	All but windows plastic covered	0.10	0.15	0.58	0.57	0.32

Source: Alzona et al. (1979).

TABLE 5-25. MEASUREMENTS IN VARIOUS CLOSED ROOMS

Case	Number of runs	Type of room	Number of windows	I/O Ca	Fe	Zn	Pb	Br
A	1	10 m^2, new univ. bldg.	0		<0.1	--	<0.1	<0.1
B	1	50 m^2, old univ. bldg.	2		0.33	--	0.25	0.43
C	1	30 m^2, bedroom, tight home	8		0.27	--	0.70	0.58
D	1	20 m^2, attic, tight home	2		0.10	0.36	0.40	0.29
E	1	20 m^2, bedroom, leaky home	2	0.05	0.33	--	0.47	0.22
F	1	Chevrolet Vega	6		0.27	--	0.41	0.36
G	1	Datsun 440	6		0.09	0.21	0.12	0.24
H	2	20 m^2, old chem. lab	(3)	0.08	0.13	0.37	0.31	0.25
I	2	20 m^2, new univ. bldg.	3	0.15	0.54	0.55	0.47	0.58
J	3	12 m^2, old univ. bldg.	(3)	0.10	0.17	0.52	0.49	0.33
Average (except A)				0.10	0.24	0.41	0.42	0.36

Source: Alzona et al. (1979).

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5-56 presents annual average values for all sites in the six cities. In all cities except Steubenville, Ohio, the indoor fine particle level was higher than outdoors. Steubenville, and industrialized community, also had the highest annual average outdoor level. Table 5-26 presents arithmetic averages for all homes in this study stratified by numbers of smokers in the household (Dockery, 1979). It is apparent that in the absence of smoking, indoor and outdoor levels of fine particle mass are almost the same. However, smoking contributes very significantly to indoor levels. With two or more smokers in the household, indoor fine particle mass is about three times outdoor levels. Figure 5-57 presents monthly values for fine particle mass for all sites stratified by smoking. The monthly trends for smoking households are consistently higher than for non-smokers over a period of more than two years. Dockery (1979) has calculated that a one pack/day smoker contributes about 18 $\mu g/m^3$ to inside fine particle moss, and this level is increased by the use of air conditioning, presumably because of recirculation, to 43 $\mu g/m^3$.

TABLE 5-26. RESPIRABLE PARTICULATE CONCENTRATIONS OUTDOORS AND INDOORS BY AMOUNT OF SMOKING[a]

Location	Number of homes	Number of samples	Mean concentration, $\mu g/m^3$	Standard deviation of home means
Outdoor	74	2598	22.3	12.7
Indoor, no smokers	38	1328	24.0	11.4
Indoor, 1 smoker	22	712	42.8	22.2
Indoor, 2+ smokers	9	323	74.5	37.9

[a]Data averaged across network of samples in six communities for 1977.

Dockery and Spengler (1979) have also reported that indoor sulfate (a fine particle component) levels are nearly the same as outdoor except that gas cooking stoves can increase levels by about 1 $\mu g/m^3$. Yocom et al. (1971) have also shown that lead indoor/outdoor ratios are greater than TSP ratios. Taken with the previously mentioned Alzona (1979) study, it appears that most fine particle components analyzed are found in high proportion indoors.

A number of studies have reported indoor measurements of smoke shade or coefficient of haze, both estimates of fine particle carbon. Whitby et al. (1957), Shephard et al. (1958), and Weatherly (1966) have all found smoke shade values inside and outside buildings to be

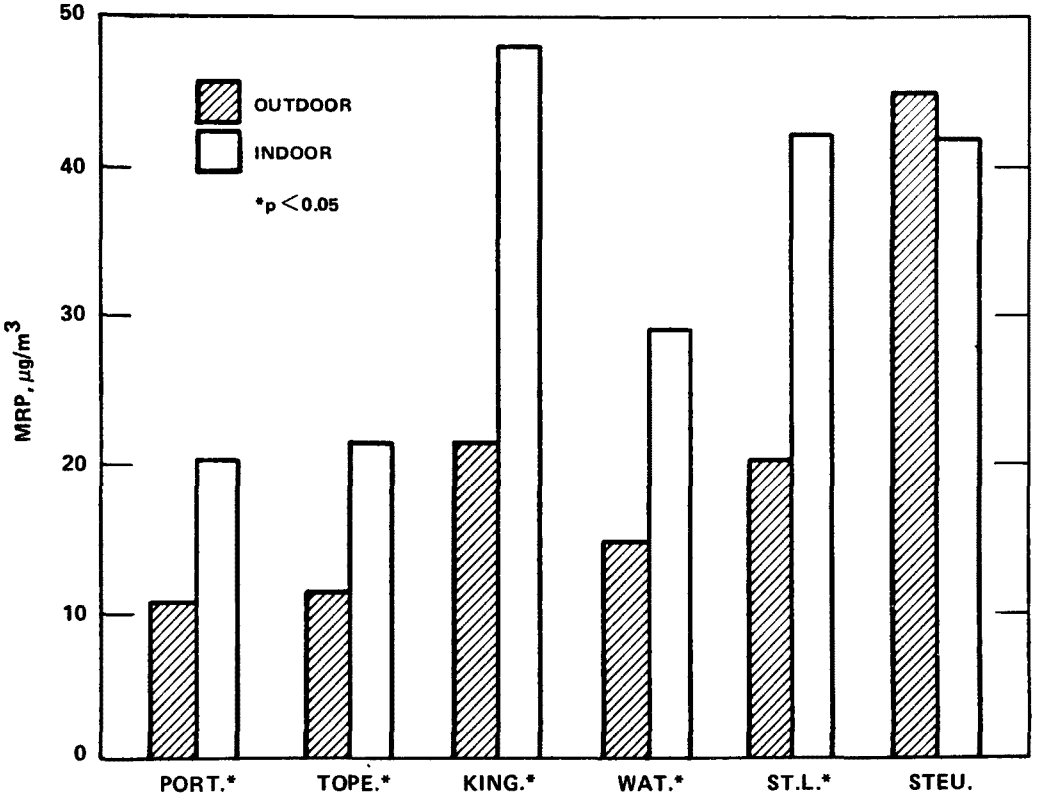

Figure 5-56. Annual respirable particulate concentrations averaged across each community's indoor and outdoor network (May 1977 – April 1978).

Source: Spengler et al. (1980).

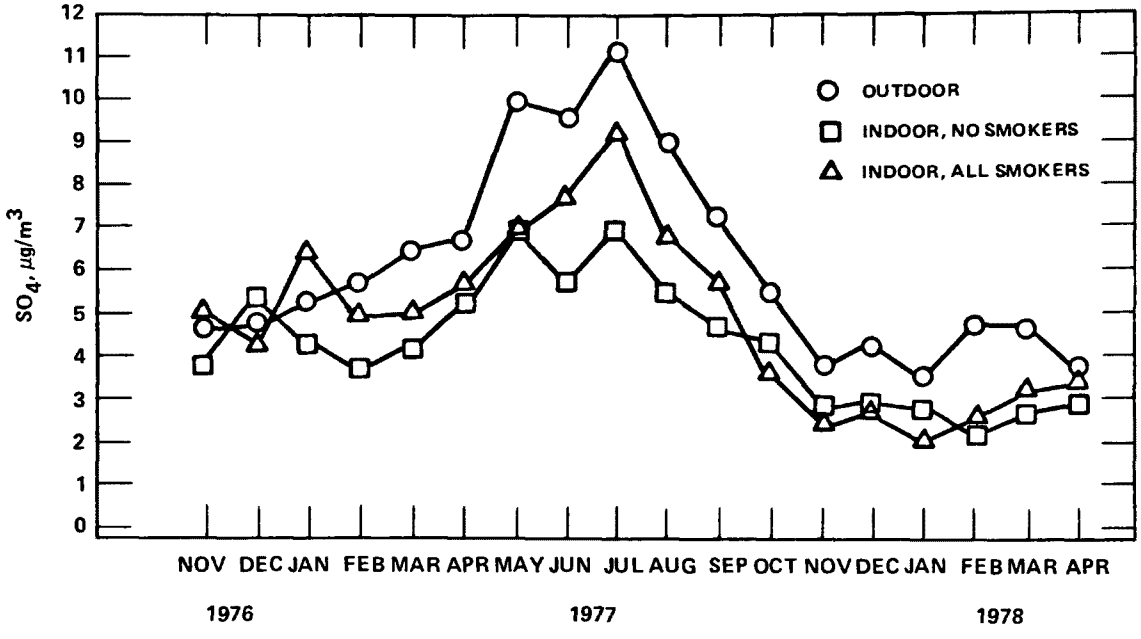

Figure 5-57. Monthly outdoor and indoor (by smoking) respirable sulfate concentrations averaged across six-city network (November 1976 – April 1978).

Source: Spengler et al. (1980).

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nearly equal. Goldwater et al. (1961) found indoor smoke about 75 percent of the outside levels in 30 New York sites, but that difference was not significant. Jacobs (1962) found no indoor/outdoor differences in a follow-up New York study. Anderson (1972) found nearly equal and highly correlated smoke values in a classroom in Denmark. Biersteker et al. (1965), on the other hand, found no correlation between indoor and outdoor smoke in a winter study of 60 homes in Rotterdam. Whitby et al. (1957) and Yocom et al. (1971) both report that indoor coefficient of haze values are much closer to outdoors than either dustfall or TSP. Apparently, the fine carbon particles measured by these techniques effectively penetrate buildings.

The similar conclusion is reached in indoor-outdoor light scattering studies. Since scattering of visible light is caused by the narrow range of particles from about 0.4 to 0.7 μm, measurements using this technique provide another index of fine particle mass. Indoor and outdoor light scattering values were found to be the same and highly correlated in Japan (Ishido, 1959; Ishido et al., 1956), in Italy (Parvis, 1952; Romagnol, 1961), and in New York (Jacobs et al., 1962).

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

5.8.4 Monitoring and Estimation of Personal Exposures

In previous sections of this chapter, the spatial and time-variations in the concentrations of SO_2 and of fine and coarse particles and their components are summarized for both outdoor and indoor exposures. However, looking forward to health effects summarized in Chapters 11-14, there is still one element of exposure remaining for discussion. In addition to the particle concentrations measured by long integrating time monitors, i.e., long-term doses of pollutants, people are exposed to short-term high concentrations. Unfortunately, sufficient data do not exist to establish the relative importance of concentration and time of exposure. There is, however, evidence (cited in Chapter 12) for gaseous SO_2 and for particles as well, that long-term exposures can cause adverse health effects. There is also evidence that a short burst of pollutant exposure can cause adverse health effects. Therefore, these peaks in exposure are likely to be important and there is some evidence that peaks occur both indoors and outdoors. For example, earlier in this chapter it was noted that high levels of SO_2 occur periodically close to intense sources. Obviously, people passing through such an area, even though they are not resident there, receive a high short-term dose. On roadways particle concentrations tend to be very high because of resuspension of road dust. Clearly, travelers experience such concentrations at least for the time they are in traffic. As pointed out earlier in this section, an individual's daily activities, the places visited, and activities in the home all play a role in that person's exposure.

For example, Spengler et al. (1980) have followed an individual's daily exposure with a portable particle monitor and correlated these measurements with activities. Figure 5-58 shows

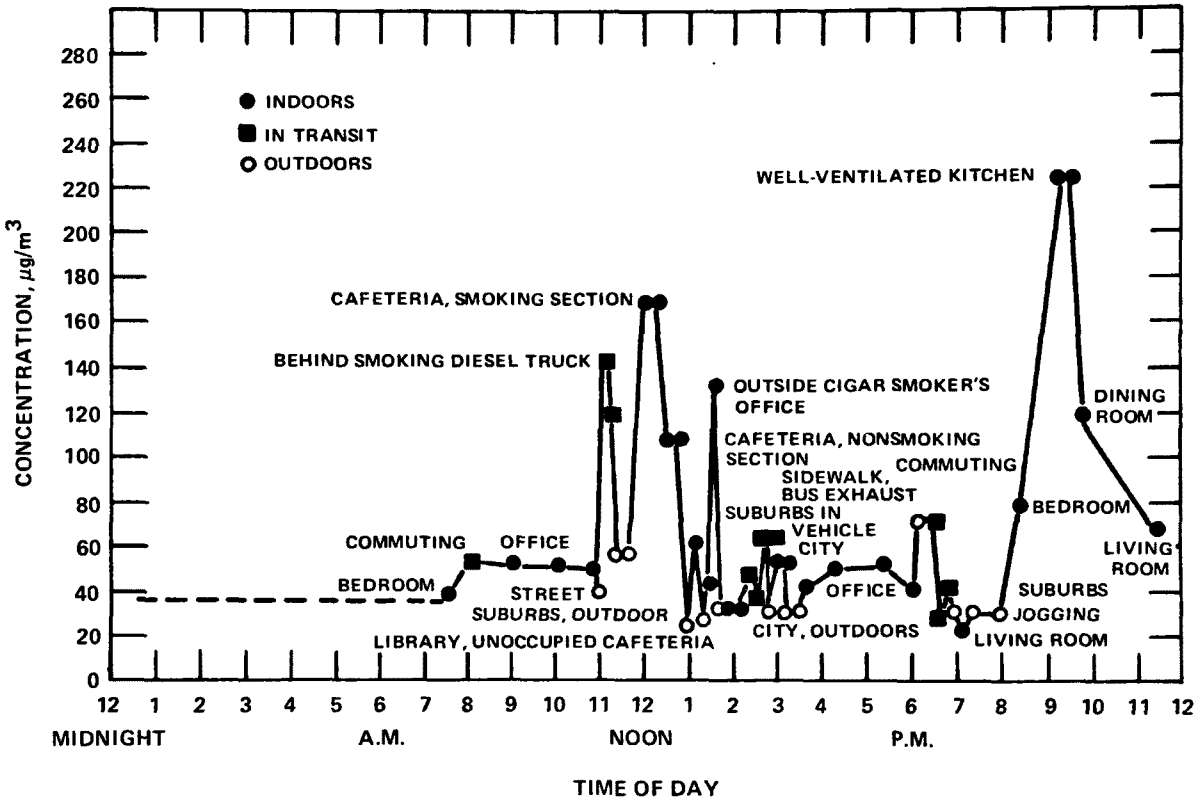

Figure 5-58. Personal exposure to respirable particles.

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time series plots of particulate material concentrations to which James Repace was exposed on October 16, 1979. Sharp peaks are evident in traffic, in indoor smoking areas and in his own home, particularly in the kitchen. Obviously, controlling outdoor air pollutant levels would have little influence on his exposure to short-term doses of particles except for roadways. There have been other recent reports of statistical studies of the relationships among personal, indoor and outdoor particle concentrations.

In a personal monitoring study designed to test the relationships between outdoor concentrations and personal exposures, and to estimate activity-concentrations, Spengler et al. (1980a) collected 12-hour respirable particulate samples for 15 days on 45 individuals in Topeka, KS. The correlations between personal and indoor concentrations and the outdoor levels were less than 0.2. Correlation of men's exposures to the indoor concentrations was 0.5 and of women's exposures to indoor concentrations was 0.7. The correlation between exposures of husbands and wives was 0.5. The mean personal concentrations were 2 and a half times the mean outdoor level. It was apparent that somewhere in the person's daily activities he/she was experiencing higher concentrations than those outside. Passive smoke exposure accounted for a significant portion of this additional exposure. Figure 5-59 plots the histograms of concentrations for both volunteers who reported no passive smoke exposure during the day and those who reported some exposure to passive smoke. The means were 20 $\mu g/m^3$ for non-smoke-exposed samples vs. 40 $\mu g/m^3$ for smoke-exposed samples.

In Figure 5-60 the daily mean concentrations for all outdoor, indoor, and personal samples are presented. There is the suggestion that the variation in outdoor concentrations causes variations in indoor and personal concentrations. However, variations in indoor concentration cause considerable variance in individual exposures.

As an alternative to direct measurement (monitoring), typical personal exposures may be estimated on the basis of information on indoor and outdoor concentrations and human activity patterns.

The exposure to particles and gases that one experiences will be ultimately determined by location and activity. Certainly, locational and activity patterns are very complex in our society. They are functions of age, sex, social, economic, and educational factors. While a limited data base exists on activity patterns within our population and on the distribution of smokers, housing stock, and various other building factors, an exhaustive discussion is not appropriate for this document.

Time budget studies of the United States population indicate that on the average, 90 percent of an individual's time is spent indoors. Between 5 and 10 percent of the time is spent in transit in a vehicle. Considering these figures, the indoor environment is very important in determining the time weighted average exposure.

However, the time weighted average is only one measure of pollution exposure. Time spent outdoors is variable. The time outdoors varies by the time of day, by time of year, between regions of the country and among different categories of people. Therefore, in the concern

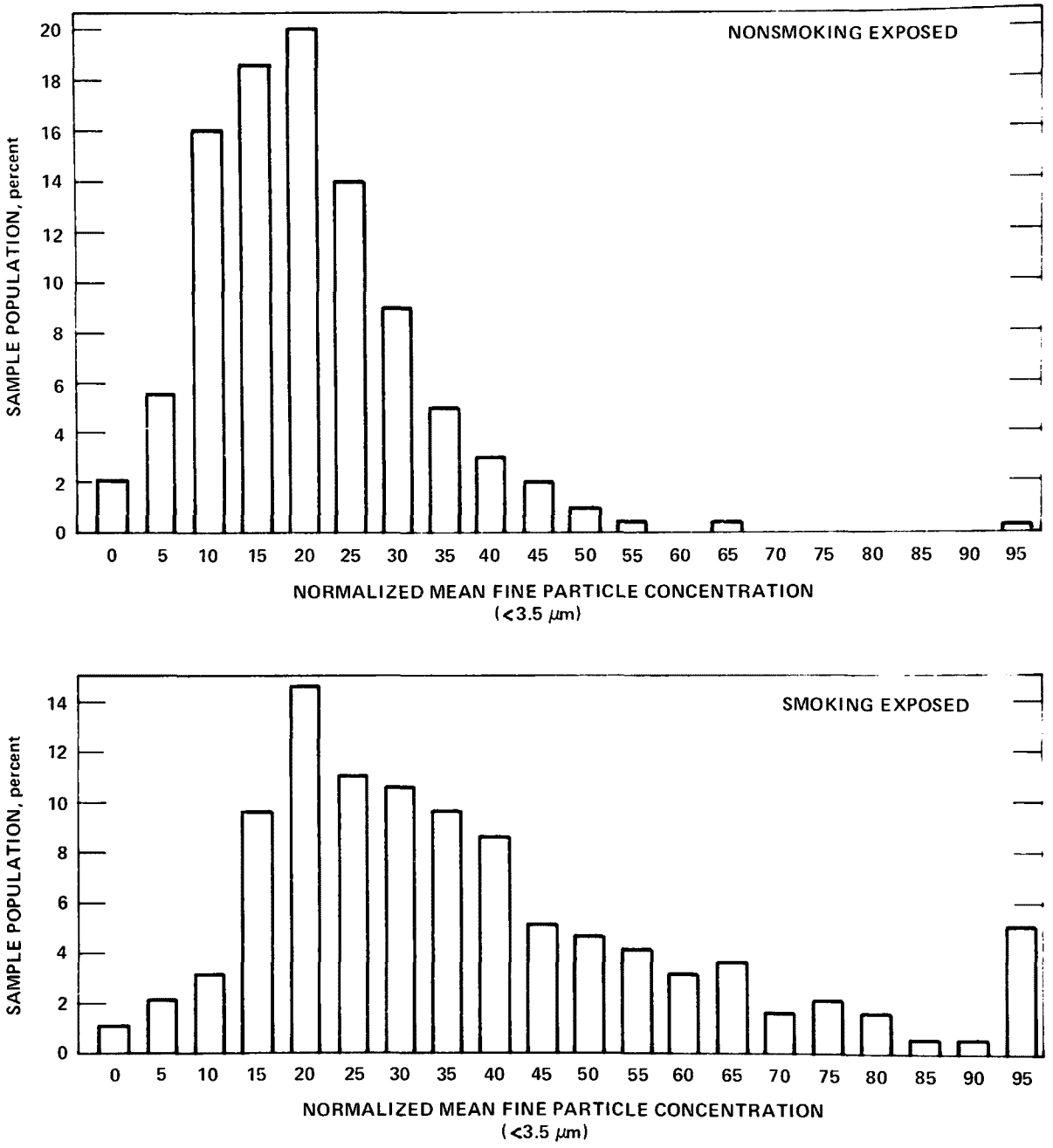

Figure 5-59. Normalized distribution of personal (12-hour) exposure samples ($\mu m/m^3$) for non-smoke exposed and smoke exposed samples.

Note: Normalized mean fine particle concentration $= \frac{\text{concentration, } \mu g/m^3}{\text{average concentration, } \mu g/m^3} \times 100$

Source: Spengler et al. (1980a).

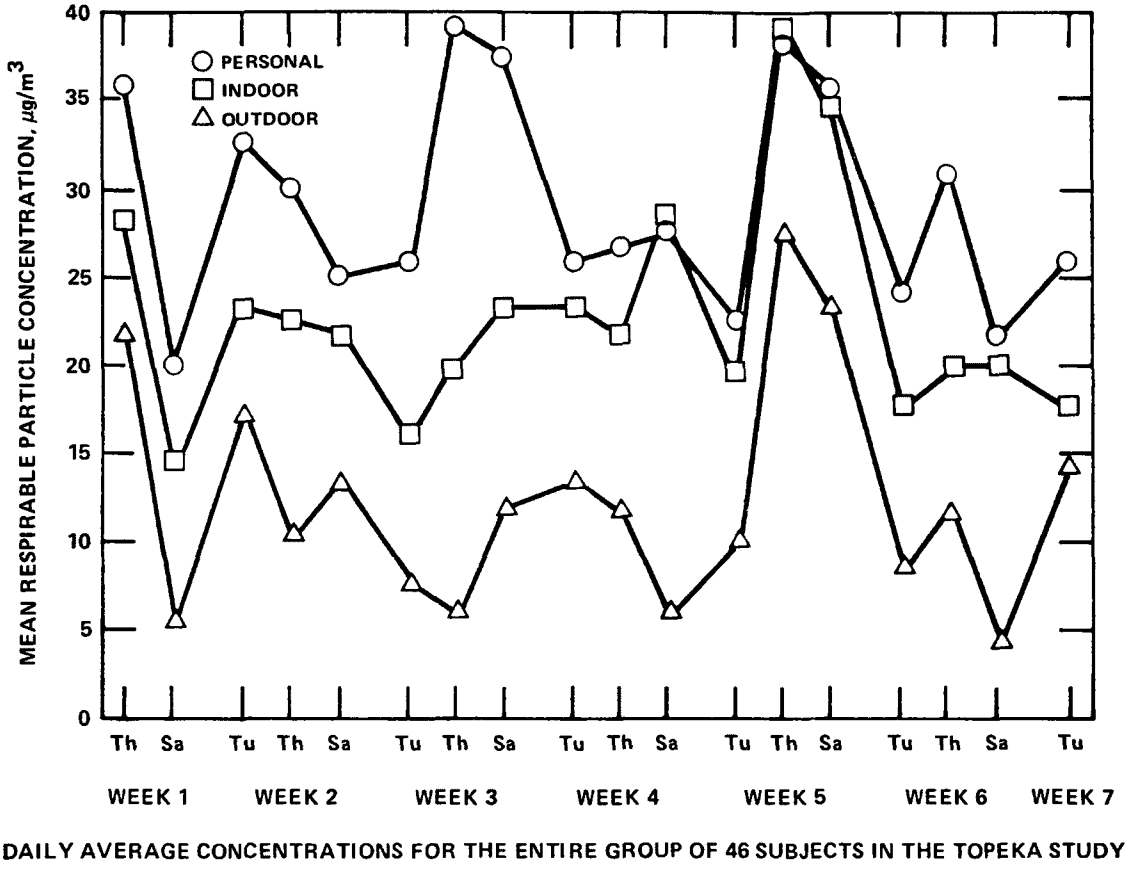

Figure 5-60. Daily mean indoor/outdoor and personal concentrations ($\mu g/m^3$) of respirable particles. Daily means averaged over 24 homes and outdoor locations and up to 46 personal samples. Samples collected during May and June 1979.

Source: Spengler et al. (1980a).

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for indoor pollution, we should not lose sight of the fact that short-term peak ambient concentration may be the important component of exposure.

Much work remains to be done on personal exposures to gases and particles. Based on current understanding, the following qualitative statements can be made:

1. Depending on spatial gradients in ambient air, personal exposures to SO_2 should be less than the outdoor concentrations.

2. Depending on activity times and building characteristics, the longer-term exposure could be less than half the ambient concentrations.

3. For estimates of personal exposure to particle mass concentration, the ambient measurement appears to be a poor predictor. While ambient concentrations exert an effect, personal activities and indoor concentrations cause personal exposures to vary substantially.

4. Tobacco smoke is an important contributor to indoor and personal exposures.

5. Personal exposures to the components of suspended particulate matter that is of outdoor origin and contained in the micron and submicron size fraction may be estimated by ambient measurements. The smaller size particles of toxic trace elements (V, Cd, Ni, Br, Se, etc.) and some organic and inorganic compounds ($SO_4^{=}$, NO_3^{-}) which are exclusively of outdoor origin penetrate the indoor environment in a predictable way. Outdoor measurements of primary and secondary fine fraction aerosols in non-industrialized communities may prove to be adequate to characterize population exposures and trends. This last statement assumes no important indoor sources for this typical outdoor component. This question certainly needs verification and quantification in field studies.

5.9 SUMMARY OF ENVIRONMENTAL CONCENTRATIONS AND EXPOSURE

The purpose of this chapter is to document the existing concentrations of sulfur oxides and particulate material in the environment. Since the damage caused by these pollutants to man and other living things and to valuable objects varies with time, place and other circumstances, a wide variety of exposure conditions are relevant for these pollutants.

Sulfur oxide concentrations in the air have been markedly reduced over the past 15 years because of fuel sulfur restrictions, control technology implementation on major sources, and redistribution of power plant exhaust to regions outside cities through the use of taller stacks. There are still some areas with very high SO_2 concentrations though, and hourly values of 4000 to 6000 $\mu g/m^3$ are rather common near large smelters. In about 100 U.S. locations, maximum hourly values above 1000 $\mu g/m^3$ are found, but much of the nation is basically in compliance with the current National Ambient Air Quality Standard for sulfur dioxide. In the last two years SO_2 has resumed an upward trend because of increasing use of high sulfur coal.

After a downward trend from 1970 to 1974, total suspended particulate material concentrations have changed very little in recent years despite major reductions in stationary source emissions inventories. Dusty arid regions of the country still have high TSP as do industrialized cities in the east and far west. Ninetieth percentile values of 24-hour TSP (the

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values which are exceeded 10 percent of the time) are above 85 $\mu g/m^3$ in every region of the country except Alaska. Regional mean TSP values range from about 50 $\mu g/m^3$ in EPA Region I to 77 $\mu g/m^3$ in EPA Region IX.

Ambient air particles exist in two distinct size ranges, fine particles below about 1 μm and coarse particles above about 3 μm. Rather little mass is in intermediate sizes. Except that both sizes are captured on filters, the two kinds have very little in common. Fine and coarse particles differ in origin, chemical composition, geographical distribution and physical behavior.

Fine particles are composed mainly of sulfate, nitrate, and ammonium ions and organic substances from atmospheric photochemical conversions, and of carbon, organics, and metallic components directly emitted from combustion sources. Sulfate in its acidic and neutral form is the principal component, often accounting for 40 percent of fine particle mass. Sulfate and nitrate ions are present in high concentrations during both summer and winter episodes over very large sections of the Eastern U.S. This area experiences 10 $\mu g/m^3$ or greater sulfate levels for one or two periods up to a month or more every year. The affected region is so large in scope that no real background levels of fine particles are available for measurement east of the Mississippi. Sulfate and fine particle levels are nearly the same in cities and in rural areas. Southern California experiences high levels of sulfate and nitrate, particularly during photochemical incidents. In that area high levels of fine organic aerosols are also found, often exceeding 100 $\mu g/m^3$.

Toxic organics and metals are mainly emitted from combustion and industrial sources and their concentrations are highest in cities. Trends in these fine particle components have been mostly down because of control measures taken, such as lead reductions in gasoline.

Coarse particles in air are stirred up by the wind and by machinery. Since these particles settle fairly rapidly, they tend to be high close to sources. In most cases the coarse particles account for 2/3 of TSP in dry regions like Phoenix, Oklahoma City, El Paso, or Denver in the summer. The overwhelming cause of high TSP is local dust, but in industrialized cities there is evidence that large contributions of soot, fly ash, and industrial fugitive emissions are also present.

Coarse particles are mainly composed of silica, calcium carbonate, clay minerals, and soot. Chemical constituents found in this fraction include the elements silicon, aluminum, potassium, calcium and iron together with other alkaline earth and transition elements. Organics are also found in coarse particles although their source is unknown.

Much of this coarse material is road dust suspended by traffic action and street levels of resuspended dust can be very high. Traffic on unpaved roadways can generate huge amounts of dust which deposits on vegetation and can be resuspended by wind action. Rain and snow cover can reduce these emissions, but one study suggests that salting of roadways can be a major source of winter TSP. Industrial fugitive emissions can be even greater sources of

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coarse particles, particularly from unpaved access roads, construction activity, rock crushing and cement manufacturing.

The problem of tracing existing levels of particles to sources is being solved in part by a number of calculational methods generally categorized as source apportionment or source-receptor models. The results from chemical element balance calculations or factor analysis are available now for several cities. Apportionments for these cities are presented as examples of results to be expected in the future by application of these powerful methods.

Although outdoor concentrations of pollutants can be measured at particular sites, our highly mobile population can be exposed to either higher or lower values than community monitors show. Indoor values of SO_2 tend to be lower than outdoor levels because walls, floors and furniture absorb SO_2. Indoor particle levels can be high because of smoking, cleaning operations, or just people's activities. Exposure of individuals to sulfur oxides and particulate material can vary more than community monitors show.

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