External Review Draft No. 2
February 1981

Draft
Do Not Quote or Cite

Air Quality Criteria for Particulate Matter and Sulfur Oxides

Volume I

NOTICE

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

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 are being 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 has been released in five volumes on a staggered schedule as the volumes were completed.

With circulation of this volume (Volume I), the release of all five volumes of this second external review draft is completed.

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 this 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, commenters 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 public comment period from March 6 to May 5, 1981, as announced in the Federal Register. There will be no extensions of this comment period, for the reasons set forth in the Federal Register, which primarily concerns the statutory deadline for completing appropriate revisions to the criteria for PM/SO_x.

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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 I contains Chapter 1 which is the Executive Summary. A Table of Contents for Volumes I, II, III, IV, and V follows.

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1. EXECUTIVE SUMMARY

1.1 INTRODUCTION

1.1.1 Legal Requirements

The purpose of this document is to present air quality criteria for particulate matter and sulfur oxides in accordance with Section 108(a)(2) of the Clean Air Act, 42 U.S.C. §7408(a)(2), which specifies that:

> "Air quality criteria for an air pollutant shall accurately reflect the latest scientific knowledge useful in indicating the kind and extent of all identifiable effects on public health or welfare which may be expected from the presence of such pollutant in the ambient air, in varying quantities. The criteria for an air pollutant, to the extent practicable, shall include information on--
>
> (A) those variable factors (including atmospheric conditions) which of themselves or in combination with other factors may alter the effects on public health or welfare of such air pollutant;
>
> (B) the types of air pollutants which, when present in the atmosphere, may interact with such pollutant to produce an adverse effect on public health or welfare."

National ambient air quality standards are based on such criteria [Clean Air Act Section 109(b), 42 U.S.C. §7409(b)]. Both the criteria and standards are to be reviewed and, as appropriate, revised at five year intervals beginning not later than December 31, 1980 [Section 109 (d)(1), 42 U.S.C. §7409(d)(1)].

This combined document constitutes a revision of separate documents previously issued for particulate matter (AP-49) and sulfur oxides (AP-50). A combined document has been prepared for several reasons: (1) the transformation of significant amounts of gaseous sulfur dioxide into particulate sulfate by chemical processes in the atmosphere; (2) difficulty in separating the relative contributions of sulfur oxides and particulate matter to mortality and morbidity effects observed in community health epidemiological studies; and (3) the recommendation or example of other organizations, notably the World Health Organization and EPA's advisory committee on air quality criteria document-related matters, the Clean Air Scientific Advisory Committee of EPA's Science Advisory Board.

This document describes what is known or anticipated with regard to both the health and welfare effects of particulate matter (PM)* and sulfur oxides (SO_x). With regard to health, the document is intended to report on the nature and significance of all identifiable effects of PM and SO_x. Under Section 109(b) of the Clean Air Act, the Administrator is to consider such information in this document in judging which effects are to be considered adverse, and set national primary ambient air quality standards which, based on the criteria and allowing an adequate margin of safety, are requisite to protect the public health. This requires the careful assessment of the relationship between levels of exposure to PM and SO_x via all routes

*For purposes of this document, PM is considered to consist of any airborne solid particles and low vapor pressure liquid droplets with an effective diameter smaller than a few hundred micrometers. Important particle size fractions within this broad range are identified in subsequent sections of this summary (see Section 1-2, for example).

and averaged over appropriate time periods, and the biological responses to those levels and interactions with other variable factors. This assessment must take into consideration the temporal and spatial distribution of PM and SO_x, and is complicated by such factors as breathing patterns, individual activity levels, effects on sensitive populations, and the complex and diverse chemical composition of PM.

The welfare effects which must be identified in the criteria document include effects on soils, water, crops, vegetation, man-made materials, animals, wildlife, weather, visibility, climate, damage to and deterioration of property, and hazards to transportation, as well as effects on economic values and personal comfort and well-being [Clean Air Act Section 302(h), 42 U.S.C. §7602(h)]. Under Section 109(b) of the Clean Air Act, the Administrator must consider such information in this document and set national secondary ambient air quality standards which are based on the criteria and are requisite to protect the public welfare from any known or anticipated adverse effects associated with the presence of such pollutants.

1.1.2 Organization of the Document

The present document consists of 14 chapters, currently organized into five separate volumes as follows:

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).

Volume I, the present volume, contains the general introduction and the executive summary and conclusions for the entire document. Chapters 2 through 5, contained in volume II, provide background information on: physical and chemical properties of PM and SO_x; approaches for the collection and measurement of such air pollutants; their sources of emissions; their ambient air concentrations; and factors affecting exposures of the general population to them.

The third volume, containing Chapters 6 through 8, provides information on: atmospheric transport, transformation and fate of PM and SO_x; their contribution to and involvement in acidic deposition processes and effects; and their effects on vegetation. Volume IV contains Chapters 9 and 10, which describe effects on visibility and damage to materials presently attributable to either PM or SO_x.

The fifth volume, containing Chapters 11 through 14, focuses on information concerning the health effects of PM and SO_x. Chapter 11 discusses respiratory tract uptake and deposition of sulfur dioxide (SO_2), sulfur-related particulate matter species (e.g., sulfates and sulfuric acid), and other types of PM, as well as factors affecting their deposition and biological fate. Chapters 12 and 13, on the other hand, respectively discuss information derived from controlled toxicological studies in animals and controlled human exposure studies, whereas Chapter 14 discusses community health epidemiological studies.

The extensive literature on PM and SO_x is critically reviewed and evaluated in the present document with emphasis on discussion of studies selected on the basis of their validity and

relevance for the assessment of human health and welfare effects. Consideration of air quality information and measurement techniques in early chapters of the document is limited to elucidating aspects of environmental pathways by which PM and SO_x move from natural and manmade sources of emissions to receptor sites (i.e., biological organisms or materials affected by them) most germane to understanding relationships between atmospheric levels of PM and SO_x and health and welfare effects discussed later in the document. As indicated by the discussion of air quality information, airborne particles of a wide variety of sizes, shapes, and chemical composition are found in the ambient air of the United States in highly variable quantities and combinations in different geographic locations and at various times at the same site. Analysis of the effects of airborne particles is further complicated by complex transformations of various particulate matter species or their precursor substances during atmospheric transport from sources of emissions that may be hundreds or thousands of miles away from human populations, other biological organisms, or materials ultimately affected by the pollutants. Sulfur dioxide (SO_2), a gaseous air pollutant exerting notable health and welfare effects in its own right, is also the main precursor substance emitted from anthropogenic sources which contributes to the secondary formation of sulfuric acid and sulfate salts representing major constituents of PM present in urban aerosols to which large segments of the U.S. population are exposed. SO_2 and sulfur-related PM species and their associated health and welfare effects are accordingly discussed in considerable detail in the present document. Other specific PM species of concern, however, are not discussed in as much detail here; but, rather the reader is referred to other EPA air quality criteria or health assessment documents where the effects of such substances are thoroughly reviewed. See, for example, Air Quality Criteria for Lead (EPA, 1977), Air Quality Criteria for Oxides of Nitrogen (EPA, 1981), and so on.

In evaluating available information on the health effects of PM and SO_x in man, the main focus is on the effects of inhalation of these substances as the most direct and important route of exposure, although it is recognized that biological effects may also be exerted by some PM species via other routes of exposure, such as ingestion or contact with skin. Important issues considered include: (1) patterns of respiratory tract uptake, deposition, and biological fate of SO_2, sulfur-related PM, and other PM substances in relation to size and other physical and chemical properties; (2) mechanisms of action by which such substances may exert biological effects of potential concern from a health viewpoint; (3) qualitative characterization of such biological effects and quantitative characterization of dose/response or exposure/effect relationships for such effects in relation to air concentrations of SO_2 and PM (defined either in general or, whenever possible, in terms of varying size or chemical composition); and (4) identification of population subgroups at special risk for the induction of effects by PM and SO_x.

In relation to the evaluation of welfare effects of PM and SO_x, consideration is not only accorded to direct, acute effects of such substances on visibility, manmade materials, and plant and animal species. Rather, as appropriate, there are assessed more-indirect, long-term

effects that might be reasonably anticipated to occur as a consequence of repeated or continuous chronic exposures to low levels of such pollutants, their interactions with other agents such as meteorological variables, and their secondary deposition on and movement through aquatic and terrestial ecosystems.

In the summary materials that follow, citations are made only to selected, crucial references that provide evidence in support of key points addressed. Complete bibliographic information for each citation is provided in the reference list for the later chapter where the particular point is discussed in more detail.

1.2 PHYSICAL AND CHEMICAL PROPERTIES OF SULFUR OXIDES AND PARTICULATE MATTER

1.2.1 Sulfur Oxides

Of four known sulfur oxides (sulfur monoxide, sulfur dioxide, sulfur trioxide, and disulfur monoxide), only sulfur dioxide (SO_2) occurs at significant concentrations in the atmosphere. SO_2 is a colorless gas with a pungent odor emitted from combustion of sulfur-containing fossil fuels, such as coal and oil. Its physical and chemical properties are summarized in Chapter 2.

Oxidation of SO_2 to form sulfate particles is one mechanism by which this gas is removed from the atmosphere; SO_2 is also removed directly by dry deposition on surfaces. Oxidation of SO_2 to produce sulfate particles takes place by a variety of mechanisms, such as photochemical reactions and catalysis by constituents of ambient aerosols. SO_2 interactions with airborne particles have been studied for a variety of solids such as ferric oxide, lead oxide, aluminum oxide, salt, and charcoal. One research group concluded that the main reaction between SO_2 and particulate matter is adsorption, with most catalytic reactions occurring at high temperatures near the combustion source.

SO_2 is readily soluble in water, forming a dilute solution of sulfurous acid including the following species: $SO_2 \cdot H_2O$; HSO_3^- (bisulfite); and $SO_3^=$ (sulfite).

1.2.2 Particulate Matter

Airborne particles exist in diverse sizes and compositions that can fluctuate widely under the changing influences of source contributions and meteorological conditions. In broad terms, however, airborne particle mass tends to cluster in two principal size groups: coarse particles mostly larger than 2-3 micrometers (μm) in diameter, and fine particles mostly smaller than 2-3 μm in diameter. The dividing line between the coarse and the fine sizes is frequently given as 2.5 μm but the separation is neither sharp nor fixed; it can depend on the contributing sources, on meteorology, and on the age of the aerosol. The curves in Figure 1-1 exemplify the influences of these parameters.

Fine particles can occur in two mass modes. Those in the nuclei mode--from 0.005 to 0.05 μm diameter--form near sources by condensation of vapors produced by high temperature processes such as fossil-fuel combustion. Particles in the accumulation mode--from 0.05 to about 2 μm--form principally by coagulation or growth through vapor condensation of the short-lived nuclei mode particles. Typically, 80% or more of atmospheric sulfate particle mass occurs in

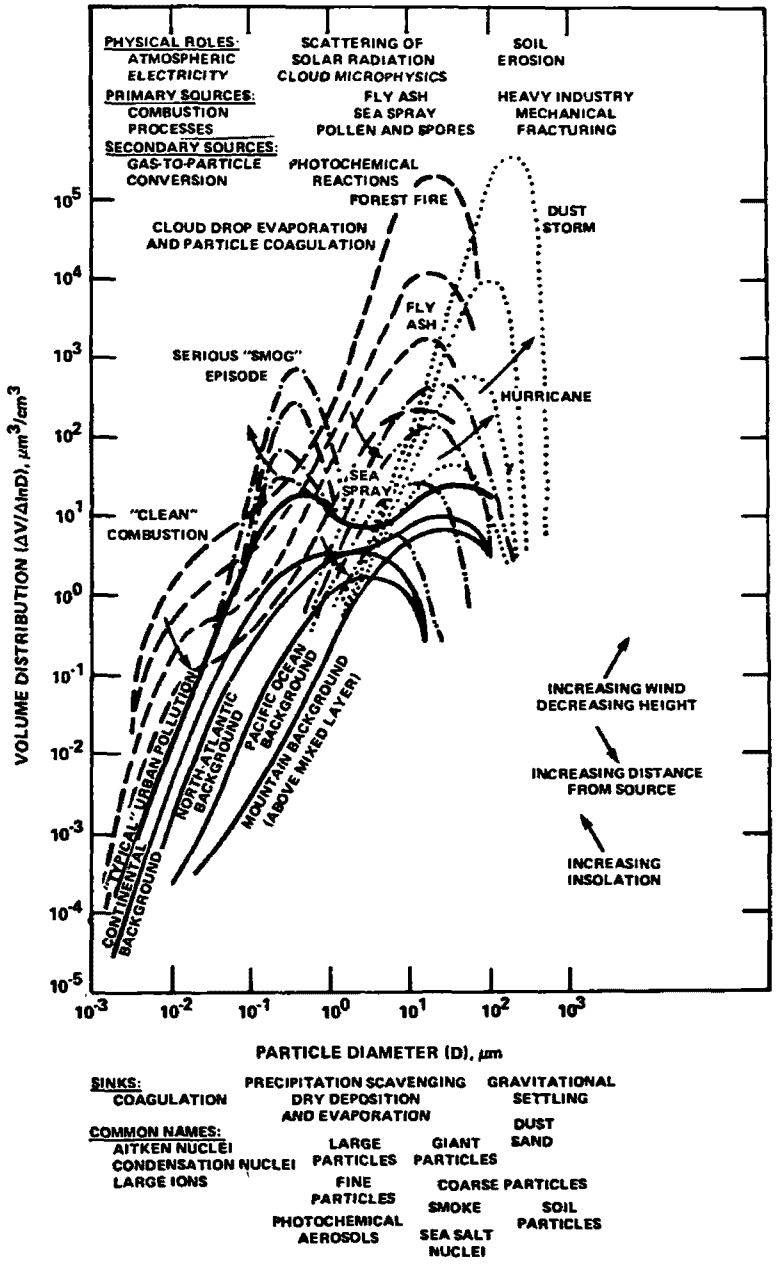

Figure 1-1. Size distribution of atmospheric particulate volume under a variety of conditions/source locations. Atmospheric particle volume is roughly proportional to mass. Particle volume tends to be bimodally distributed, although the relative amounts and peaks of both modes can vary significantly.

Source: W.G.N. Slinn. Dry Deposition and Resuspension of Aerosol Particles-a New Look at Some Old Problems. In: Atmosphere-Surface Exchange of Particulate and Gaseous Pollutants (1974), Proceedings of a Symposium, Battelle Pacific Northwest Laboratories and U.S. Atomic Energy Commission, Richland, Washington, September 4-6, 1974. ERDA Symposium Seroes 38, Energy Research and Development Administration, Oak Ridge, TN, January 1976. pp. 1-40.

the accumulation mode. Accumulation mode particles normally do not grow into the coarse mode--those larger than about 2-3 μm. Coarse particles include re-entrained surface dust and particles formed by anthropogenic processes such as grinding.

Primary particles are directly discharged from manmade or natural sources. Secondary particles form by chemical and physical reactions in the atmosphere, and most of the reactants involved are emitted to the air as gaseous pollutants.

In the atmosphere, particle growth and chemical transformation occur through gas-particle and particle-particle interactions. Gas-particle interactions include condensation of low-vapor-pressure molecules, such as sulfuric acid (H_2SO_4), which occurs principally on fine particles. The only particle-particle interaction important in atmospheric processes is coagulation among fine particles.

As shown in Figure 1-2, major components of fine atmospheric particles include sulfates, carbonaceous material, ammonium, lead, and nitrate. Coarse particles consist mainly of oxides of silicon, aluminum, calcium, and iron, as well as calcium carbonate, tire particles, vegetation-related particles and sea salt. Note that some overlap into fine versus coarse size distributions occurs for many chemical species found predominantly in one or the other size mode.

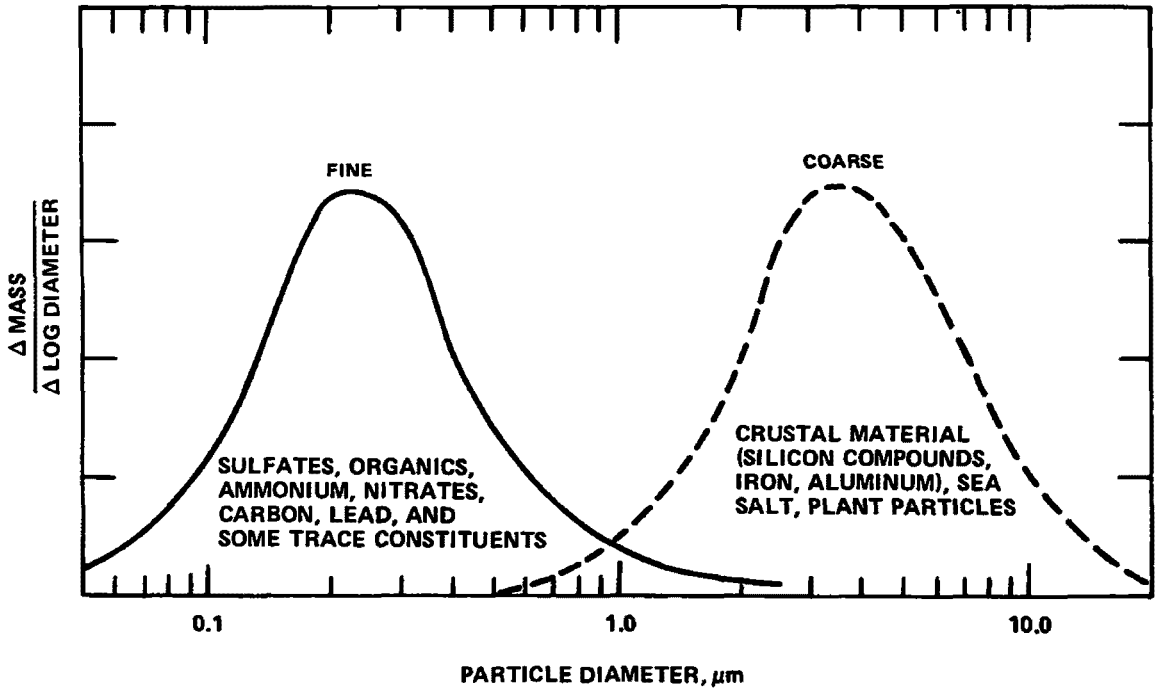

Figure 1-2. Idealized representation of typical fine and coarse particle mass and chemical composition distribution in an urban aerosol. Although some overlap exists, note substantial differences in chemical composition of fine versus coarse modes. Chemical species of each mode are listed in approximate order of relative mass contribution.

Source: After Husar et al. (1978).

The carbonaceous component of fine particles contain both elemental carbon (graphite and soot) and nonvolatile organic carbon (hydrocarbons emitted in combustion exhaust and secondary organics formed by photochemistry). In many urban and nonurban areas, these particles may be the most abundant fine particle species after sulfates. Secondary organic particles form by oxidation of primary organics, ozone, and nitrogen oxides. Atmospheric reactions of nitrogen oxide gases yield nitric acid vapor (HNO_3) which may accumulate as nitrate in fine and coarse particles. Chemical pathways for forming nitrate particles and secondary organics are not well established, and much doubt exists regarding the validity of historical nitrate data bases.

Most atmospheric sulfates and nitrates are water soluble and hygroscopic (absorb moisture). Hygroscopic growth of sulfate-containing particles has a profound effect on their size, reactivity and other physical properties, which in turn influence their deposition in the respiratory tract, toxicity, removal efficiency, and effects on weather and climate. Deliquescence, or sudden uptake of water when relative humidity exceeds a certain level, is exhibited by a number of organic and inorganic compounds, primarily salts.

1.3 TECHNIQUES FOR COLLECTION AND ANALYSIS

Since publication of the 1970 criteria documents, advances in technology have resulted in a substantial number of new measurement techniques together with information on the quality of data collected by older techniques, as discussed in Chapter 3 of the present document. This summary focuses on those techniques principally used in health and welfare studies.

1.3.1 Sulfur Oxides

Three main measurement methods or variations thereof have been employed in generating data cited for sulfur dioxide (SO_2) levels in community health epidemiological studies: (1) sulfation rate (lead dioxide) methods; (2) hydrogen peroxide measurements and (3) the West-Gaeke (pararosanaline) method.

Sulfation rate methods involve reaction of airborne sulfur compounds with lead dioxide in a paste spread over an atmospherically-exposed plate or cylinder. Rates of reaction of sulfur compounds with surface paste compounds are expressed in $SO_3/cm^2/day$. However, the reactions are not specific for SO_2, and atmospheric concentrations of SO_2 or other sulfur compounds cannot be accurately extrapolated from the results, which are markedly affected by factors such as temperature and humidity. Lead dioxide gauges were widely used in the United Kingdom prior to 1960 and provided aerometric data reported for SO_2 in some pre-1960s British epidemiological studies; sulfation rate methods were also used in certain American studies.

Use of the hydrogen peroxide method was gradually expanded in the United Kingdom during the 1950s, often being coupled in tandem with apparatus for particulate matter (smoke) monitoring. The hydrogen peroxide method was adopted in the early 1960s as the standard SO_2 method used in the National Survey of Air Pollution throughout the United Kingdom and, as an OECD-recommended method, elsewhere in Europe. The method can yield reasonably accurate estimates of atmospheric SO_2 concentrations expressed in $\mu g/m^3$; but results obtained with routine

ambient air monitoring can be affected by factors such as temperature, presence of atmospheric ammonia and titration errors. Very little quality assurance information exists on sources and magnitudes of errors encountered in use of the method in obtaining SO_2 data reported in specific epidemiological studies, making it difficult to assess the accuracy and precision of reported SO_2 values. Only in the case of the British National Survey has extensive quality assurance information been reported (Warren Spring Laboratory, 1961; 1962; 1966; 1967; 1975; 1977; OECD, 1964; Ellison, 1968) for SO_2 measurements made in the United Kingdom and used in various British epidemiological studies.

The West-Gaeke (pararosanaline) method has been more widely employed in the United States for measurement of SO_2. The method involves absorption of SO_2 in potassium tetrachloromercurate (TCM) solution, producing a chemical complex reacted with pararosanaline to form a red-purple color measured colorimetrically. The method, suitable for sampling up to 24 hrs, is specific for SO_2 if properly implemented to minimize interference by nitrogen or metal oxides, but results can be affected by factors such as temperature variations and mishandling of reagents. Only limited quality assurance information (Congressional Investigative Report, 1976) has been reported for some American SO_2 measurements by the West-Gaeke methods.

In recent years, a number of automated methods have gained widespread use for air monitoring. Some of these have been used in studying the effects of SO_2 on vegetation. Continuous analyzers based on a variety of measurement principles have been designated by EPA as equivalent methods for measurement of SO_2 in the atmosphere. Testing by EPA has verified their performance and has demonstrated excellent comparability with the federal reference method under typical monitoring conditions.

1.3.2 Particulate Matter

Sampling particulate matter suspended in ambient air presents a complex task because of the spectrum of particle sizes and shapes. Particle separation by aerodynamic size provides a simplification by accounting for variations in particle shape and particle settling velocity. Samplers can be designed to collect specific size fractions or match specific deposition patterns. Mass concentration measurements using gravimetric analysis provide direct measures of atmospheric particulate matter levels. High-volume samplers, dichotomous samplers, cascade impactors, and cyclone samplers are the most common examples of this type of measurement.

Mass concentrations have also been estimated using methods which do not employ direct weighing. These methods utilize techniques which measure an integral property of particles other than mass, such as optical reflectance. Examples of commonly used indirect methods include the American Iron and Steel Institute (AISI) tape sampler version of the ASTM method, the integrating nephelometer, and beta attenuation analysis.

Three main measurement approaches or variations thereof were used to obtain PM data reported in community health studies. (1) the British Smokeshade light reflectance method or variations used in the United Kingdom and elsewhere in Europe; (2) the American Society for

Testing and Materials (ASTM) filter soiling method based on light transmittance and used in the United States; and (3) the high-volume sampling method most widely employed in the United States.

As discussed in Chapter 3, the British Smoke (BS) method and various standard variations of it typically have a D_{50} cut-point of ≅ 4.5 μm in field use (McFarland, 1979). Thus, regardless of whether or not larger coarse-mode particles were present in the atmosphere during the sampling period, the BS method collected predominantly small particles. The D_{50} of the instrument may, however, shift slightly at higher wind speeds. The BS method neither directly measures the mass nor determines chemical composition of collected particles. Rather, it primarily measures light absorption of particles as indicated by reflectance from a stain formed by the particles collected on filter paper, which is somewhat inefficient for collecting very fine particles (Lui, 1978). The reflectance of light from the stain depends both on density of the stain or amount of PM collected in a standard period of time and optical properties of the collected materials. Smoke particles composed of elemental carbon of the type found in incomplete fossil fuel combustion products typically make the greatest contribution to the darkness of the stain, especially in urban areas. Thus, the amount of elemental carbon, but not organic carbon, present in the stain tends to be most highly correlated with BS reflectance readings. Other non-black, non-carbon particles also have optical properties such that they can affect the reflectance readings (Pedace and Sansone, 1972).

Since highly variable relative proportions of atmospheric carbon and non-carbon PM can exist from site to site or from one time to another at the same site, then the same absolute BS reflectance reading can be associated with markedly different amounts (or mass) of particles collected or, even, carbon present. Site-specific calibrations of reflectance readings against actual mass measurements obtained by collocated gravimetric monitoring devices are therefore necessary in order to obtain approximate estimates of atmospheric concentrations of PM based on the BS method. A single calibration curve relating mass or atmospheric concentration (in $\mu g/m^3$) of particulate matter to BS reflectance readings obtained at a given site may serve as a basis for crude estimates of PM (mainly small particle) levels at that site over time, so long as the chemical composition and relative porportions of elemental carbon and non-carbon PM do not markedly change. Of crucial importance for evaluation of BS data is the fact that the actual mass or smoke concentration present at a particular site may differ markedly from the corresponding mass or concentration (in $\mu g/m^3$) associated with a given reflectance reading on either of the two most widely used standard curves; great care must be applied in interpreting exactly what any reported BS value in $\mu g/m^3$ means at all.

The ASTM or AISI light transmittance method is similar in approach to the British smoke technique. The instrument has a D_{50} cut-point of ≅5 μm and utilizes an air flow intake apparatus similar to that used for the BS method, depositing collected material on a filter paper tape periodically advanced to allow accumulation of another stain over a standard time

period. Opacity of the stain is determined by transmittance of light through the deposited material and filter paper, with results expressed in terms of optical density or coefficient of haze (CoHs) units per 1000 linear feet of air sampled (rather than mass units). CoHs readings, however, are somewhat more markedly affected by non-carbon particles than BS measurements. The ASTM method does not directly measure mass or determine chemical composition of the PM collected. Any attempt to relate CoHs to $\mu g/m^3$ would require site-specific calibration of CoHs readings against mass measurements determined by a collocated gravimetric device, but the accuracy of such mass estimates could be subject to question.

The high-volume (hi-vol) sampler method, more widely used in the United States to measure total suspended particulates (TSP), collects particles on a glass-fiber filter by drawing air through the filter at a flow rate of approximately 1.5 m^3/min, thus sampling a higher volume of air per unit of time than the above PM sampling methods. 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). Under most conditions the particle size fraction collected (D_{50}) ranges from 0 to 25 - 30 μm. 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.

One consequence of the broader size range of particles sampled by the hi-vol method versus the BS or ASTM methods are severe limitations on intercomparisons or conversions of PM measurements by those methods to equivalent TSP units or vice versa. As shown by several studies, no consistent relationship typically exists, for example, between BS and TSP measurements taken at various sites or even during various seasons at the same site (Commins and Waller, 1967; Lee, 1972; Ball and Hume, 1977; Holland et al., 1979). The one exception appears to be that, during severe London air pollution episodes when low wind speed conditions resulted in settling out of larger coarse-mode particles and fine-mode particles markedly increased to constitute most of the PM present, then TSP and BS levels (in excess of ≅ 500 $\mu g/m^3$) tended to converge as would be expected when both methods are essentially sampling predominantly fine-mode particles (Holland et al., 1979).

An extensive list of techniques is available to analyze particles collected on a suitable substrate. Many of the techniques are 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, etc.). Not all analyses can be performed on all particle samples because of factors such as incompatible sub-

strates and inadequate sample size. Misinterpretation of analytical results occur when samples have not been 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, the 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, no single sampler meets all requirements, but samplers are available which can meet a majority of typical requirements.

A variety of devices including hi-vol samplers, size-selective samplers, nephelometers, and precipitation collectors have been used to study the contributions of sulfur oxides and particulate matter to such welfare effects as visibility reduction, soiling, and acidic deposition.

1.4 SOURCES AND EMISSIONS

Both natural and manmade sources emit particulate matter and SO_2 into the atmosphere. Natural emissions include dust, sea spray, volcanic emissions, biogenic emanations (such as organic aerosols from plants), and emissions from wild fires. Manmade emissions originate from stationary point sources, fugitive sources (such as roadway and industrial dust), and transportation sources (vehicle exhausts). Reliable estimates for natural emissions of PM and SO_x specific to the U.S. are not available. Proportional interpolations from global estimates indicate that in the U.S. natural sources emit 84 million metric tons of particles; estimates of biogenic sulfur emissions from the northeast quadrant of the U.S. suggest a regional total in the range of 0.1 million metric tons as SO_2. Additional contributions from coastal and oceanic sources may also be significant. Manmade sources emit 125 million to 383 million metric tons of particulate matter and 27 million metric tons of sulfur oxides (mostly SO_2) per year in the United States. These numbers should not be considered more than estimates because of the assumptions and approximations inherent in emissions calculations.

The proximity of emissions to humans often is more important than relative intensity. Emissions from combustion of home-heating fuels and transportation sources are minor on a national level. However, they are emitted in densely populated areas and close to ground level, thereby increasing the possibility of effects on human health and welfare. For such reasons, certain manmade sources, particularly stationary point sources, have been given special attention in this document. Historical trends in emissions of particulate matter (excluding fugitive emissions) and sulfur oxide are shown in Table 1-1.

TABLE 1-1 (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 1-1 (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)

1.4.1 Sulfur Oxides

Most manmade sulfur oxide emissions come from stationary point sources, and more than 90 percent of these discharges are in the form of SO_2. The balance consists of sulfates. Most natural sulfur is emitted as reduced sulfur compounds, some portion of which probably becomes oxidized in the atmosphere to SO_2 and sulfates.

1.4.2 Particulate Matter

Characteristics of particle emissions vary with the source and a host of other factors. Primary particles from natural sources tend to be coarse. About 50 percent are smaller than 10 μm. Particles from non-industrial fugitive sources, such as unpaved roads and wind-eroded farmland, are significant on a mass basis--an estimated 110 to 370 million metric tons a year. However, only about 20 percent of this particulate matter is less than 1 μm in size. On the other hand, most particles emitted by stationary and transportation sources are less than 2.5 μm in diameter. In addition, the variety of different toxic elements found in fine material from stationary point sources tends to exceed that typically found in emissions from manmade or natural fugitive sources.

Fugitive dust emissions exceed those from stationary point sources in most Air Quality Control Regions with high total suspended particle loadings. However, the impact of this pollution on populated areas may be lessened because: (1) a major portion of these emissions consists of large particles which settle out in a short distance, and (2) most sources, such as unpaved roads, exist in rural areas and their emissions spread over areas with low population densities.

1.5 CONCENTRATIONS AND EXPOSURE

1.5.1 Sulfur Oxides

Sulfur oxide concentrations in the air have been markedly reduced during the past 15 years by restrictions on sulfur content in fuels, control devices on stationary and other major sources, and tall stacks which relocate power-plant exhausts. Currently, only 1 percent of the SO_2 monitoring sites show levels above 80 μg/m^3, as compared with 16 percent of the monitoring stations which reported annual means above this level in 1970. Despite this, some areas still report very high short-term SO_2 concentrations (see Figure 1-3). Hourly values of 4000 to 6000 μg/m^3 (1.5 to 2.3 ppm) are common near large smelters. Maximum hourly values above 1000 μg/m^3 (0.4 ppm) exist in about 100 U.S. locations. Near isolated point sources, such peaks may be reached very rapidly and be of only short duration (see, for example, Figure 1-4).

1.5.2 Particulate Matter

Following a downward trend from 1970 to 1974, TSP concentrations have not changed significantly in recent years. Dusty, arid regions of the country still have high TSP values, as do industralized cities in the east and far west. Ninetieth percentile values of 24-hr TSP (values exceeded 10 percent of the time) above 85 μg/m^3 are reported in every region of the United States except Alaska (Figure 1-5). Annual mean TSP values range from 50 μg/m^3 in the New England region to 77 μg/m^3 in the California-Nevada-Arizona region.

As discussed in Section 1.2, particulate matter is generally distributed in fine and coarse mode size ranges of differing chemical compositions. A comparison of coarse, fine, and hi-vol particle measurements for selected urban suburban, and rural sites is shown in Figure 1-6. Fine particles typically contribute about one-third of TSP mass in urban areas. Sulfates often account for 40 percent of fine-particle levels which, in the eastern U.S., are

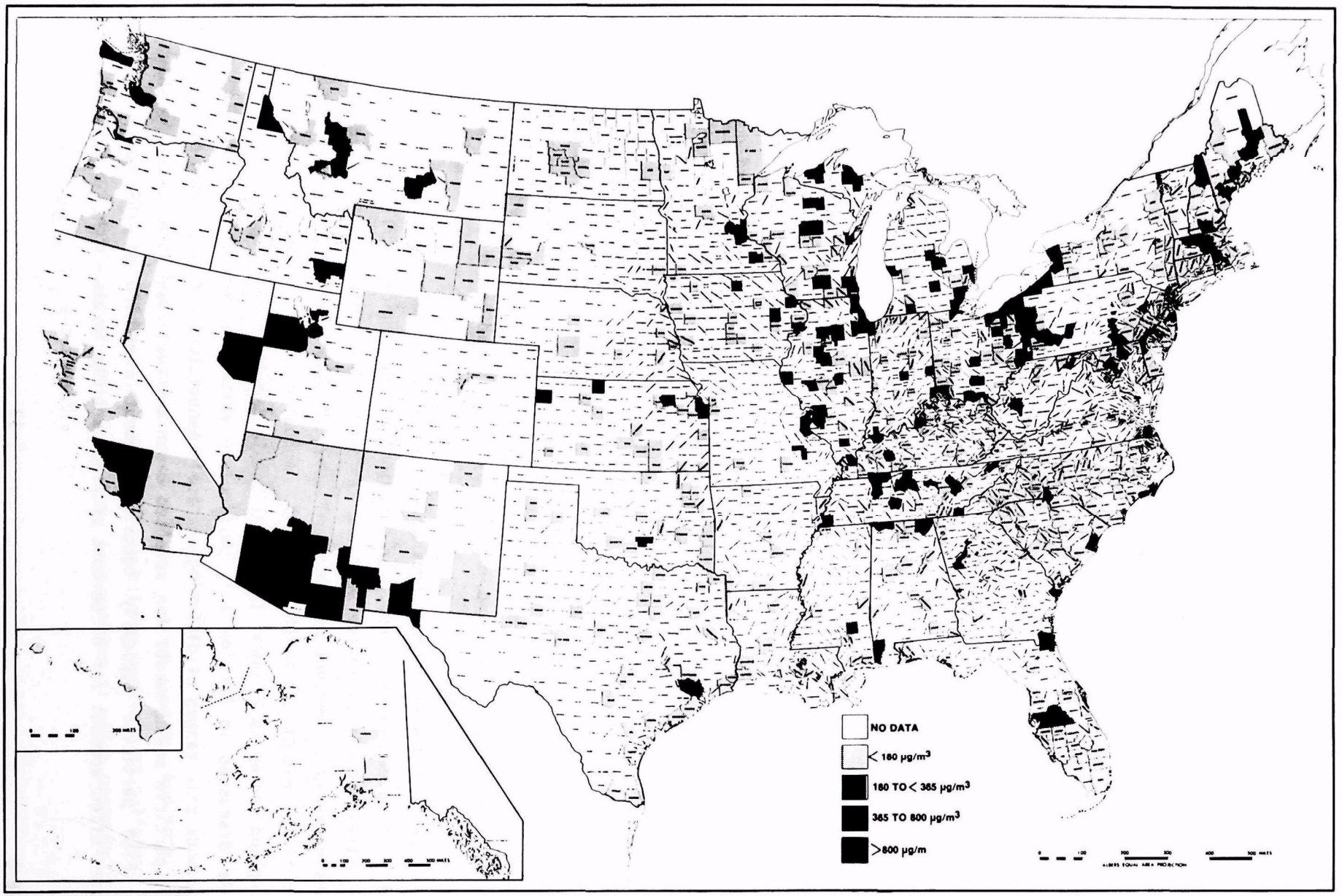

Figure 1-3. Sulfur dioxide second maximum 24-hour average by county, 1974-1976.

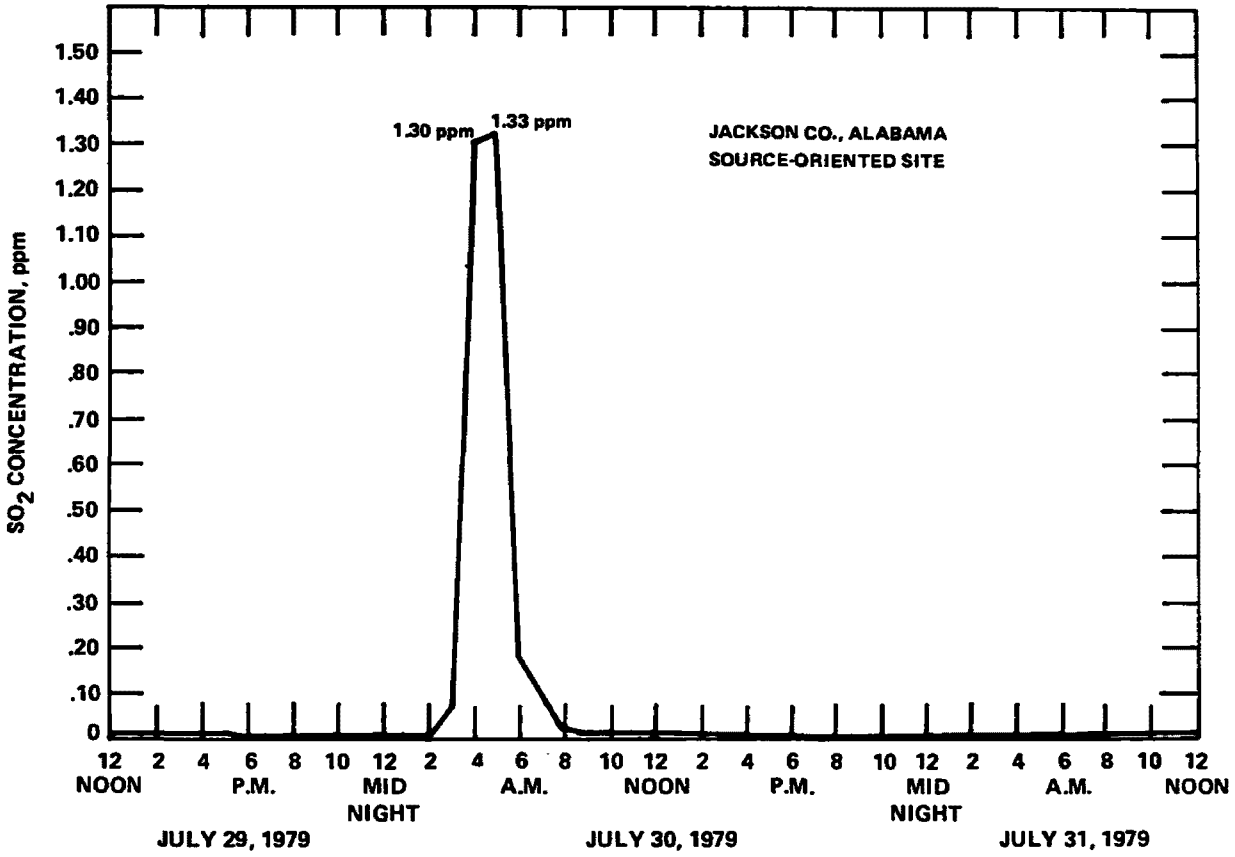

Figure 1-4. One example of rapid increase in ambient sulfur dioxide concentration from near zero to 1.30 ppm (3410 $\mu g/m^3$) during a period of approximately two hours is shown.

Source: Sulfur Dioxide One-Hour Values, National Aerometric Data Bank Standards Report for July 1979, Monitoring and Data Analysis Division, Office of Air Quality Planning and Standards, US Environmental Protection Agency, Research Triangle Park, NC, (1981).

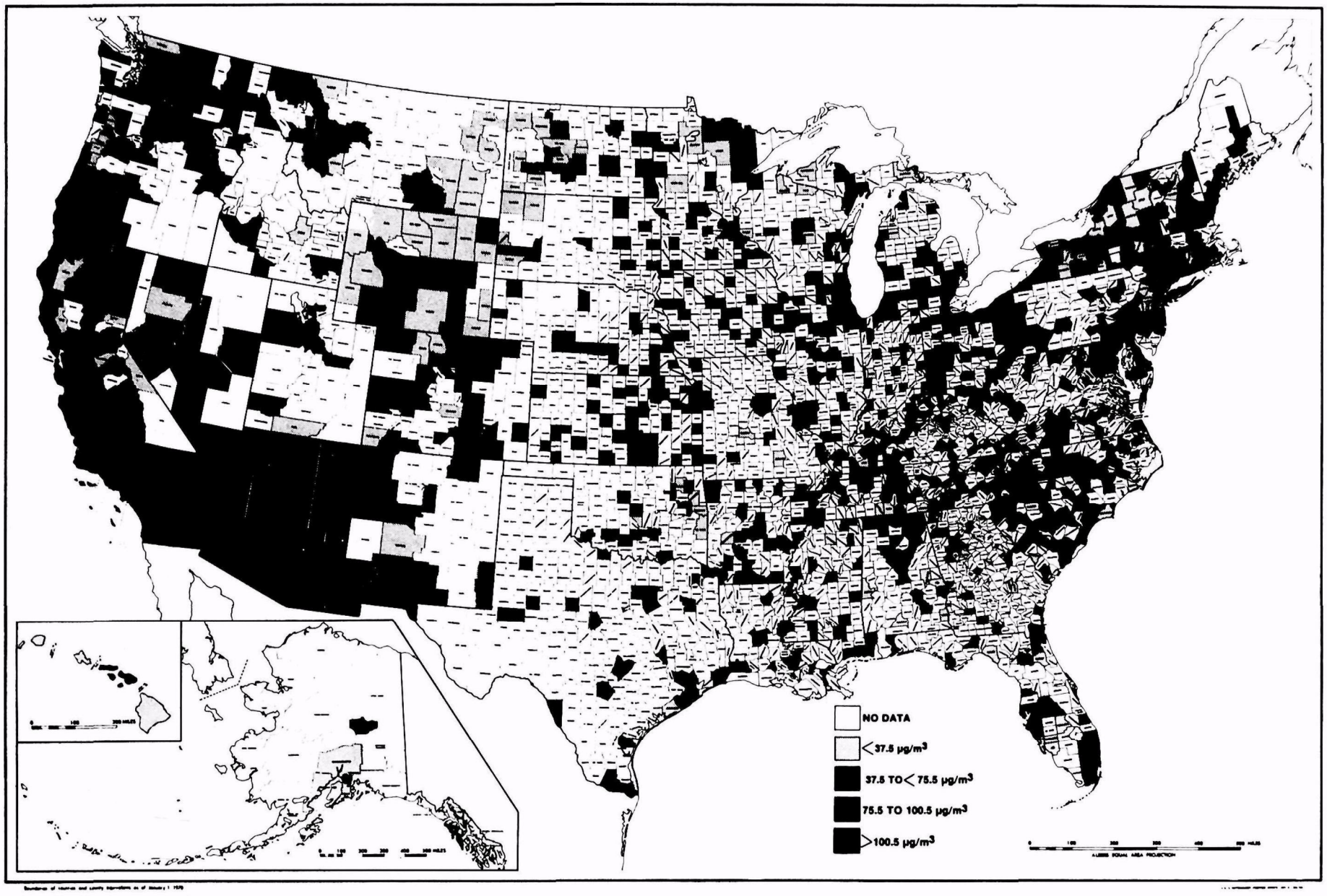

Figure 1-5. Total suspended particulate maximum annual average by county, 1974-1976.

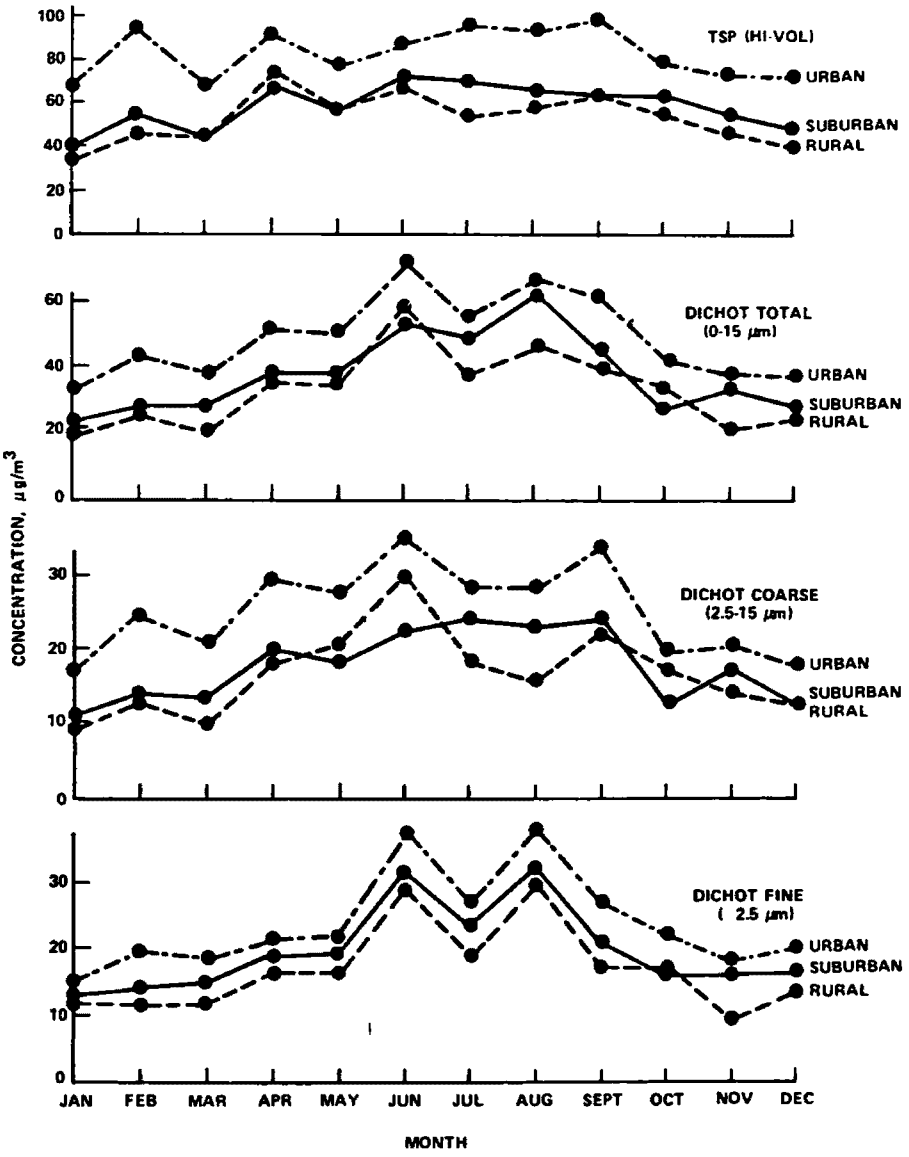

Figure 1-6. Seasonal variations in urban, suburban, and rural areas are shown for four size ranges of particles. This represents monitoring data from a relatively small sumber of sites.

Source: After Trijonis et al. (1980).

nearly the same in cities and rural areas. Sulfate and nitrate ions occur in high concentrations during both summer and winter. Large areas of the United States experience 10 $\mu g/m^3$ or greater sulfate levels for one or two periods of a month or more every year. These areas are so large that no background levels of fine particles are available for measurement east of the Mississippi River. Southern California experiences high levels of sulfate and nitrate, particularly during photochemical (smog) incidents. Extremely high levels of organic aerosols also occur in this area; from 2 to 4 p.m., during intensive periods of ozone formation, levels above 100 $\mu g/m^3$ have been found. These organic aerosols consist largely of dicarboxylic acids and other polyfunctional compounds. Concentrations of toxic organics and trace metals are highest in cities. Levels of some fine-particle components have decreased because of control measures, such as reduction of lead in gasoline.

Coarse particles tend to settle close to sources. In most cases, these particles account for 2/3 of TSP. During the summer, in dry regions such as Phoenix, Oklahoma City, El Paso, or Denver they may contribute even higher proportions. The primary cause of high TSP appears to be local dust, but in industrialized cities evidence exists for large contributions of soot, fly ash, and industrial fugitive emissions.

Coarse particles are mainly composed of silica, calcium carbonate, clay minerals, and soot. Chemical constituents in this fraction include silicon, aluminum, potassium, calcium, and iron, together with other alkaline-earth and transition elements. Organic materials are also found in coarse particles, including plant spores, pollens, and diverse biogenic detritus. Much of this coarse material is road dust suspended by traffic action. Street levels of resuspended dust can be very high. Traffic on unpaved roads generates huge amounts of dust which deposit on vegetation and can be resuspended by wind action. Rain and snow can reduce these emissions, but one study suggests that salting of roads is a major source of winter TSP. Industrial fugitive emissions, particularly from unpaved access roads, construction activity, rock crushing, and cement manufacturing can be major sources of coarse particles.

A number of calculational methods, generally categorized as source-apportionment or source-receptor models, are being used to trace particle levels to their sources. The results from chemical-element balance calculations or factor analysis are available for several cities. Apportionments for these cities are presented in Chapter 5 as examples of results to be expected in the future by application of these methods.

Although outdoor concentrations of pollutants can be measured at particular sites, the highly mobile population can be exposed to either higher or lower values than community monitors show. Some individuals in "clean" cities receive greater exposures than some individuals in "polluted" cities. Indoor levels of SO_2, which tend to be lower than outdoor levels because walls, floors, and furniture absorb the gas, are almost entirely due to penetration from outdoors. Presence or absence of air conditioning, air exchange rates, and activity levels that resuspend dust all influence indoor particulate matter values. Also, outdoor fine particles penetrate into buildings. Peak indoor TSP levels correlate to some degree with outdoor values after a time which depends on a building's air-exchange rate. Stationary ambient

air pollution monitors provide general statistics on composite population exposures; it is extremely difficult to predict an individual's actual exposure to sulfur oxides and particulate matter on the basis of community air-monitoring data alone.

1.6 ATMOSPHERIC TRANSPORT, TRANSFORMATION, AND DEPOSITION

The concentration of a pollutant at some fixed time and place beyond its source depends on: (1) rate of emission and configuration of the source, (2) chemical and physical reactions that transform one pollutant species to another, (3) transport and diffusion (dilution) as a result of various meteorological variables, and (4) removal of the pollutant through interaction with land and water surfaces (dry deposition) and interaction with rain droplets or cloud particles (wet deposition). Figure 1-7 schematically illustrates some of these processes.

Processes governing transport and diffusion, chemical transformation, and wet and dry removal of SO_2 and particulate matter are extremely complex and not completely understood. The oxidation rate of SO_2 observed in urban and rural atmospheres is only partially accounted for by gas-phase reactions. Liquid-phase catalytic reactions involving manganese and carbon are possible contributing sources to observed rates, but further research is required to quantify these processes under typical atmospheric conditions.

Dry deposition of SO_2 is fairly well understood as a result of extensive measurements over various vegetation canopies. Particle deposition has focused on physical aspects of the process; that is, the aerodynamics, and little supportive measurement data exist on particles with compositions typical of those in polluted atmospheres. It is apparent that coarse particles are removed from the atmosphere much more rapidly than fine particles. Because of this, the residence time of fine particles in the atmosphere appears to be in the order of 1 week and their transport distance can exceed 500 km.

Understanding of wet removal of SO_2 has progressed considerably in recent years, including increased knowledge of solution-phase chemistry within rain droplets. Removal of particles, as well as gases, depends mainly on the physical character of precipitation events, which in many instances may be the determining factor in accurate wet-removal prediction.

Characterization of the dynamics of the planetary boundary layer is essential to an adequate understanding of pollutant transport and diffusion over all spatial scales. Though considerable advances have been made in this area, ability to predict mean transport and diffusion over long distances is less than adequate. This is due in part to the wide scatter, spatially and temporally, of upper-air wind observations.

The long-range transport of the fine particle/SO_2 complex results in the superposition and chemical interaction of emissions from many different types of sources. Present long-range transport models are characterized by simple parameterization for chemical transformation and wet and dry removal, and by varying degrees of sophistication in treatment of transport and diffusion. None of the models adequately treats the dynamics of the planetary boundary. With further research and development, long-range transport models, though limited

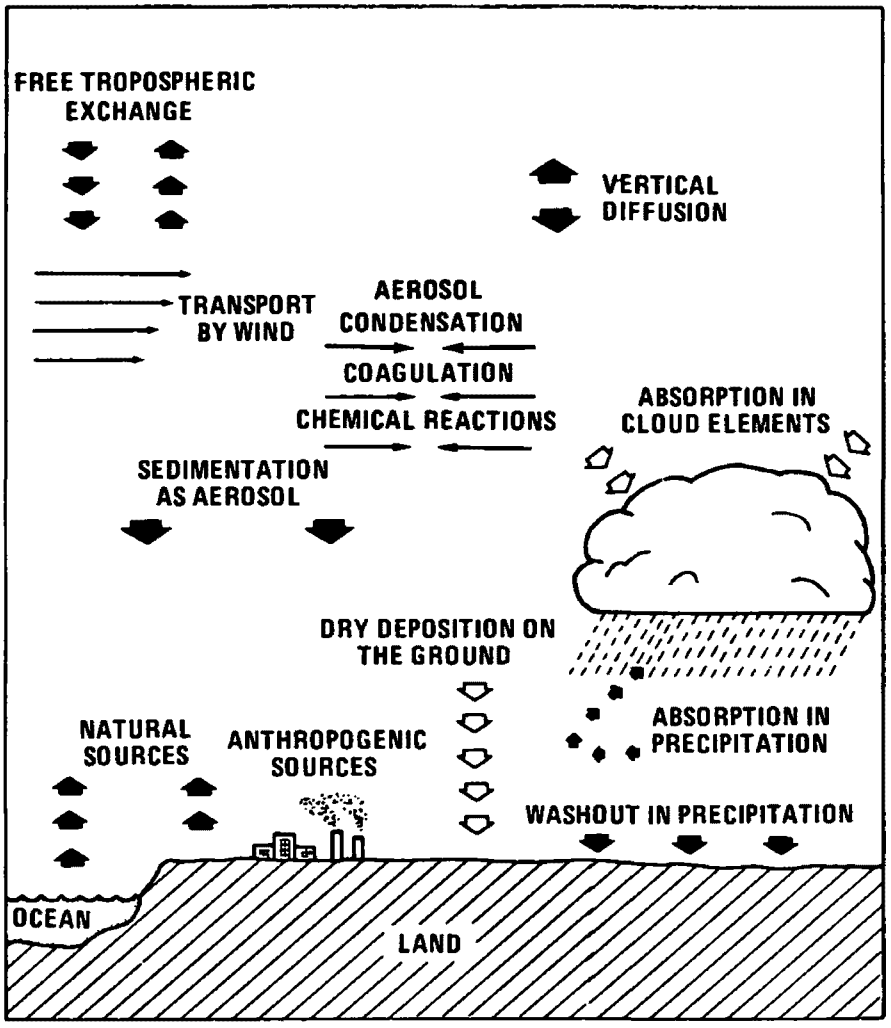

Figure 1-7. Complex processes affecting transport and transformation of airborne particulate matter and sulfur oxides.

Source: Adapted from Drake and Barrager (1979).

by a lack of data bases, should prove adequate for addressing issues associated with movement of pollutant emission over long distances.

1.7 ACIDIC DEPOSITION

The occurrence of acidic deposition, especially in the form of acidic precipitation, has become a matter of concern in many regions of the United States, Canada, northern Europe, Taiwan and Japan. Acidic precipitation in the Adirondack Mountains of New York State, in Maine, in northern Florida, in eastern Canada, in southern Norway and in southwest Sweden has been associated with acidification of waters in ponds, lakes and streams with a resultant disappearance of animal and plant life. Acidic precipitation (rain and snow) is also believed to have the potential to: (1) leach nutrient elements from sensitive soils, (2) cause direct and indirect injury to forests, (3) damage monuments and buildings made of stone, and (4) corrode metals.

Sulfur and nitrogen oxides have been most clearly implicated as pollutants contributing to acidic deposition phenomena; and Chapter 7 of this document emphasizes the effects of wet deposition of sulfur and nitrogen oxides and their products on aquatic and terrestrial ecosystems. Dry deposition also plays an important role, but contributions by this process have not been well quantified. Because sulfur and nitrogen oxides are so closely linked in the formation of acidic precipitation, no attempt has been made to limit the present discussion solely to a main topic of this document, sulfur oxides. A more thorough general review of acidic deposition processes and associated environmental problems will be presented in a future EPA document.

Sulfur and nitrogen oxides are considered to be the main precursors in the formation of acidic precipitation. Emissions of such compounds involved in acidification are attributed chiefly to the combustion of fossil fuels such as coal and oil. Emissions may occur at ground level, as from automobile exhausts, or from stacks at times 1000 feet or more in height. Emissions from natural sources are also involved; however, in highly industrialized areas, emissions from manmade sources markedly exceed those from natural sources. In the eastern United States the highest emissions of sulfur oxides derive from electric power generators using coal. However, emissions of nitrogen oxides, mainly from automotive sources, tend to predominate in the West. (Information regarding sources and emissions is discussed in Chapter 4 and is summarized in Sections 1.4 and 1.5 of this chapter.)

The fate of sulfur and nitrogen oxides, as well as other pollutants emitted into the atmosphere, depends on their dispersion, transport, transformation and deposition. Sulfur and nitrogen oxides or their transformation products may be deposited locally or transported long distances from the emission sources (Altshuller and McBean, 1976; Pack, 1978; Cogbill and Likens, 1974). Residence time in the atmosphere, therefore, can be brief if the emissions are deposited locally or may extend to days or even weeks if long range transport occurs. The chemical form in which emissions ultimately reach the receptor, i.e., the biological organism or material affected, is determined by complex chemical transformations that take place between

the emission sources and the receptor. Long range transport over distances of hundreds or thousands of miles allows time for many chemical transformations to occur.

Sulfates and nitrates are among the products of the chemical transformations of sulfur oxides (especially SO_2) and nitrogen oxides. Ozone and other photochemical oxidants are believed to be involved in the chemical processes that form sulfates and nitrates. When sulfates and nitrates combine with atmospheric water, dissociated forms of sulfuric (H_2SO_4) and nitric (HNO_3) acids result; and when these acids are brought to earth in rain and snow, acidic precipitation occurs. Because of long range transport, acidic precipitation in a particular state or region can be the result of emissions from sources in states or regions many miles away, rather than from local sources. To date, however, the complex nature of the chemical transformation processes has not made it possible to demonstrate a direct cause and effect relationship between emissions of sulfur and nitrogen oxides and the acidity of precipitation. (Transport, transformation, and deposition of sulfur compounds are discussed in Chapter 6 of this document; analogous information on nitrogen oxides is discussed in a separate document, Air Quality Criteria for Oxides of Nitrogen, U.S. EPA, 1981).

Acidic precipitation has been arbitrarily defined as precipitation with a pH less than 5.6, because precipitation formed in a geochemically clean environment would have a pH of approximately 5.6 due to the combining of carbon dioxide with air to form carbonic acid. Currently the acidity of precipitation in the northeastern United States usually ranges from pH 3.0 to 5.0; in other regions of the United States precipitation episodes with a pH as low as 3.0 have also been reported in areas with average pH levels above 5.0 (see Figure 1-8).

The pH of precipitation can vary from event to event, from season to season and from geographical area to geographical area. Other substances in the atmosphere besides sulfur and nitrogen oxides can cause the pH to shift by making it more acidic or more basic. For example, dust and debris swept up in small amounts from the ground into the atmosphere may become components of precipitation. In the West and Midwest soil particles tend to be more basic, but in the eastern United States they tend to be acidic. Also, in coastal areas sea spray strongly influences precipitation chemistry by contributing calcium, potassium, chlorine and sulfates. In the final analysis, the pH of precipitation is a measure of the relative contributions of all of these components (Whelpdale, 1978).

It is not presently clear as to when precipitation in the U.S. began to become markedly acidic. Some scientists argue that it began with the industrial revolution and the burning of large amounts of coal and others estimate that it began in the United States with the introduction of tall stacks in power plants in the 1950's. However, other scientists disagree completely and argue that rain has always been acidic. In other words, no definitive answer to the question exists at the present time. Also, insufficient data presently exist to characterize with confidence long-term temporal trends in changes in the pH of precipitation in the United States, mainly due to the pH of rain not having been continuously monitored over extended periods of time.

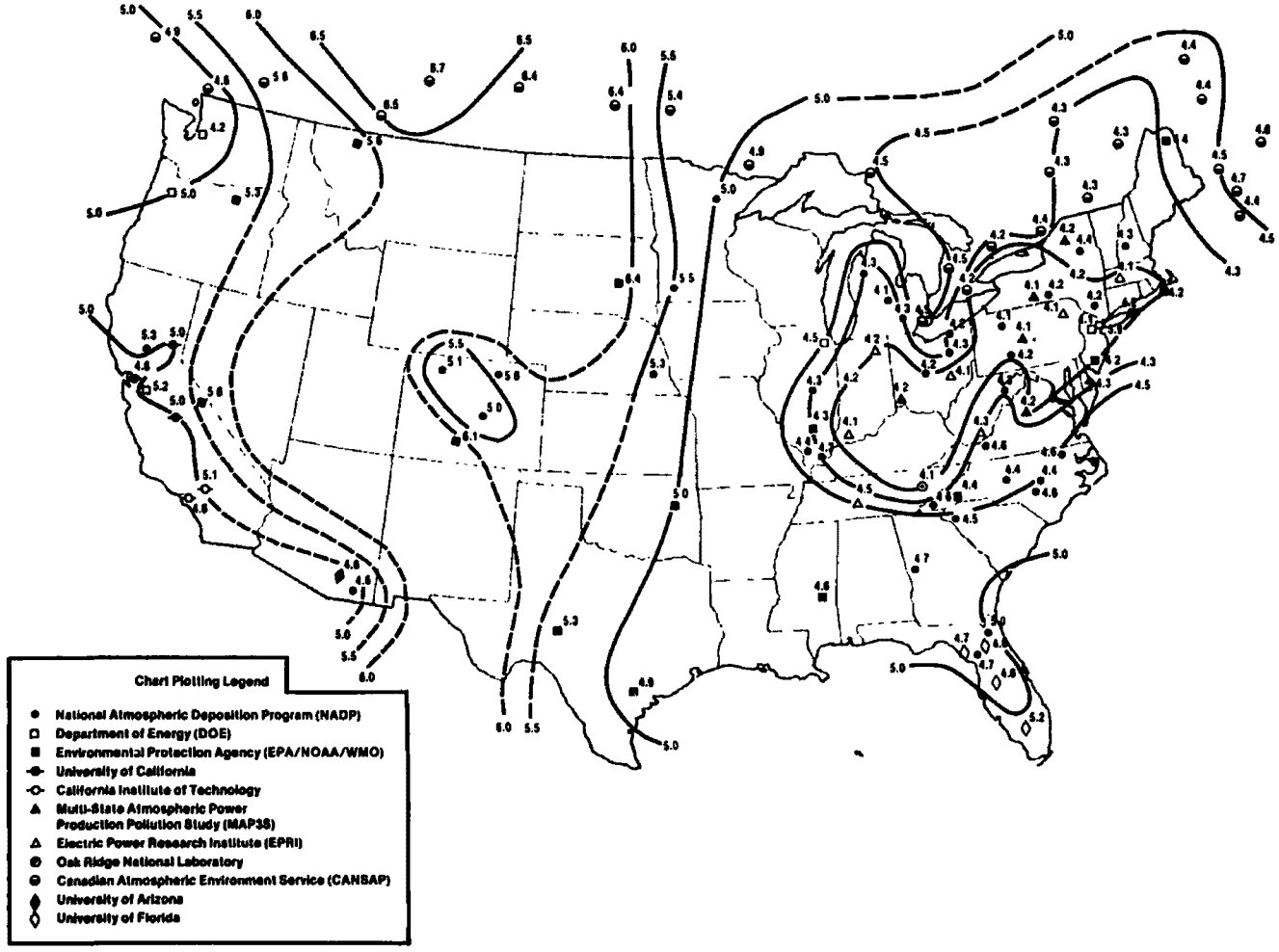

Figure 1-8. pH of rain sample as measured in the laboratory used in combination with the reported amount of precipitation.

Although acidic precipitation (wet deposition) is usually emphasized, it is not the only process by which acids or acidifying substances are added to bodies of water or to the land. Dry deposition also occurs. Dry deposition processes include gravitational sedimentation of particles, impaction of aerosols and the sorption and absorption of gases by objects at the earth's surface or by the soil or water. Dew, fog, and frost are also involved in the deposition processes but do not strictly fall into the category of wet or dry deposition (Galloway and Whelpdale, 1980; Schmel, 1980; Hicks and Wesley, 1980). Dry deposition processes are not as well understood as wet deposition at the present time; however, all of the deposition processes contribute to the gradual accumulation of acidic or acidifying substances in the environment.

The most visible changes associated with acidic deposition, that is both wet and dry processes, are those observed in the lakes and streams of the Adirondack Mountains in New York State, in Maine, in northern Florida, in the Pre-cambrian Shield areas of Canada, in Scotland, and in the Scandinavian countries. In these regions, the pH of the fresh water bodies has decreased, causing changes in animal and plant populations.

The chemistry of fresh waters is determined primarily by the geological structure (soil system and bedrock) of the lake or stream catchment basin, by the ground cover and by land use. Near coastal areas (up to 100 miles inland) marine salts also may be important in determining the chemical composition of the stream, river or lake. Sensitivity of a lake to acidification depends on the acidity of both wet and dry deposition plus the same factors--the soil system of the drainage basin, the canopy effects of the ground cover and the composition of the waterbed bedrock. The capability, however, of a lake and its drainage basin to neutralize incoming acidic substances is determined largely by the composition of the bedrocks (Wright and Gjessing, 1976; Galloway and Cowling, 1978; Hendrey et al., 1980). Soft water lakes, those most sensitive to additions of acidic substances, are usually found in areas with igneous bedrock which contributes few solids to the surface waters, whereas hard waters contain large concentrations of alkaline earths (chiefly bicarbonates of calcium and sometimes magnesium) derived from limestones and calcareous sandstones in the drainage basin. Alkalinity is associated with the increased capacity of lakes to neutralize or buffer the incoming acids. The extent to which acidic precipitation contributes to the acidification process has yet to be determined.

The survival of natural living ecosystems in response to marked environmental changes or perturbations depends upon the ability of constituent organisms of which they are composed to cope with the perturbations and to continue reproduction of their species. Those species of organisms most sensitive to particular environmental changes are first removed. However, the capacity of an ecosystem to maintain internal stability is determined by the ability of all individual organisms to adjust and survive, and other species or components may subsequently be impacted in response to the loss of the most susceptible species.

The capacity of organisms to withstand injury from weather extremes, pesticides, acidic deposition or polluted air follows the principle of limiting factors (Billings, 1978; Odum, 1971; Moran et al., 1980; Smith, 1980). According to this principle, for each physical factor

in the environment there exists for each organism a minimum and a maximum limit beyond which no members of a particular species can survive. Either too much or too little of a factor such as heat, light, water, or minerals (even though they are necessary for life) can jeopardize the survival of an individual and in extreme cases a species. The range of tolerance (see Figure 1-9) of an organism may be broad for one factor and narrow for another. The tolerance limit for each species is determined by its genetic makeup and varies from species to species for the same reason. The range of tolerance also varies depending on the age, stage of growth or growth form of an organism. Limiting factors are, therefore, factors which, when scarce or overabundant, limit the growth, reproduction and/or distribution of an organism.

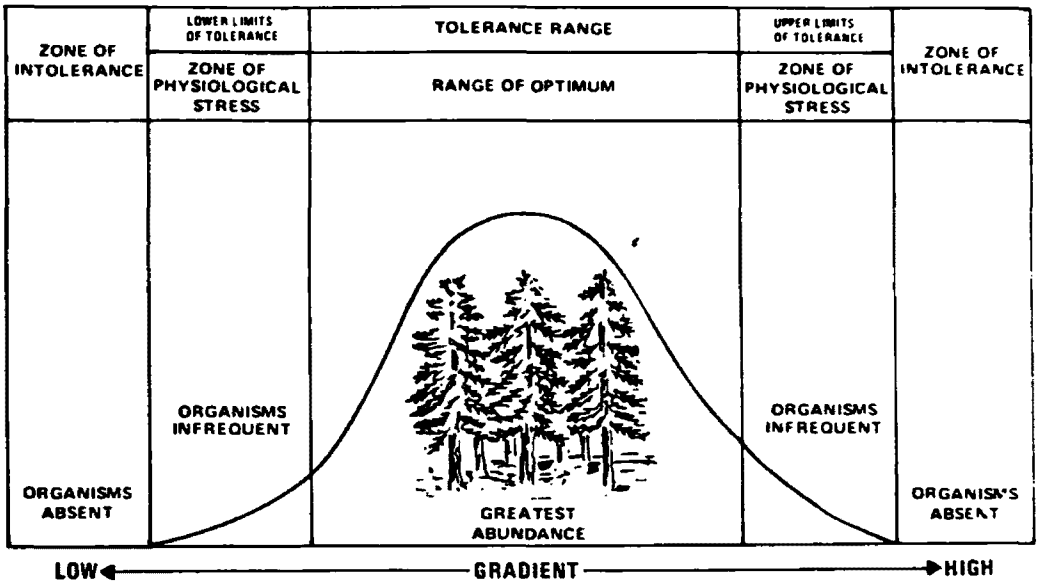

Figure 1-9. Idealized conceptual framework illustrating the "law of tolerance," which postulates a limited tolerance range for various environmental factors within which species can survive.

Source: Adapted from Smith (1980).

Continued or severe perturbation of an ecosystem can overcome its resistance or prevent its recovery, with the result that the original ecosystem will be replaced by a new system. In the Adirondack Mountains of New York State, in eastern Canada, and parts of Scandinavia the original aquatic ecosystems have been and are continuing to be replaced by ecosystems different from the original due to acidification of the aquatic habitat. Forest ecosystems, however, appear thus far to have been resistant to changes due to perturbation or stress from acidifying substances.

The impact of acidic precipitation on aquatic and terrestrial ecosystems is typically not the result of a single or several individual precipitation events, but rather the result of continued additions of acids or acidifying substances over time. Wet deposition of acidic substances on freshwater lakes, streams, and natural land areas is only part of the problem. Acidic substances exist in gases, aerosols, and particulate matter transferred into the lakes,

streams, and land areas by dry deposition as well. Therefore, all the observed biological effects should not be attributed to acidic precipitation alone.

The disappearance of fish populations from freshwater lakes and streams is usually one of the most readily observable signs of lake acidification. Death of fish in acidified waters has been attributed to the modification of a number of physiological processes by a change in pH. Two patterns related to pH change have been observed. The first involves a sudden short-term drop in pH and the second, a gradual decrease in pH with time. Sudden short-term drops in pH may result from a winter thaw or the melting of the snow pack in early spring and the release of the acidic constituents of the snow into the water.

Long-term gradual increases in acidity, particularly below pH 5, interfere with reproduction and spawning, producing a decrease in population density and a shift in size and age of the population to one consisting primarily of larger and older fish. Effects on yield often are not recognizable until the population is close to extinction; this is particularly true for late maturing species with long lives. Even relatively small increases (5 to 50 percent) in mortality of fish eggs and fry can decrease yield and bring about extinction.

In some lakes, concentrations of aluminum may be as crucial or more important than pH levels as factors causing a decline in fish populations in acidified lakes. Mobilization of certain aluminum compounds in the water upsets the osmoregulatory function of blood in fish. Aluminum toxicity to aquatic biota other than fish has not been assessed.

Although the disappearance of and/or reductions in fish populations are usually emphasized as significant results of lake and stream acidification, also important are the effects on other aquatic organisms ranging from waterfowl to bacteria. Organisms at all trophic (feeding) levels in the food web appear to be affected. Species reduction in number and diversity may occur, biomass (total number of living organisms in a given volume of water) may be altered and processes such as primary production and decomposition impaired.

Significant changes that have occurred in aquatic ecosystems with increasing acidity include the following:

1. Fish populations are reduced or eliminated.
2. Bacterial decomposition is reduced and fungi may dominate saprotrophic communities. Organic debris accumulates rapidly, tying up nutrients, and limiting nutrient mineralization and cycling.
3. Species diversity and total numbers of species of aquatic plants and animals are reduced. Acid-tolerant species dominate.
4. Phytoplankton productivity may be reduced due to changes in nutrient cycling and nutrient limitations.
5. Biomass and total productivity of benthic macrophytes and algae may increase due in part to increased lake transparency.
6. Numbers and biomass of herbivorous invertebrates decline. Tolerant invertebrate species, e.g., air-breathing insects may become abundant primarily due to reduced fish predation.
7. Changes in community structure occur at all trophic levels.

An indirect effect of acidification potentially of concern to human health is the possible contamination of edible fish and of water supplies. Studies in Canada and Sweden reveal high mercury concentrations in fish from acidified regions. Lead has been found in plumbing systems with acidified water, and persons drinking the water could be affected by the lead. However, no examples have yet been documented of such human effects having actually occurred in response to acidic precipitation processes.

Soils may become gradually acidified from an influx of hydrogen (H^+) ions. Leaching of the mobilizable forms of mineral nutrients may occur. The rate of leaching is determined by the buffering capacity of the soil and the amount and composition of precipitation. Unless the buffering capacity of the soil is strong and/or the salt content of precipitation is high, leaching will in time result in acidification. Anion mobility is also an important factor in the leaching of soil nutrients. Cations cannot leach without the associated anions also leaching. The capacity of soils to adsorb and retain anions increases as the pH decreases, when hydrated oxides of iron and aluminum are present.

Sulfur, like nitrogen, is essential for optimal plant growth. Plants usually obtain sulfur in the form of sulfate from organic matter during microbial decomposition. Wet and dry deposition of atmospheric sulfur is also a major source. In soils where sulfur and nitrogen are limiting nutrients, such deposition may increase growth of some plant species. The amounts of sulfur entering the soil system from atmospheric sources is dependent on proximity to industrial areas, the sea coast, and marshlands. The prevailing winds and the amount of precipitation in a given region are also important (Halsteand and Rennie, 1977). Near fossil-fueled power plants and industrial installations the amount of sulfur in precipitation may be as much as 150 pounds per acre (168 kg/ha) or more (Jones, 1975).

At present there are no documented observations or measurements of changes in natural terrestrial ecosystems or agricultural productivity directly attributable to acidic precipitation. The information available regarding vegetational effects concerns the results of a variety of controlled research studies, mainly using some form of "simulated" acidic rain, frequently dilute sulfuric acid. The simulated "acid rains" have deposited hydrogen (H^+), sulfate ($SO_4^=$) and nitrate (NO_3^-) ions on vegetation and have caused necrotic lesions in a wide variety of plants species under greenhouse and laboratory conditions. Such results must be interpreted with caution, however, because growth and morphology of leaves under such conditions are not necessarily typical of field conditions.

Damage to monuments and buildings made of stone, corrosion of metals and deterioration of paint may also result from acidic precipitation. Because sulfur compounds are a dominant component of acidic precipitation and are deposited during dry deposition as well, the effects resulting from the two processes cannot be clearly distinguished. Also, deposition of sulfur compounds on stone surfaces may provide a medium for microbial growth that can result in deterioration.

Several aspects of the acidic precipitation problem remain subject to debate because existing data are ambiguous or inadequate. Important unresolved issues include: (1) the rate at which rainfall is becoming more acidic and the rate at which the problem is becoming geographically more widespread; (2) the quantitative contributions of various acids to the overall acidity of rainfall; (3) the relative extent to which the acidity of rainfall in a region depends on local emissions of nitrogen and sulfur oxides versus emissions transported from distant sources; (4) the relative importance of changes in total mass emission rates compared to changes in the nature of the emission patterns (ground level versus tall stacks) in contributing to regional acidification of precipitation; (5) the relative contribution of wet and dry deposition to the acidification of lakes and streams; (6) the geographic distribution of natural sources of NO_x, SO_x and NH_3 and the significance and seasonality of their contributions; (7) the existence and significance of anthropogenic, non-combustion sources of SO_x, NO_x and HCl; (8) the dry deposition rates for SO_x, NO_2, sulfate, nitrate and HCl over various terrains and seasons of the year; (9) the existence and reliability of long-term pH measurements of lakes and headwater streams; (10) the acceptability of current models for predicting long range transport of SO_x and NO_x and for acid tolerance of lakes; (11) the feasibility of using liming or other corrective procedures to prevent or reverse acid damage and the costs of such procedures; (12) the effects of SO_x and NO_x and hydrogen ion deposition on ecosystem dynamics in both aquatic and terrestrial ecosystems; (13) the effectiveness of fertilization resulting from sulfate and nitrate deposition on soils; (14) the effects, if any, of acidic deposition on agricultural crops, forests and other native plants; and (15) the effects of acidic deposition on soil microbial processes and nutrient cycling. A more comprehensive evaluation of scientific evidence bearing on these issues is being prepared as part of a forthcoming EPA document on acidic deposition.

1.8 EFFECTS ON VEGETATION

The widespread occurrence of particulate matter, sulfur dioxide and other substances in the atmosphere frequently results in exposure of terrestrial vegetation simultaneously to these pollutants as well as other phytotoxic pollutants. More is known about the effects of sulfur dioxide on vegetation than about the effects of particulate matter. Studies of the effects of particulate matter have generally focused on the effects of heavy accumulations and the reduction in photosynthesis resulting from these accumulations. The more subtle effects of particulate matter on vegetation have not been extensively investigated and are, therefore, not well understood. Plant response following exposure to sulfur oxides and particulate matter in combination is even less well understood. Chapter 8 of this document discusses the effects of sulfur oxides and particulate matter on vegetation.

Sulfur dioxide and particulate sulfate are the main forms of sulfur in the atmosphere, and a plant may be exposed to these pollutants in several different ways. Dry deposition of particulate matter and wet deposition of gases and particles bring sulfur compounds into

contact with plant surfaces and soil substrates. The effects of such exposure are more difficult to assess than those associated with the entry of SO_2 through plant stomata.

Most sulfur dioxide enters leafy plants through the stomata (Chamberlain, 1980). After entering the stomata and passing into cells within the leaf, sulfur dioxide is converted to sulfite and bisulfite, which may then be oxidized to sulfate. Sulfate appears to be less toxic than sulfite and bisulfite. As long as the absorption rate of SO_2 in plants does not exceed the rate of conversion to sulfate, the only effects of exposure may be changes in opening or closing of stomata or undetectable changes in the biochemical or physiological systems. Such effects may abate if SO_2 concentrations are reduced. Both negative and positive influences on crop productivity have been noted following low-dose exposures.

Symptoms of SO_2-induced injury in higher plants may be quite variable since response is governed by pollutant dose (concentration x duration of exposure), the kinetics of the exposure (e.g., day vs. night, peak vs. long-term); the physiological status of the plant, the maturation stage of plant growth, environmental influences on the pollutant/plant interaction, and the environmental influences on the metabolic status of the plant itself. Although the product of time and concentration may remain constant, the effect of exposure may vary for a given dose. The relation of exposure to injury is generally more sensitive to changes in concentration than to changes in duration of exposure. Plant response to dynamic physical factors such as light, leaf surface moisture, relative humidity, and soil moisture may influence pollutant uptake through internal physiological changes as well as stomatal opening and closing and hence play a major role in determining sensitivities of species and cultivars or the time of sensitivity of each on a seasonal basis. Dose-response relationships are significantly conditioned by environmental conditions before, during, and following exposure to SO_2.

Plants may respond to exposures of SO_2 and related sulfur compounds in the following ways: (1) no detectable response, (2) increased growth and yield resulting from fertilization, (3) injury manifested as reductions in growth and yield without visible symptoms appearing on the foliage or with only very mild symptoms that would be difficult to perceive as induced by air pollution without comparing them with a control set of plants grown in pollution-free conditions, (4) injury exhibited as chronic or acute symptoms on foliage with or without associated reduction in growth and yield, and (5) death of plants and plant communities.

Under certain conditions, atmospheric SO_2 can have beneficial effects on agronomic vegetation (Noggle and Jones, 1979). The amount of sulfur accumulated from the atmosphere by leaf tissues is influenced by the amount of sulfur in soil relative to the sulfur requirement of the plant. After exposure to low doses of SO_2, plants grown in sulfur-deficient soils have exhibited increased productivity.

Some species of plants are sensitive to low concentrations of SO_2, and some of these plants may serve as bioindicators in the vicinity of major sources of SO_2. Even these sensitive species may be asymptomatic, however, depending on the environmental conditions before, during, and after SO_2 exposure. Various species of lichens appear to be among the most sensitive plants.

Because of space limitation, it is not possible to list all plants that are known to be sensitive to various doses of SO_2. It has also been demonstrated that plant response to air pollutants varies at the genus, species, variety, and cultivar levels. Lists of sensitive plants have been prepared on the basis of the expression of visible symptoms by any given plant. Analyses of injury expressed in terms of growth or yield losses, however, have been limited due to the relative lack of empirical data quantifying such losses in relation to SO_2 exposures.

Jacobson and Hill (1970) included a listing of plants sensitive to the major phytotoxic air pollutants. Linzon (1972) has listed 36 tree species as being tolerant, intermediate, and sensitive to SO_2. Many of these sensitivity lists have not attempted to identify the dose required to induce visible injury on indicator species. However, Jones et al. (1974) have published such details based upon observations over a 20-year period of 120 species growing in the vicinity of coal-fired power plants in the southeastern United States (Table 1-2).

TABLE 1-2. SULFUR DIOXIDE CONCENTRATIONS CAUSING VISIBLE INJURY TO VARIOUS SENSITIVITY GROUPINGS OF VEGETATION[a] (ppm SO_2)

Maximum average concentration	Sensitivity grouping		
	Sensitive ppm SO_2	Intermediate ppm SO_2	Resistant ppm SO_2
Peak	1.0-1.5	1.5-2.0	>2.0
1-hr	0.5-1.0	1.0-2.0	>2.0
3-hr	0.3-0.6	0.6-0.8	>0.8
	Ragweeds	Maples	White oaks
	Legumes	Locust	Potato
	Blackberry	Sweetgum	Upland cotton
	Southern pines	Cherry	Corn
	Red and black oaks	Elms	Dogwood
	White ash	Tuliptree	Peach
	Sumacs	Many crop and garden species	

[a]Based on observations over a 20-year period of visible injury occurring on over 120 species growing in the vicinities of coal-fired power plants in the southeastern United States. Source: Jones et al., 1974.

McLaughlin (1980) used symptom data as collected by Dreisinger and McGovern (1970) on 31 species of forest and agricultural plants following SO_2 exposure and plotted the average, maximum, and minimum tolerances of individual species (Figure 1-10). The injury threshold for most sensitive plants was 0.41, 0.37, 0.28, and 0.12 ppm SO_2 at averaging intervals of 1, 2, 4, and 8 hours, respectively.

As SO_2 exposure levels increase, plants develop more predictable and more obvious visible symptoms. Foliar symptoms advance from chlorosis or other types of pigmentation changes to necrotic areas and the extent of necrosis increases with exposure. Studies of the effects of SO_2 on growth and yield have demonstrated a reduction in the dry weight of foliage, shoots, roots, and seeds, as well as a reduction in the number of seed. At still higher doses, reductions in growth and yield increase. Extensive mortality has been noted in forests continuously exposed to SO_2 for many years.

The presence of acute or chronic foliar injury is not necessarily associated with growth or yield effects. Furthermore, the degree of foliar injury, when present, may not always be a reliable indicator of subsequent growth or yield effects.

Plant response to SO_2 may occur at many levels. However, two parameters, visible damage to foliage and plant productivity, provide the most functional basis for evaluating response. Both can be quantified as a "cost" to economic or ecological performance of many plant species.

Dose-response relationships involving visible injury may be expressed in terms of the level of injury (percent leaf area destroyed) produced for a single species, or as the upper and lower limits of sensitivity of a group of species. The latter approach is presented here because it provides data more applicable to responses of plant populations and because of the difficulties in quantifying a dependable relationship between degree of visible injury and growth responses (see Section 8.2.7). Data on generalized concentrations at which sensitive, intermediate, and resistant species may be injured by SO_2 were presented earlier in Table 1-2. In Figure 1-10, the data of Dreisinger and McGovern (1970) are graphed to show upper and lower concentration limits of susceptibility of 31 species of herbs, trees, and shrubs to visible foliar injury. Plotted as a function of SO_2 concentration and exposure time, these data demonstrate a number of important points. First, the most sensitive plants at each concentration were injured at SO_2 levels 6 to 7 times lower than the most resistant plants; secondly, the dose or product of concentration x time (ppm-hr) required to cause injury was 30 to 60 percent lower for 1-hr than 8-hr exposures. This emphasizes the importance of differences in exposure duration when comparing specific degrees of injury associated with different exposure concentrations. Finally, exposure to SO_2 at 0.5 ppm for 3 hr represents a rather close estimate of the injury threshold for about 50 percent of the species studied.

A second approach to defining dose-response relationships focuses on the numbers of individuals in a plant population which may be injured as function of exposure concentration. As an example, a "worst-case" situation of SO_2 exposures and vegetation effects near a rural coal-fired power plant in the southeastern United States provides some interesting data

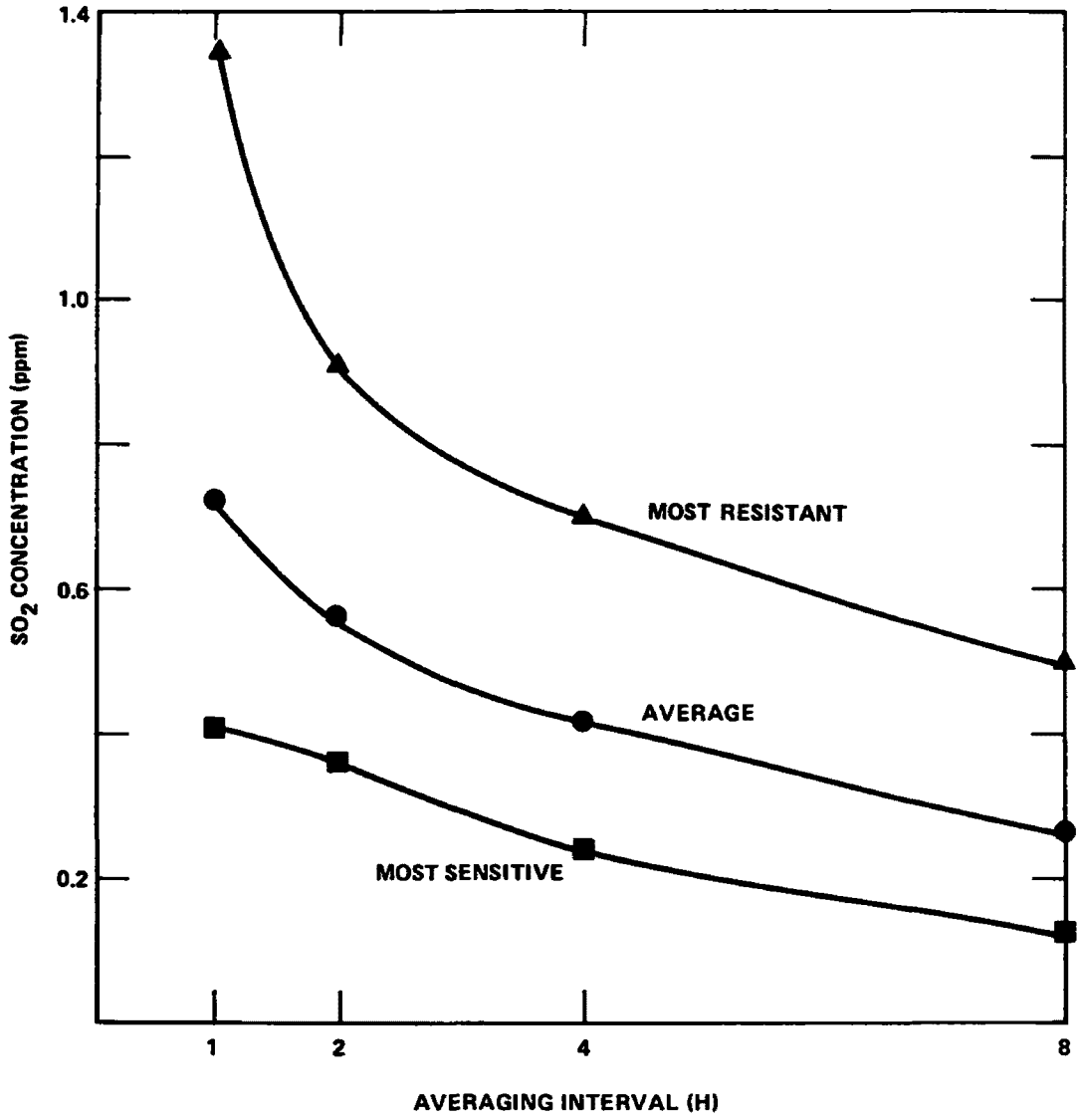

Figure 1-10. Exposure thresholds for minimum, maximum, and average sensitivity of 33 plant species to visible foliar injury by SO_2.

Source: Dreisinger and McGovern (1970) as applied by McLaughlin (1980).

(McLaughlin and Lee, 1974). During the period 1970-1973 (before partial sulfur scrubbing and stack elevation improved surrounding air quality), surveys of vegetation in the vicinity of this plant documented foliar injury of 84 plant species growing in the vicinity of continuous SO_2 monitoring stations. Plotting of these data (Figure 1-11) as a function of exposure

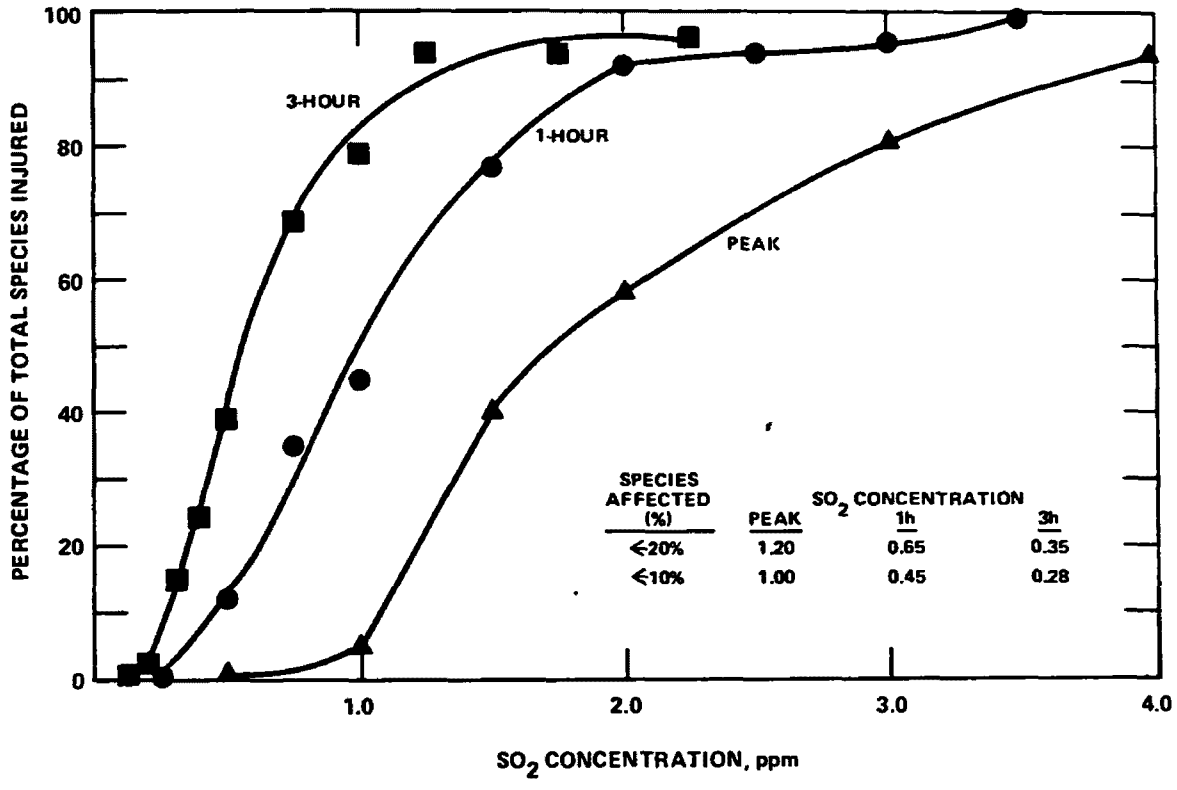

Figure 1-11. Percentage of plant species visibly injured as a function of peak, 1-hour, and 3-hour SO_2 concentrations.
Source: McLaughlin and Lee (1974); McLaughlin (1980).

concentration provides an index of probability of injury of species in a plant community as a function of SO_2 concentration. Note, for example, 10 percent of the plant population (here 8 of 84 species) is injured at peak, 1-hr, and 3-hr concentrations of ≅1.00, ≅0.50, and ≅0.30 ppm.

For agricultural crops, data on SO_2 effects on plant growth and yield, in most cases, provide the most relevant basis for studying dose-response relationships. As a whole-plant measurement, plant productivity is an integrative parameter which considers the net effect of multiple factors over time. Productivity data are presently available for a wide range of species under a broad range of experimental conditions. Because results would not be expected to be closely comparable across these sometimes divergent experimental techniques, data have been tabulated separately for controlled field exposures (see Chapter 8, Table 8-3), laboratory studies with agronomic and horticultural crops (see Chapter 8, Table 8-4) and tree species (see Chapter 8, Tables 8-5 and 8-6), and a variety of studies with native plants (see Chapter 8, Table 8-7).

Many presently available dose-response data sets have been derived from studies of controlled exposures in the laboratory or in field chambers. In spite of the variety of species studied and experimental protocols utilized, it is possible to derive potentially useful generalizations from these data:

(1) The concentration threshold for visible injury is generally lower than the threshold for effects on growth and yield, especially for acute exposure effects. Doses causing visible injury to 10 percent of a variety of southeastern plant species were 0.30 ppm for a 3-hr exposure and 0.50 for a 1-hr exposure.

(2) Visible injury data emphasize the greater relative biological effectiveness of short-term higher concentrations than longer exposures with the same total dose.

(3) Plant responses to SO_2 may be positive, neutral, or negative over a rather wide range of exposure dose. Positive responses were generally restricted to a very few species or conditions when plants were known to have been grown in sulfur-deficient soils. Negative responses constituted approximately 85 percent of all responses noted above threshold levels for visible injury.

(4) Data derived from continuous or intermittent controlled chronic exposures ($\geq$4 weeks) of six species or cultivars in field chambers provided a basis for estimating yield responses from total logarithmically transformed exposure dose. Regression analysis of these data provided a no-effects limit of approximately 6.0 ppm-hr. Yield losses of 10 percent and 20 percent were similarly estimated at 10 and 27 ppm-hr, respectively.

(5) An attempt to analyze data from 23 species or cultivars from laboratory and greenhouse exposures generally indicated greater sensitivity than the six species or cultivars tested in the field (above). A boundary line which delimited the maximum observed response over the range of concentrations employed indicated that upper-limit yield losses were approximately 10 percent and 20 percent for exposure doses of 0.9 and 17 ppm-hr, respectively. Average responses determined by regression analysis indicated that 10 and 20 percent yield losses would be produced by exposures of 0.6 ppm-hr and 4.5 ppm-hr, respectively.

In interpreting the dose-response information, it should be noted that responses of plants to SO_2 in the field may occur as a consequence of one or more short-term episodes or as a result of the cumulative dose experienced over an entire growing season. Regression analysis of data from both controlled exposures in field chambers and from laboratory and greenhouse studies showed positive and statistically significant correlations between degree of yield loss and logarithmically transformed exposure dose in ppm-hr. The plants and conditions utilized in field studies, which were heavily oriented toward crop plants, provided generally lower yield losses for the same exposure dose than did laboratory and greenhouse studies.

A critical need in evaluating the likelihood of adverse effects occurring in association with longer-term SO_2 exposures is the identification of the fraction of the total SO_2 exposure

which may constitute a stress to plant growth and development. A review of dose-response data indicates that this level may be approximately 0.05 ppm for some sensitive crop species or lower (≅0.02 ppm) for certain types of sensitive native vegetation (e.g., pines and lichens) under field conditions. Data from studies involving SO_2 alone and in combination with other pollutants may provide a more accurate basis for determining this level.

At present, data concerning the interactions of SO_2 with other pollutants indicate that, on a regional scale, SO_2 occurs at least intermittently at concentrations high enough to produce significant interactions with other pollutants, principally O_3. A major weakness in the approach to pollutant interactions, however, is the lack of in-depth analysis of existing regional air quality data sets for the three principal pollutants (SO_2, O_3, and NO_2). These data should determine how frequently and at what concentrations the pollutants occur together both spatially and temporally within regions of major concern. The relative significance of simultaneous versus sequential occurrence of these pollutants to effects on vegetation is also not well documented and is critical in evaluating the likelihood and extent of potential pollutant interactions under field conditions.

A few studies have reported that combinations of particulate matter and SO_2, or particulate matter and other pollutants, increase foliar uptake of SO_2, increase foliar injury of vegetation by heavy metals, and reduce growth and yield. Because of the complex nature of particulate pollutants, conventional methods for assessing pollutant injury to vegetation, such as dose-response relationships, are poorly developed. Studies have generally reported vegetational responses relative to a given source and the physical size or chemical composition of the particles. For the most part, studies have not focused on effects associated with specific ambient concentrations. Coarse particles such as dust directly deposited on the leaf surfaces result in reduced gas exchange, increased leaf surface temperature, reduced photosynthesis, chlorosis, reduced growth, and leaf necrosis. Heavy metals deposited either on leaf surfaces or on the soil and subsequently taken up by the plant can result in the accumulation of toxic concentrations of the metals within the tissue.

Natural ecosystems are integral to the maintenance of the biosphere and disturbances of stable ecosystems may have long-range effects which are difficult to predict. Within the United States anthropogenic contributions to atmospheric sulfur exceed natural sources and in the Northeast, approximately 60 percent of the anthropogenic emissions into the atmosphere are deposited (wet and dry deposition) on terrestrial and aquatic ecosystems. The fate and distribution of anthropogenic sulfur deposited in these systems is not well understood. Wet deposition of sulfur compounds is discussed in Chapter 7.

Data relating ecosystem responses to specific doses of SO_2 and other pollutants are difficult to obtain and interpret because of the generally longer periods of time over which these responses occur and because of the many biotic and abiotic factors which modify them.

Vegetation within terrestrial ecosystems is sensitive to SO_2 toxicity, as evidenced by changes in physiology, growth, development, survival, reproductive potential and community

composition. Indirect effects may occur as a result of habitat modification through influences on litter decomposition and nutrient cycling or through altered community structure. At the community level chronic exposure to SO_2, particularly in combination with other pollutants such as O_3, may cause shifts in community structure as evidenced by elimination of individuals or populations sensitive to the pollutant. Differential effects on individual species within a community can also occur through direct effects on sensitive species and through alteration of relative competitive potential of species with which they compete within the plant community.

Particulate emissions have their greatest impact on terrestrial ecosystems near large emission sources. Particulate matter in itself constitutes a problem only in those few areas where deposition rates are very high. Ecological modification may occur if the particles contain toxic elements, even though deposition rates are moderate. Solubility of particle constitutents is critical, since water-insoluble elements are not mobile within the ecosystem. Most of the material deposited by wet and dry deposition on foliar surfaces in vegetated areas is transferred to the soil where accumulation in the litter layer occurs.

1.9 EFFECTS ON VISIBILITY AND CLIMATE

Atmospheric visibility is often used by airport weather observers and others to connote visual range. Visual range is generally defined as the farthest distance at which one can see a large, black object against the horizon sky. In the everyday sense, however, visibility relates to the perceived characteristics of viewed surroundings including contrast and color of objects and sky and atmospheric clarity. Pollution-derived effects on visibility can be classified as: (1) coherent plumes or haze layers visible because of contrast with background, (2) widespread, relatively homogeneous haze that reduces contrast of viewed targets and reduces visual range. The kind and degree of effects are determined by the distribution and characteristics of atmospheric particulate matter and nitrogen dioxide, which scatter and absorb light.

Reductions in visibility can adversely affect transportation safety, property values, and aesthetics. When visibility (visual range) drops below 3 miles, FAA regulations restrict flight in controlled air to those aircraft equipped with IFR instrumentation. Assessment of the social, psychological, and economic value of visibility is difficult. Preliminary studies of the economic value of visibility conducted in both urban and non-urban settings show promise but are currently too limited and premature to permit any large-scale evaluation.

Current U.S. visibility as indicated by regional airport visual range data is depicted in Figure 1-12. Such human observations are subject to some limitations, but the data indicate regional trends. The best visibility occurs in the mountainous Southwest where annual median visibility exceeds 70 miles (110 km). East of the Mississippi and south of the Great Lakes annual median visibilities are less than 15 miles (24 km) and are significantly lower in the summer time, particularly during periodic episodes of regional haze.

On a regional scale, visibility reduction is generally dominated by light scattering and by fine particles, particularly those in the 0.1 to 2 μm size range. In urban areas, absorption of light by fine carbanaceous particles and, to a lesser extent, NO_2 can become important.

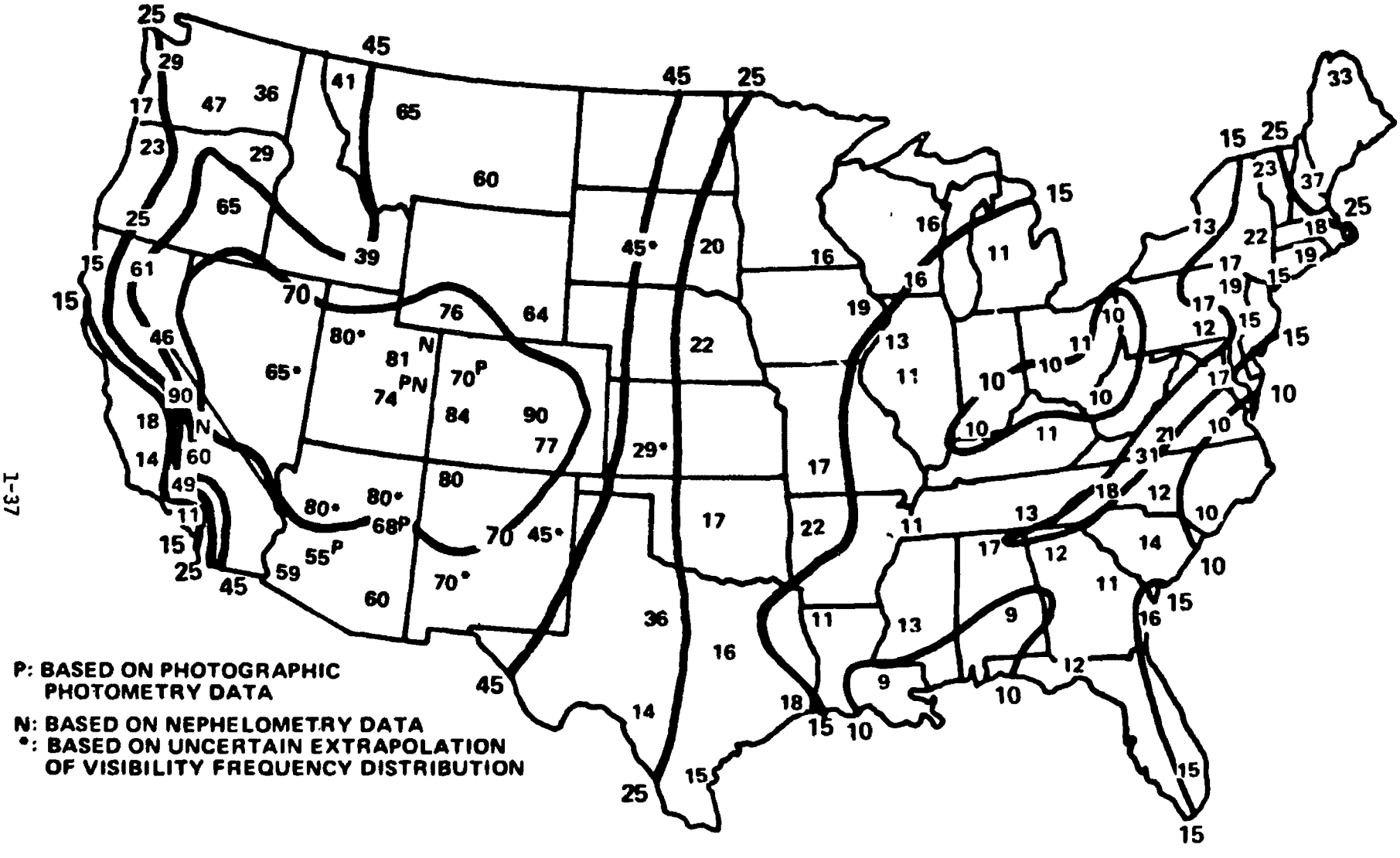

Figure 1-12. Map shows median yearly visual range (miles) and isopleths for suburban/nonurban areas, 1974-1976.

Source: Trijonis and Shapland (1978).

*
Total extinction is the sum of scattering and absorption by pollutants and Rayleigh or "blue sky" scatter by air molecules. Visual range is inversely related to total extinction and can be estimated, if extinction is known, by the Koschmieder relationship (see Figure 1-13). Because extinction is wavelength and sun angle dependent, particle-derived haze may appear bluish, white, grey, or brown under varying conditions.

Extinction due to scattering is closely proportional to the fine particle mass concentration (Figure 1-14) with typical extinction/mass ratios (for <70 percent humidity) in the range of 0.003 to 0.005 $km^{-1}/\mu g/m^3$. Measurements in general areas suggest that the extinction due to fine particle scattering will increase by a factor of two to three as relative humidity is increased from 70 to 90 percent. This is due to absorption of atmospheric water vapor by aerosol constituents such as sulfates. The major constituents of fine particles from natural and anthropogenic sources contribute in varying degrees to visibility impairment. Theoretical and empirical results suggest that two constituents, sulfates and elemental carbon, generally tend to be most significant. Sulfate, with associated ammonium and water, often dominates the fine mass and visibility impairment, while elemental carbon can be a major visibility-reducing specie in urban areas. Significant variations can occur at different times and sites. Our knowledge of the roles of several possibly important species such as organics is hindered by the lack of sufficient good data.

Studies of trends in Eastern airport visibility indicate that, while wintertime visibilities improved in some Northeastern locations, overall Eastern visibility declined (Figure 1-15). Summer, often the season of best visibility in the early fifties, is currently the worst season. From 1948 to 1974, summertime haze (extinction) increased by more than 100 percent in the central Eastern States, by 50 to 70 percent for the Midwest and Eastern sunbelt States, and by 10 to 20 percent for the New England area. Although the results of airport surveys should be viewed with caution, the results are consistent from site to site. Similarities exist in the long-term record of the spatial and seasonal trends in airport visibility and trends in sulfates, point source sulfur oxides emissions, and coal use. These similarities suggest, but do not prove, that historical visibility trends in the East were caused, at least in part, by regional sulfur oxides emissions and resultant sulfate aerosols.

The currently available visibility monitoring methods measure different aspects of visibility impairment. Generally, contrast type measurements (such as photography, telephotometry, and human eye observations) relate well to the perception of visual air quality, while extinction or scattering measurements (such as transmissometry and nephelometry) relate to the cause of visibility degradation. Each of the above measurement methods can be used to approximate visual range. No single method has been proven totally effective in measuring light absorption. The methods used thus far include determining the difference between extinction and scattering, several filtering methods, and a refractive index method.

The longer residence time and light attenuating properties of fine particles may also lead to slow and subtle changes in the nature of the atmosphere and, possibly, in climate. For

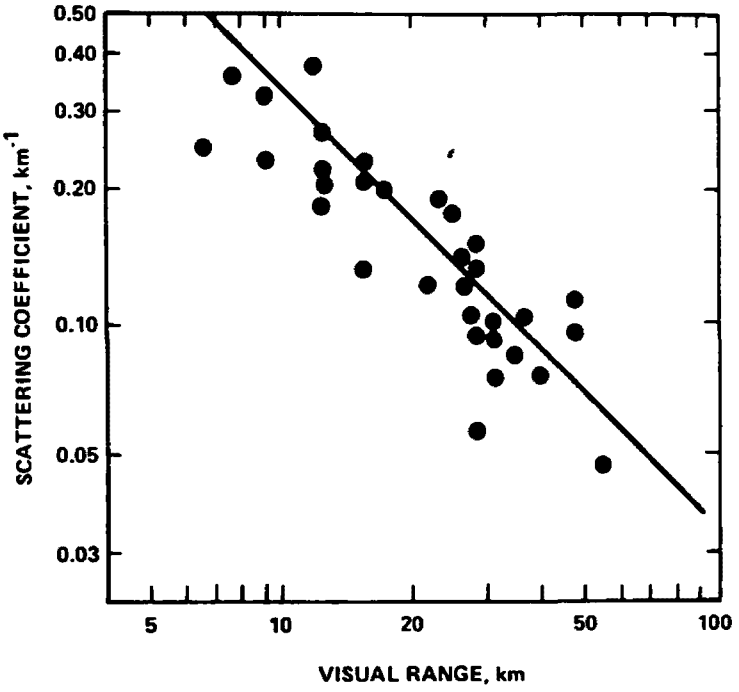

Figure 1-13. Inverse proportionality between visual range and the scattering coefficient, b_{scat}, was measured at the point of observation. The straight line shows the Koschmieder formula for non-absorbing ($b_{ext} = b_{scat}$) media. $V = 3.9/b_{scat}$. The linear correlation coefficient for V and $1/b_{scat}$ is 0.89.

Source: Horvath and Noll (1969).

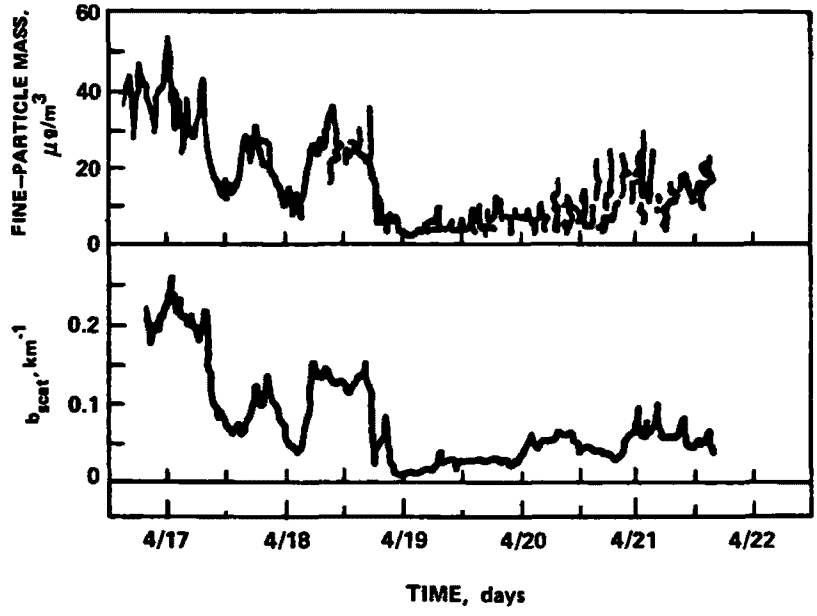

Figure 1-14. Simultaneous monitoring of b_{scat} and fine-particle mass in St. Louis in April 1973 showed a high correlation coefficient of 0.96, indicating that b_{scat} depends primarily on the fine-particle concentration.

Source: Macias and Husar (1976).

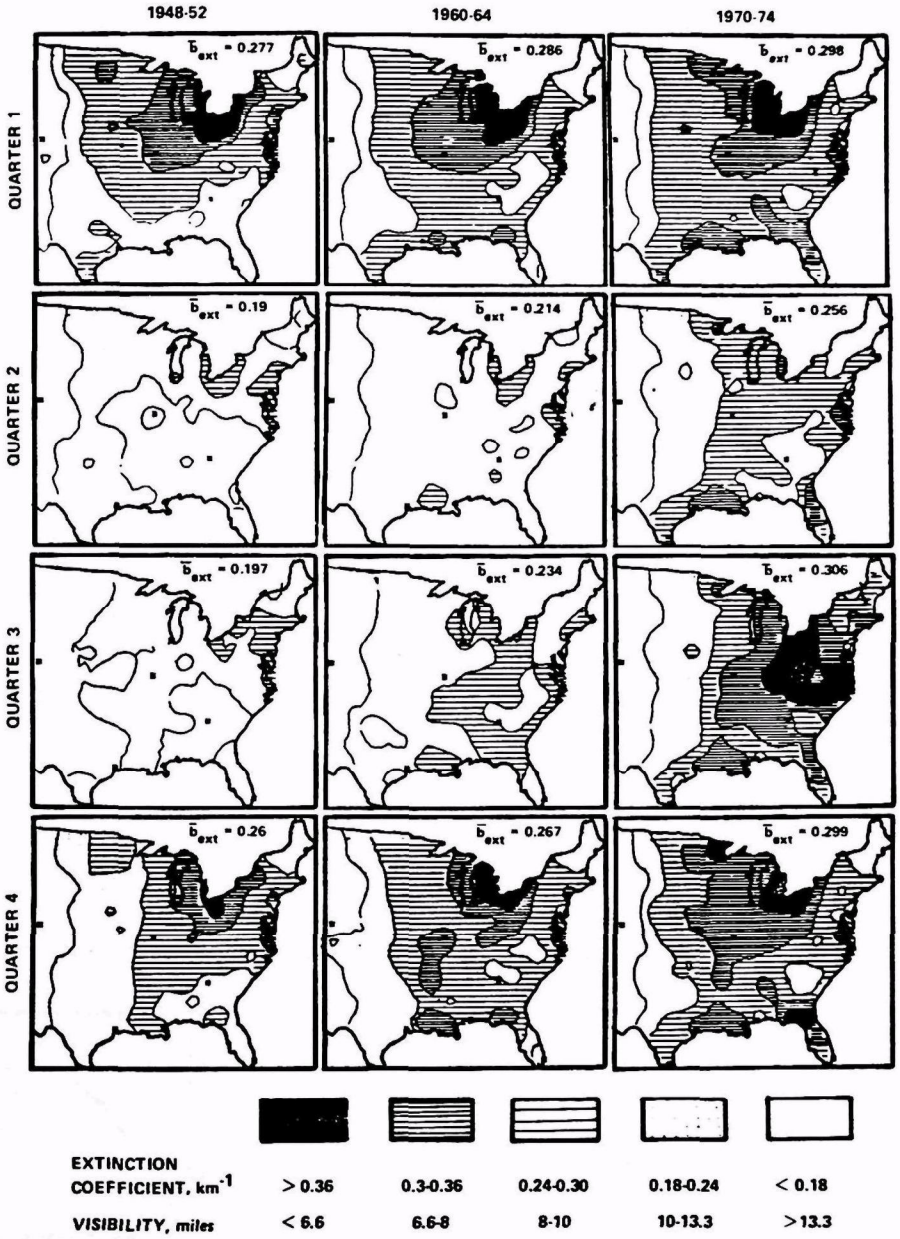

Figure 1-15. The spatial distribution of 5-year average extinction coefficients shows the substantial increases of third-quarter extinction coefficients in the Carolinas, Ohio River Valley, and Tennessee-Kentucky area. In the summers of 1948-52, a 1000-km size multistate region centered around Atlanta, GA, had visibility greater than 15 miles; visibility has declined to less than 8 miles by the 1970's. The spatial trend of winter (first quarter) visibility shows improvements in the Northeast megalopolis region and some worsening in the Sunbelt region. Both spring and fall quarters exhibit moderate but detectable increases over the entire eastern United States.

Source: Husar et al. (1979).

example, a fraction of the solar radiation may be absorbed by aerosols, further reducing the amount of radiation reaching the earth's surface and, at the same time, heating the aerosol layer itself. On a hazy day, the direct solar radiation is reduced to about one-half of that on a clear day, but most of the energy reappears as diffuse skylight. However, there is an overall loss of up to about 10 to 20 percent of the radiation reaching the surface.

If there are no clouds between the observer and the sun, the intensity of direct solar radiation for a given solar elevation depends on the variable amount of dust, haze, and water vapor in the atmosphere. The extinction produced by these constituents is called "atmospheric turbidity." During hazy episodes, turbidity coefficients of 0.6 to 1.0 are often reported, resulting in a condition in which 75 to 90 percent of the solar radiation is removed from the direct beam, 7.5 to 18 percent is lost to space and 7.5 to 18 percent is lost as atmospheric heating. One of the consequences of such a hazy atmosphere is the disappearance of shadow contrast. Long-term trends in atmospheric turbidity in the eastern U.S. are qualitatively consistent with those for airport visibility (Figure 1-16).

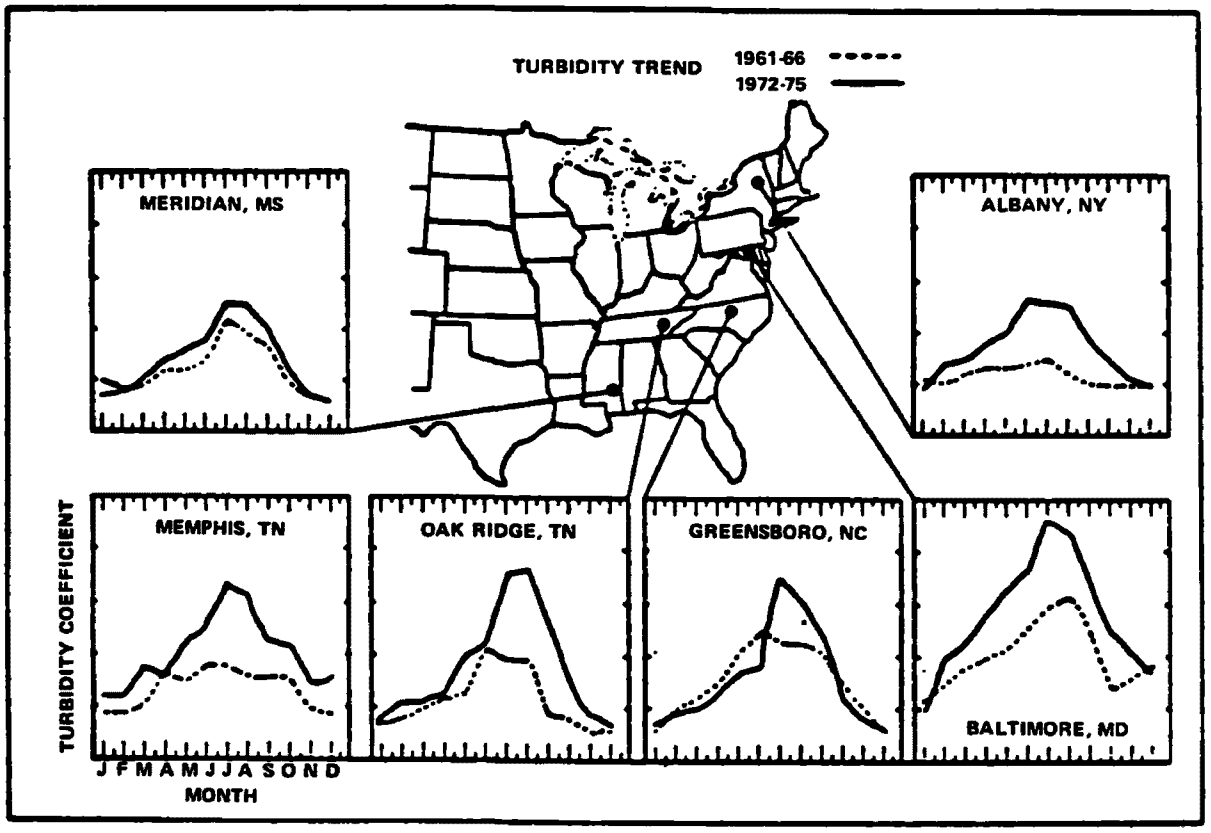

Figure 1-16. Seasonal turbidity patterns for 1961-66 and 1972-75 are shown for selected regions in the Eastern United States.

Source: Flowers et al. (1969).

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The attenuation of solar radiation from scattering and absorption by particles in the atmosphere is probably an important factor in climatic change on all scales. On local scales associated with urban and industrial areas, any significant attenuation of radiation by air pollution can, in addition to other well-recognized factors, result in changes in local weather. It is possible that local- and regional-scale changes in solar radiation caused by human activity may ultimately influence the heat and water vapor content of the atmosphere on very large scales, but solar radiation and aerosol levels measured at stations remote from pollutant sources have not as yet displayed any trend that can be related to human activity.

Cloud- and precipitation-forming processes may be divided into two broad classes: macrophysical and microphysical processes. Macrophysical processes involve the rise and descent of air masses and the amount of water vapor available for condensation. Atmospheric aerosols, primarily those that are strongly hygroscopic, influence the microphysics of cloud formation. The incorporation of particles into rain and fog droplets can change the "quality" of precipitation by changing its chemical composition. However, the complex interactions of cloud- and precipitation-forming processes obscure the specific role of manmade aerosols.

1.10 EFFECTS ON MATERIALS

The nature and extent of physical damage to materials by sulfur oxides and particulate matter have been investigated by field and laboratory studies. Various approaches are used to estimate economic damage; economic determinations may directly relate ambient pollutant levels to economic damage estimates or may estimate economic damage based on physical damage functions. The latter method of determination, termed here the physical damage function approach, has been the past method of choice. Other studies, especially in the last decade, have employed the first approach. Both approaches share a common element--an estimation of willingness to pay.

Physical damage function approaches have been most widely used and, therefore, have received the most extensive treatment. The damage function, which is a mathematical expression linking exposure to damage, is expressed in terms appropriate to the interaction of the pollutant and material. For example, corrosion of metal would be expressed in units of thickness lost, and deterioration of paint in units of reflectance or thickness lost. A major problem in establishing reliable damage functions involves separating influences of the target pollutant from that of meteorological parameters, (e.g., temperature, relative humidity, sunlight, wind speed, wind direction) and other air pollutants. For the corrosion of metals, time of wetness is the most important variable.

Economic valuations may require determinations of a critical damage level. This level represents the point at which the service life or utility of the material ends or is severely impaired. When this point is reached, replacement or repair costs are incurred. For example, if a typical coat of paint is 60 μm thick, the critical damage level at which repainting is necessary may be about 50 μm. Monetary value is determined through economic damage functions which may be developed from physical damage functions. This approach includes exposure, replacement cost, protection cost, and other data, but it cannot account for damage to irre-

placeable items, such as works of art, where the only measurable cost is that of preservation. However, only a few of the functions developed to date are relatively reliable in determining damage and none has been generally accepted for estimating costs.

The best documented and most significant damage from sulfur oxides and particulate matter involves: acceleration of metal corrosion; erosion and soiling of paint; and soiling of buildings and other structures. Erosion of stone and other building materials due to sulfur oxides is also well established, but the importance of sulfur oxides relative to other pollutants is not clear. Although evidence of damage to fibers (cotton and nylon), paper, leather and electrical components has been reported, reliable damage functions have not been developed.

There are some general conclusions which may be drawn from studies discussed in more detail in Chapter 10. As noted above, it has been clearly established that increases in sulfur oxide concentrations accelerate corrosion. Table 1-3 displays damage functions developed for effects of SO_2 on zinc, steel, and house paint. These equations and the data from which they are derived show that temperature and total suspended particulate matter are relatively unimportant factors in metal corrosion, and that the most important factor is surface wetness (Schwartz, 1972, Barton and Bartonova, 1969, Sydberger and Ericsson, 1976, and Haynie and Upham, 1974). Corrosion will not take place when the metal surface is not wet. This dominating factor is usually approximated by a "time-of-wetness" term, that is, the amount of time the relative humidity exceeds some critical humidity; critical humidities have been identified for various metals. There are, of course, several sources of moisture: rain, snow, fog, condensation; but relative humidity is the usual proxy for contribution of moisture to the surface from all sources. Metal corrosion initiated by surface wetness is accelerated by sulfur dioxide. Increase in either sulfur dioxide concentration or relative humidity is accompanied by increase in rate of corrosion. The relative importance of the two factors in corrosion acceleration is shown in Figures 1-17 and 1-18, which reflect analysis of field data by Haynie and Upham (1976). As shown in the figures, a 100 percent increase in average sulfur dioxide concentration has about the same effect as a 10 percent increase in relative humidity above a critical humidity. In some areas of the country (see Figure 1-19) this humidity level is usually exceeded; in others, rarely.

This fact has obvious and major implications for the probability of producing an accurate aggregated national estimate of damage to metals related to SO_2 exposure. Average annual relative humidity can vary 10 percent even within one region of the country; for instance, included in the data base for Figures 1-17 and 1-18 are average relative humidities of 29 and 39 percent for Las Vegas and Phoenix, respectively. The range in RH for all 57 sites (covering 34 states and the District of Columbia) was 29 to 76 percent. Average sulfur dioxide concentrations measured at these sites ranged from 9 $\mu g/m^3$ to 374 $\mu g/m^3$ during the same period. As noted by Haynie and Upham (1976), this wide variation is useful and desirable in regression analysis for development of damage functions, but is quite the opposite in estimates of aggregate damage. Not only do both relative humidity and SO_2 concentrations vary spatially,

TABLE 1-3. SELECTED PHYSICAL DAMAGE FUNCTIONS RELATED TO SO_2 EXPOSURE

Material	Reference	Dose-Response relationships	R^2
Zinc	Haynie and Upham, 1970	$Y = 0.001028\ (RH - 48.8)\ SO_2$	0.92
Galvanized steel	Haynie et al., 1976	$corr = (0.0187\ SO_2 + e^{41.85 - 23{,}240/RT})t_w$	0.91
Galvanized steel	Haynie, 1980	$corr = 2.32\ t_w + 0.0134 v^{0.781} SO_2 t_w$	
Oil-base house paint	Spence et al., 1975	$Y = 14.3 + 0.0151\ SO_2 + 0.388\ RH$	0.61
Enameling steel	Haynie and Upham, 1974	$corr = 325\ t^{\frac{1}{2}}\ e^{(0.00275\ SO_2 - 163.2/RH)}$	
Weathering steel	Haynie et al., 1976	$corr = [5.64\ \sqrt{SO_2} + e^{(55.44 - 31{,}150/RT)}]\ \sqrt{t_w}$	0.91

corr = corrosion, μm
Y = corrosion/erosion rate, μm/yr
SO_2 μg/m^3
R ≡ gas constant (1.98 cal/gm mol/°K)
RH = percent average annual relative humidity

t_w = time-of-wetness in years
v = wind velocity in m/s
T ≡ °K
t ≡ time of exposure, years

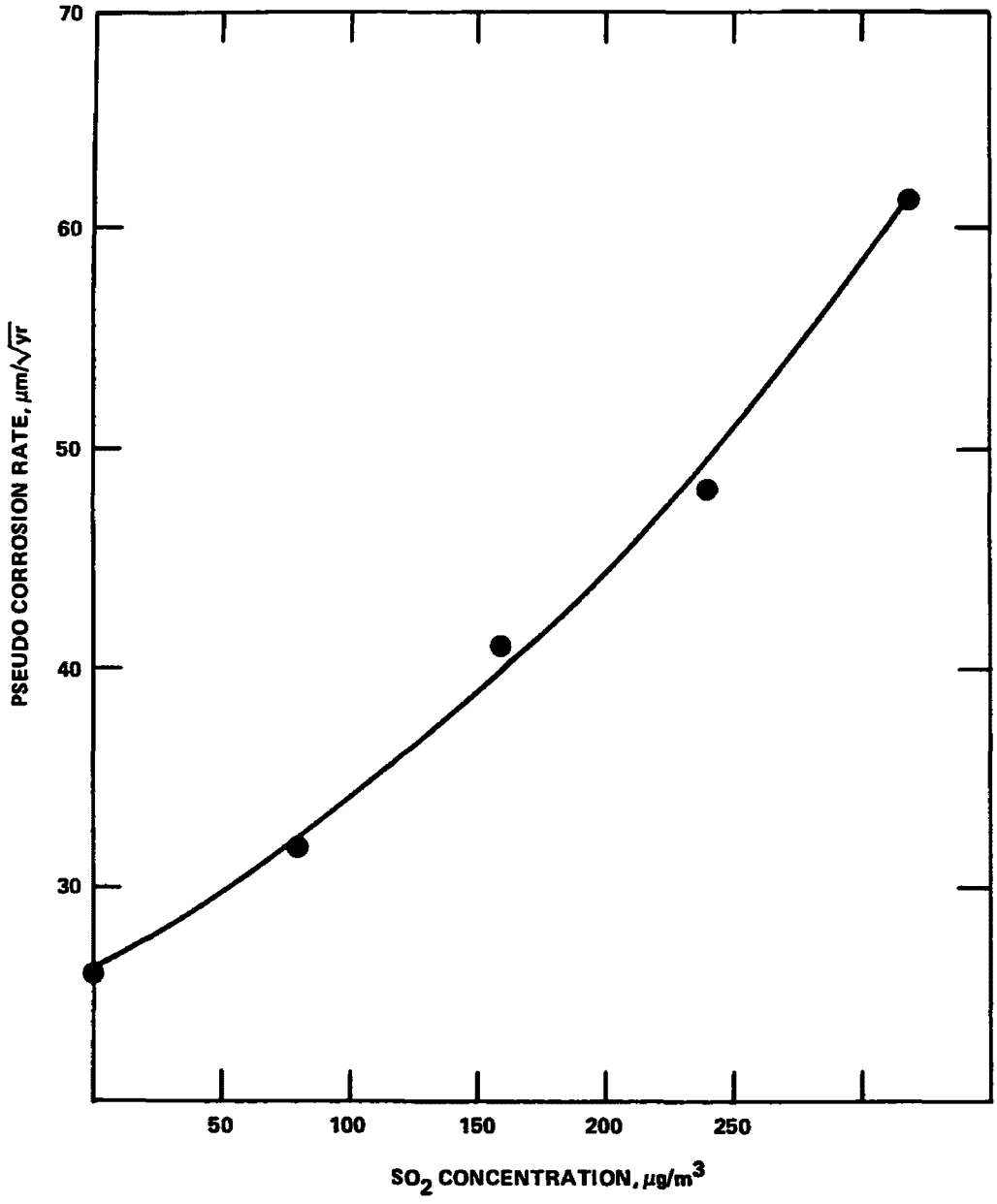

Figure 1-17. Steel corrosion behavior is shown as a function of average SO_2 concentration at 65% relative humidity.

Source: Adapted from Haynie and Upham (1974).

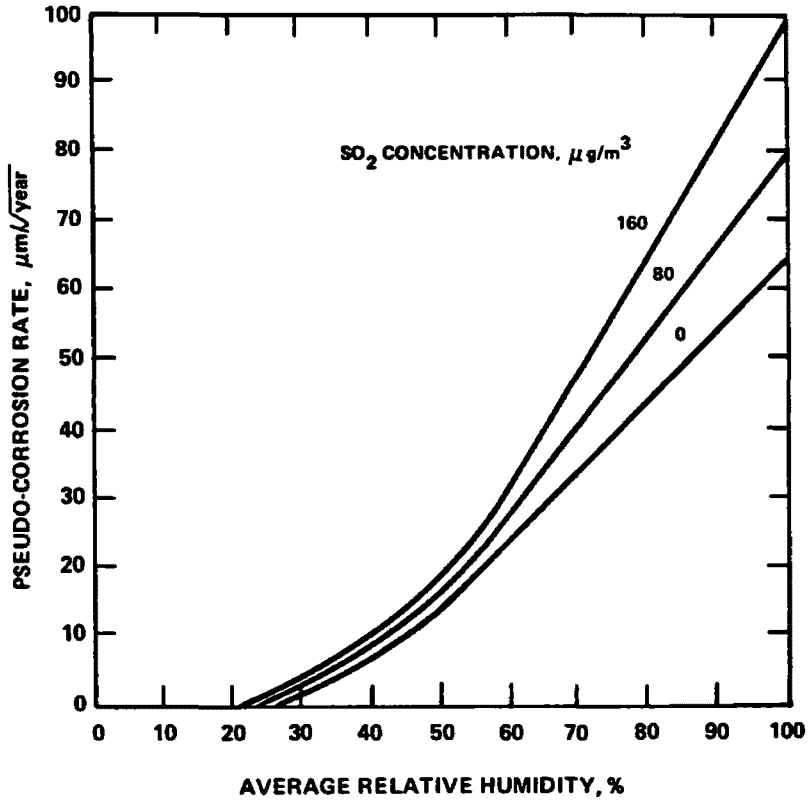

Figure 1-18. Steel corrosion behavior is shown as a function of average relative humidity at three average concentration levels of sulfur dioxide.

Source: Haynie and Upham (1974).

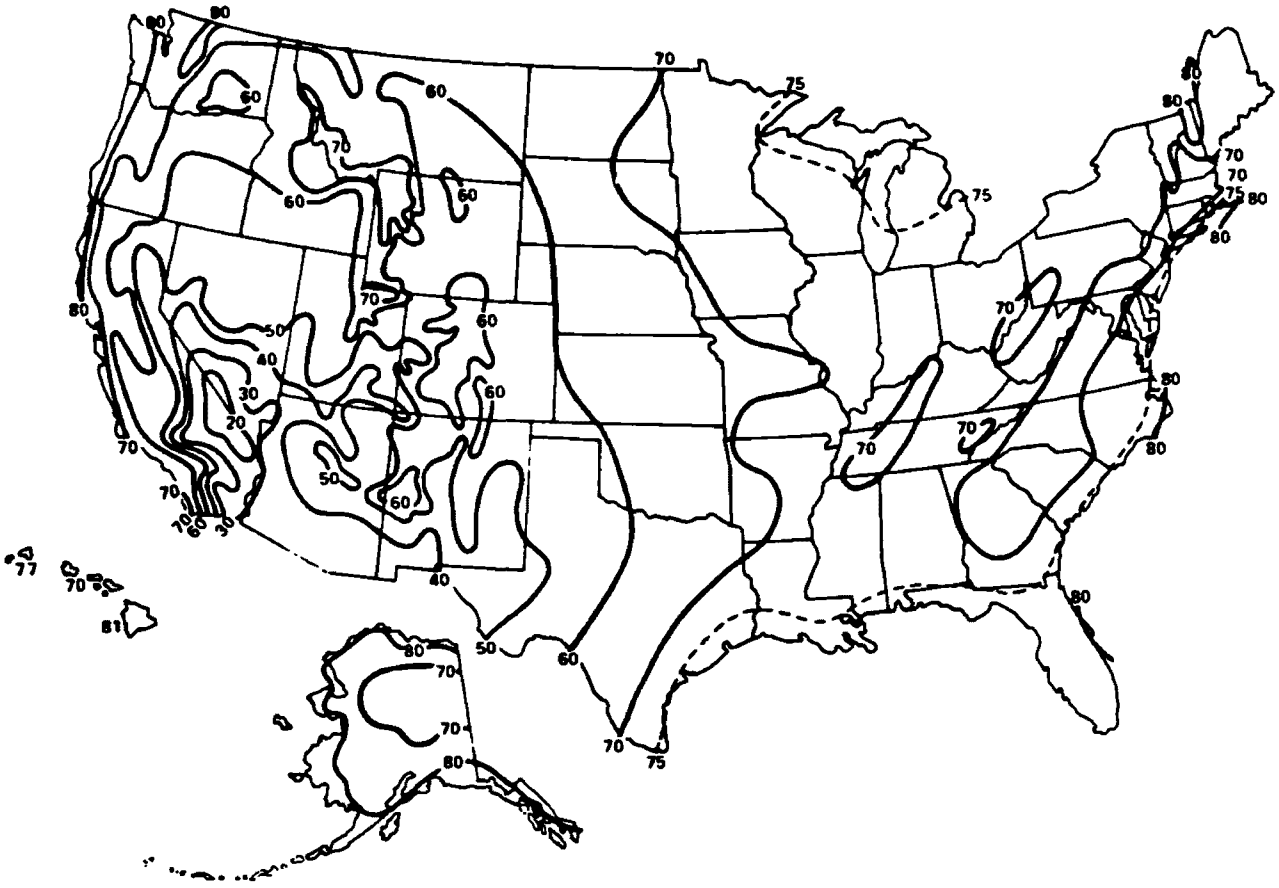

Figure 1-19. Annual mean relative humidity (RH) in various U.S. areas.

Source: Office of Air Quality Planning and Standards. Protecting Visibility: An EPA Report to Congress, EPA-450/5-79-008, U.S. Environmental Protection Agency, Research Triangle Park, N.C. October 1979.

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they also vary seasonally. These spatial and temporal variations, further, are not the same across the country (See Chapter 5). In some areas, then, the highest SO_2 concentrations coincide with periods of highest relative humidity; in other areas, the reverse is true.

Setting all these uncertainties aside, even if there were a means to predict with perfect precision that X level of SO_2 would result in Y μm corrosion to a metal surface, it would still be difficult to arrive at an acceptable aggregate damage estimate. This is true because one would have to know both the total thickness of the metal surface in question, the critical thickness below which repair or replacement is necessary, and the total area of surface exposed. This information is not available. Various surrogates have been used, typically annual production modified by some service life factor. These surrogates do not account, however, for such influences as indoor versus outdoor use, use of protective coatings, or subjective judgments as to the point at which the object in use should or could be repaired or replaced. This latter judgment is influenced both by willingness to pay and ability to pay and is tied to the economic status of the individual, the corporation, the region, or the nation, as appropriate. All of these difficulties discussed are reasons why the trend in more recent attempts to relate atmospheric pollutant levels to economic damage has been toward development of direct relationships between pollutant concentrations and economic benefit or disbenefit.

The kinds of limitations in available data necessary to estimate total metal corrosion associated with ambient concentrations of sulfur dioxide also exist for estimates of total erosion of paint or building materials. Factors such as humidity, nature and extent of exposure, and critical damage points are quantifiable only with a great deal of uncertainty for the national case. Costs assigned to repair or replacement are often necessarily arbitrary. Furthermore, existing damage functions for those materials are much less well documented than those for metals.

The least reliable of the "significant" damage functions are those for soiling from particulate matter. Shown in Table 1-4 are the results of a regression analysis for soiling of building materials, including paint, as a function of total suspended particulate exposure. It is apparent from the results that reflectance, which formed the basis of the analysis, is not the only property of particulate matter important to soiling. Also of importance is particle size. The minimum deposition velocity for a particle is in a size range of 0.1 to 1.0 μm diameter (see Chapter 6). Those characteristics (stickiness, oiliness, tarriness) which would increase adherence of deposited particles to a surface should also be considered. There is at present no single technique which combines all relevant measurements: reflectance, adherence, and particle size.

These limitations in physical damage estimates, as related to both sulfur oxides and particulate matter, have presented major obstacles to accurate estimation of total material damage and soiling by application of physical damage functions. Estimates of resultng economic damage based primarily on this approach have varied over a wide range, and have been

TABLE 1-4. RESULTS OF REGRESSION FOR SOILING OF BUILDING MATERIALS AS A FUNCTION OF TSP DOSE

Material	N	A	B	S_A^2	S_B^2	S_E^2	R^2
Oil base paint	400	89.43	-0.2768	0.0641	0.000069	7.6510	0.745
Tint base paint	400	86.13	-0.2618	0.0571	0.000061	6.8265	0.738
Sheltered acrylic emulsion paint	400	91.54	-0.593	0.1156	0.000123	13.8143	0.880
Acrylic emulsion paint	720	90.79	-0.4131	0.0497	0.000026	8.3791	0.902
Shingles	48	43.50	-0.199	0.5771	0.000258	7.6992	0.769
Concrete	160	41.75	-0.0458	0.1338	0.000080	7.5011	0.143
Coated limestone	80	44.57	+0.0779	0.2464	0.000164	6.9046	0.347
Uncoated limestone	80	46.99	-0.0503	0.1500	0.000089	4.2035	0.266
Coated red brick	80	12.95	-0.0296	0.0223	0.000013	0.6255	0.459
Uncoated red brick	80	14.88	-0.0374	0.0331	0.000020	0.9274	0.477
Coated yellow brick	80	45.05	-0.1133	0.5337	0.000317	14.9533	0.342
Uncoated yellow brick	80	43.21	-0.1133	0.2740	0.000168	7.6773	0.503
Glass	45	0.2806	+0.0314	0.008077	0.000007	0.6851	0.340

Note: Equation used in this regression analysis was reflectance = $B(\text{TSP} \times \text{months of exposure})^{\frac{1}{2}} + A$.

N, Number of data sets (dependent upon the number of controlled variables in the factorial experiment).

A, Intercept of linear regression.

B, Slope of linear regression.

S_A^2, Estimated variance of intercept.

S_B^2, Estimated variance of slope.

S_E^2, Residual variance (error).

R^2, Correlation index (fraction of variability accounted for by regression).

Source: Abstracted from Beloin and Haynie, 1975.

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criticized both as underestimating total damage and overestimating it. For this reason, other estimates of economic damage effects on materials and soiling related to ambient pollutant concentrations have related ambient pollutant concentrations directly to economic benefit or disbenefit. Such approaches are in the developmental stage and are limited by difficulties in distinguishing the effects of one pollutant from another, and involve socioeconomic factors that have yet to be dealt with satisfactorily. Though they show promise for future application, to date these approaches have been found to be inadequate for decision-making guidance.

1.11 RESPIRATORY TRACT DEPOSITION AND FATE OF SULFUR OXIDES AND PARTICULATE MATTER

1.11.1 Exposures

Chapter 11 of the present document presents information on respiratory tract deposition and fate of sulfur oxides and particulate matter useful in better understanding health effects associated with such pollutants as determined by animal toxicological, controlled human exposure and epidemiological studies. In animal laboratory or human clinical studies, measurements of exposure levels can usually be made near the point of inhalation. Studies in animals can often be used to determine the relationships between exposure levels and deposited fractions or target-organ doses. The monitoring instruments used in laboratory and clinical studies may, however, be very different from those used for environmental sampling in epidemiological studies or for implementation of standards. These differences in exposure characterizations have important quantitative effects upon the dose-response relationships that may be derived from the different types of studies described in this report. They should also be taken into account in developing exposure criteria and in specifying methods to be used in complying with these criteria.

1.11.2 Deposition and Clearance

Removal of SO_2 by the upper airways during inspiration affects the penetration of SO_2 to the tracheobronchial and possibly pulmonary regions of the lung. SO_2 removal by nasal absorption, primarily under resting conditions, is nearly complete (95-99 percent) in both man and laboratory animals (Frank et al., 1969; Speizer and Frank, 1966). SO_2 removal from the respiratory tract during mouth breathing is significantly lower than during nose breathing, although regional uptake has not been studied in man during mouth or oronasal breathing. Since mouth breathing and higher airflow rates may be expected under exercise conditions, the transition from rest to increased activity levels should significantly increase SO_2 penetration in man. These findings are in agreement with controlled human exposure studies that have examined subjects under different breathing patterns (Lawther et al., 1975). Some people are compulsorily or predominantly nose breathers; others favor breathing through their mouths. However, most rely on both oral and nasal breathing under conditions of increased respiratory workload.

Increasing the activity levels and respiratory rates of individuals can increase penetration of SO_2 into the trachea and bronchial airways. For example, animal studies show that

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absorption of SO_2 can be decreased to less than 50 percent by mouth breathing at relatively high airflow rates. The presence of fine particles in inhaled air may result in gas-particle interactions that also increase penetration of the reaction products into the lower respiratory tract. Laboratory animals and people are similar in all of these aspects of SO_2 deposition.

The majority of studies on the deposition of SO_2 in animals and people have been done at concentrations greater than 2.62 mg/m^3 (1 ppm). The high deposition of SO_2 in the upper respiratory tract has not been confirmed at levels ordinarily found in ambient air [generally less than 0.1 mg/m^3 (0.038 ppm)]. It is anticipated, however, that similar deposition patterns would be observed at these concentrations of SO_2.

Of the total SO_2 inhaled, less than 15 percent is likely to be exhaled immediately. That which is deposited is quickly absorbed into the secretions lining the respiratory passages. Most of the sulfur is rapidly transferred into the systemic circulation from all regions of the respiratory tract. Only small amounts have been observed to be exhaled at later times (about 3 percent).

The deposition of inhaled particles in the respiratory tract is complex. Deposition in different regions of the respiratory tract depends upon the physical properties and aerodynamic diameters of the inhaled particles and upon breathing patterns. Detailed information on regional deposition of inhaled particles for different modes of inhalation cannot be summarized here and the reader is referred to Sections 11-1 and 11-2 in Chapter 11 of this document. These studies were made in individuals using a variety of air volumes and flow patterns, so that the data relate to the resting state and states of light to moderate exercise.

Particles inhaled through the nose have deposition patterns markedly different from particles inhaled through the mouth. In nose breathing, most particles with greater than 4 μm aerodynamic diameter are deposited in the respiratory tract (see Figure 11.3). With mouth breathing, nearly complete deposition is observed only for particles greater than 10 μm aerodynamic diameter (see Figure 11.4). Deposition of these size ranges is mainly in the extrathoracic regions. However, 20 to 30 percent of particles between 5 and 10 μm aerodynamic diameter inhaled with mouth breathing are deposited in the trachea and bronchial airways (see Figures 11-7 and 11-8) and, with light activity levels, about 10 percent of particles as large as 15 μm aerodynamic diameter are predicted to deposit in the tracheobronchial region. These deposition patterns are depicted in Figure 1-20 in relation to varying physical or aerodynamic particle diameters.

Inhaled particles with aerodynamic diameters less than about 4 μm have pulmonary deposition fractions between 20 and 70 percent (see shaded area of Figure 1-20). About 20 percent pulmonary deposition is typical for these particle sizes when inhaled through the nose; when particles between 2 and 4 μm aerodynamic diameter are inhaled through the mouth, substantially greater (30-70 percent) pulmonary deposition results. For nose breathing, as

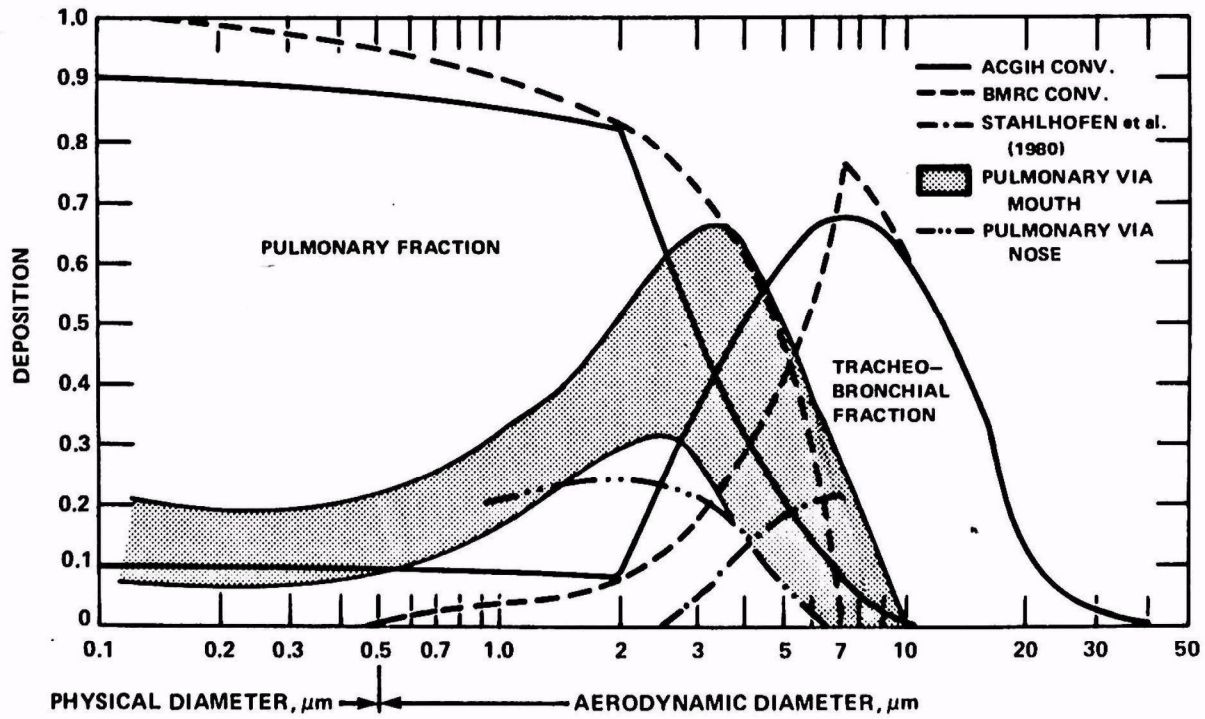

Figure 1-20. Division of the thoracic fraction into the pulmonary and tracheobronchial fractions for two sampling conventions (ACGIH and BMRC) as a function of aerodynamic diameter except below 0.5 μm where particle deposition is plotted vs. physical diameter, from International Standard Organization ad hoc group to TC-146, 1980. Also shown are the band for experimental pulmonary deposition data of Figure 11-9 and the tracheobronchial deposition data of one subject from Stahlhofen et al. (1980).

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compared to mouth breathing, the peak of the pulmonary deposition curve shifts downward from 3.5 to 2.5 μm aerodynamic diameter. Depending upon the tidal volume and breathing frequency used in various studies, pulmonary deposition of particles 5 μm in aerodynamic diameter can vary from as little as 5 percent to as much as 50 percent. Also, with mouth breathing, about 5-13 percent of particles 8-9 μm in aerodynamic diameter are deposited in the pulmonary region.

Regional deposition studies of particles less than 3 μm aerodynamic equivalent diameter have been conducted using dogs and some rodents. In these species, the relative distribution of these particles among the respiratory regions during nose breathing follows a pattern that is similar to regional deposition in man during nose breathing. Thus, in this instance, the use of rodents or dogs in toxicological research for extrapolation to humans entails differences in regional deposition of insoluble particles less than 3 μm aerodynamic equivalent diameter that can be reconciled from available data (see Section 11.2.1.5).

Although children are usually considered to be a subpopulation more susceptible to the effects of environmental pollutants, deposition data for children are not currently available, nor likely to be obtained soon. The little data that are available on other subpopulations, such as asthmatics and chronic bronchitics, indicate that tracheobronchial deposition appears to be enhanced at the expense of pulmonary deposition in most abnormal states.

Appropriate selective sampling procedures can and are being developed to provide more meaningful data on inhalation hazard potential for particles as a function of their regional deposition in the respiratory tract. Various sampler acceptance criteria reflective of selective sampling procedures for various regions of the respiratory tract are shown in Figure 11-20. By taking into account the biological effects of the material and the population at risk, air sampling procedures can be formulated which focus on the region(s) of the respiratory tract pertinent to accurate health assessment (see Section 11.4 of Chapter 11).

Particles deposited in different regions of the respiratory tract are cleared by different pathways and at different rates. Particles deposited in the anterior regions of the nasal passages are cleared forward by nose blowing and sneezing. Beyond the middle turbinate region, clearance to the pharyngeal regions occurs by mucociliary action, whereupon the particles are swallowed. Likewise, most clearance of material deposited in the oral cavity is by swallowing. All of these processes are relatively rapid and remove most of the deposited material within minutes to hours.

Insoluble particles that deposit in the tracheobronchial region are cleared upward in the respiratory tract by mucociliary action and then swallowed. This clearance is generally complete within one or two days after particle deposition. In contrast, particles deposited in the pulmonary region may be retained for several hundred days before they are cleared to the conducting airways or to the pulmonary lymphatic system.

As the particles are cleared by mechanical processes from all regions of the respiratory tract, chemical dissolution may remove soluble compounds which can then be absorbed directly

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into the systemic circulation. Since dissolution and absorption of substances from particles deposited in the respiratory tract competes with mechanical clearance processes, the amount absorbed depends upon the dissolution rate as compared to the mechanical clearance rate. The absorbed fractions are markedly different for different regions of the respiratory tract because of the large variations in clearance rates. Such variations may be calculated using the equations seen on page 11-42 (see also Figures 11-12 and 11-13 of Chapter 11).

1.12 TOXICOLOGICAL STUDIES

Chapter 12 of this document discusses information derived from toxicological studies in animals concerning the metabolism and effects of sulfur oxides and various forms of particulate matter. Such information is summarized next.

1.12.1 Metabolism of Sulfur Oxides and Particulate Matter

Although inhaled sulfur compounds are rapidly absorbed into the systemic circulation, their main effect is observed in the respiratory tract. Prior to or during inhalation, SO_2 may react with water to form sulfurous acid, or be oxidized to SO_3. The latter reacts rapidly with water to form sulfuric acid, which subsequently forms ammonium sulfate in the presence of ammonia. The sulfurous acid readily dissociates to sulfite and bisulfite ions, which are in rapid equilibrium. Bisulfite ions react with biological molecules by sulfonation, by autooxidation and by addition to cytosine. Most of the inhaled SO_2 is presumed to be detoxified by the sulfite oxidase pathway in the liver, which forms sulfate that can then be excreted in the urine.

The metabolism of toxic substances that may be inhaled with atmospheric particles is specific to the individual compounds. A discussion of the metabolism of all potentially inhalable compounds in urban air is beyond the scope of this report. Detailed studies on the deposition and clearance in laboratory animals of coal combustion products, automobile exhausts, and silicates have been reported elsewhere in the scientific literature.

1.12.2 Effects of SO_2

A great number of studies have been conducted on the effects of exposing various species of laboratory animals to differing concentrations of SO_2. Tables 1-5, 1-9, and 1-10 highlight studies demonstrating various types of effects at different exposure concentrations. The following discussion summarizes these findings and points out some of the inter- and intraspecies variability observed.

Table 1-5 summarizes several animal studies on the effects of acute exposure to SO_2 on pulmonary function. The most commonly observed response following 1 hour of exposure to SO_2 is bronchoconstriction. Only a few studies suggest acute exposure effects on pulmonary function at levels below 1 ppm, e.g., the increased airway resistance in guinea pigs reported by Amdur et al. (1970, 1978a) at concentrations as low as 0.16 ppm. However, another study by the same investigator (Amdur et al., 1978a) found no response at levels up to 0.8 ppm. It has been hypothesized that SO_2 induces bronchoconstriction by interaction with a bronchial epithelial receptor, which then initiates a reflex arc. This pathway is pharmacologically-mediated by portions of the autonomic nervous system, particularly the vagus, and apparently

TABLE 1-5. EFFECTS OF ACUTE EXPOSURES TO SULFUR DIOXIDE ON PULMONARY FUNCTION

Table	Concentration (ppm)	Duration	Species	Results	Reference
12-3	0.42 or 0.84 mg/m^3 (0.16 or 0.32 ppm) SO_2	1 hr	Guinea pig	Increase in resistance	Amdur et al., 1970, 1978a
12-3	0.52, 1.04, or 2.1 mg/m^3 (0.2, 0.4, or 0.8 ppm) SO_2	1 hr	Guinea pig	No significant increase in airway resistance.	Amdur et al., 1978c
12-3	2.62, 5.24, 13.1, or 26.2 mg/m^3 (1, 2, 5, or 10 ppm) SO_2	1 hr	Dog	Increased bronchial reactivity to aerosols of acetylcholine, a potent bronchoconstrictive agent	Islam et al., 1972
12-3	18 to 45 mg/m^3 (7 to 17 ppm) SO_2	1 hr	Guinea pig	General decrease in tidal volume and an increase in respiratory rate	Lee and Danner, 1966
12-3	0, 44.5, 83.8, 162, 233, 322, 519, or 781 mg/m^3 (0, 17, 32, 62, 89, 123, 198, or 298 ppm) SO_2	10 min	Mouse	Respiratory rate decreased proportionally to the log of the concentration; complete recovery within 30 min following all exposures. The time for maximum response was inversely related to the log of the concentration, being shortest at highest concentrations	Alarie et al., 1973d
12-3	>50 mg/m^3 (>19 ppm) SO_2	1 hr	Guinea pig	Increase in tidal volume and a decrease in respiratory rate	Lee and Danner, 1966

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involves the release of histamine (see Section 12.2.4). This hypothesis is supported partially by investigations in man (see Section 1.13).

The respiratory response to histamine aerosols is similar, if not identical, to that of SO_2. If the SO_2-initiated bronchoconstriction involves histamine release, as hypothesized above, then the broad range of response of animals (and man) to different histamine concentrations could explain the similar broad concentration range of the SO_2-bronchoconstriction dose-response curve. As much as 200-fold differences in dose have been reported for histamine-induced bronchoconstriction, for example. In addition, sensitivity to histamine may decrease with age, depending upon the species involved. Further studies are needed to substantiate this hypothesis and to determine if the variation in response to SO_2 represents sensitive subpopulations.

Another alteration in breathing mechanics caused by SO_2 is a transient decrease in respiratory rate. This may involve a chemoreceptor in the nasal passages, similar to the one thought to be responsible for bronchoconstriction, which is pharmacologically mediated by the trigeminal nerve and which may involve the release of acetylcholine (see Section 12.2.4). The SO_2-induced decrease in respiratory rate requires a higher concentration than, and differs from, bronchoconstriction in several respects (see Table 1-5), among which are a concentration-independent transience and a concentration-dependent period of desensitization.

The primary host defense mechanism of the respiratory tract is the clearance of foreign objects from the lung, whether it be by mechanical (mucociliary transport) or biological (phagocytosis or immunological function) means (See Section 12.2.5). The effects of SO_2 on these mechanisms are variable and species-dependent (See Table 12-4). For example, rats exposed to 0.1 ppm SO_2, 7 hours/day, 5 days/week, for 10 or 23 days exhibited accelerated clearance of labeled particles. In the same study, however, 1.0 ppm exposures accelerated clearance at 10 days, but depressed clearance rates after 25 days. In other studies, mucus flow in the trachea of dogs was decreased following intermittent exposure for 1 year to 1 ppm SO_2, whereas a single 30-minute exposure of 25 ppm did not affect clearance in donkeys. Also, based on limited work with infectivity models, it appears that susceptibility to bacterial infection is not affected by high concentrations of SO_2 (5 ppm up to 3 months). Antiviral defenses were compromised by SO_2 in mice at 7-10 ppm for 7 days. Chronic exposure to SO_2, however, can cause alterations of the pulmonary and systemic immune systems. In summary, acute exposure to SO_2 can alter some aspects of host defenses, but concentrations in excess of those currently found in the ambient air appear to be required. Unfortunately, few studies have examined chronic effects on these parameters.

In regard to possible respiratory tract pathology, no remarkable alterations in lung morphology were observed following chronic exposure of SO_2 in monkeys (0.14, 0.64, 1.28, and 5.12 ppm x 18 months) or dogs (5.1 ppm x 620 days) (see Section 12.2.3 and Table 12-2). However, only conventional light microscopy was used, which is a method far less sensitive than scanning or transmission electron microscopy for observing alterations in surface mem-

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branes and cilia. Shorter exposures to much higher concentrations (10-400 ppm) generally did cause morphological changes in mice, rats, and pigs (see Table 12-2).

The issue of mutagenesis is currently unresolved (see Section 12.5.2 and Table 12-15). Although mutagenesis has been shown in two microorganisms in response to SO_2, no evidence supports its occurrence in at least two higher systems, i.e., Drosophila and mouse oocytes.

With regard to the tumorigenic properties of SO_2, investigations of its in vivo potential oncogenicity are quite rare (see Section 12.5.3 and Table 12-16). Tumorigenesis after exposure to SO_2, or to a combination of SO_2 and benzo(a)pyrene, has been examined in mice and rats, respectively. In a single study involving SO_2, mice were exposed intermittently over an entire lifetime. Increased incidence of primary lung carcinoma was reported for females, but not for males. Because an adequate statistical analysis was not presented in the paper, a subsequent statistical analysis was performed and revealed the increase in primary lung carcinoma in SO_2-exposed females to be significant ($p = 0.011$). Unfortunately, the exact duration of exposure and concentration cannot be accurately determined from the publication.

Simultaneous exposure to SO_2 (4 ppm) and benzo(a)pyrene (10 mg/m^3) for a lifetime was subsequently reported for rats. The biological significance of these studies is complex and difficult to interpret, particularly since statistical analyses were not given. However, subsequent statistical analysis of the data reported for a combined exposure revealed the increased incidence of lung tumors to be significant ($p = 0.005$), whereas exposures to SO_2 and benzo(a)pyrene alone were not significant.

Numerous animal studies have investigated mortality induced by sulfur dioxide. However, SO_2 causes high mortality only at high concentrations ($\geq$50 ppm) which are not relevant to ambient air exposures (see sect. 12.2.3 and Table 12-1).

1.12.3 Effects of Particulate Matter

Characterizing exposures to particles in the atmosphere may be even more difficult than characterizing exposures to SO_2. This is due, in large part, to the fact that the toxicity of particulate matter depends greatly upon its chemical composition. In general, urban air is quite heterogeneous in composition and may vary widely from one community to the next, or even within a single community. It may contain both inert and chemically toxic fractions; the potential impact of the latter is complicated by such considerations as dissolution, solubility, and bioavailability (see Section 11.2.2). Although adequate physical and chemical information can be obtained in studies with laboratory animals exposed to well-defined particulate aerosols, the above types of data are not available for the heterogeneous mixture of particles found in the environment. Therefore, the comparisons that can be made between toxicological studies of defined, laboratory-produced aerosols and epidemiological studies of people exposed to environmental aerosols is extremely limited.

A large number of studies have been conducted on the effects of exposure to sulfates and certain other, well-defined particulate aerosols. Tables 1-6, 1-7, and 1-8 represent a summary of these studies demonstrating various types of effects at different exposure concentra-

TABLE 1-6. RESPONSES TO ACUTE SULFURIC ACID EXPOSURE

Table	Concentration	Duration	Species	Results	Reference
12-6	100 μg/m³ H_2SO_4	1 hr	Guinea pig	Pulmonary resistance +47% pulmonary compliance -27%.	Amdur et al., 1975, 1978b
12-9	500 μg/m³ H_2SO_4	1 hr	Dog	Slight increases in tracheal mucociliary transport velocities immediately and 1 day after exposure. One wk later clearance was significantly decreased.	Wolff et al., 1979a
12-6	510 μg/m³ H_2SO_4	1 hr	Guinea pig	Pulmonary resistance +60% pulmonary compliance -33%.	Amdur et al., 1978b
12-6	1000 μg/m³ H_2SO_4	1 hr	Guinea pig	Pulmonary resistance +78% pulmonary compliance -40%.	Amdur et al., 1978b
12-9	190-1400 μg/m³ H_2SO_4	1 hr	Donkey	Bronchial mucociliary clearance was slowed.	Schlesinger et al., 1978
12-9	1000 μg/m³ H_2SO_4	1 hr	Dog	Depression in tracheal mucociliary transport rate persisted at 1 wk post-exposure.	Wolff et al., 1979a
12-9	1400 μg/m³ H_2SO_4	1 hr	Donkey	No effect on tracheal transport.	Schlesinger et al., 1978

TABLE 1-7. RESPONSES TO CHRONIC SULFURIC ACID EXPOSURE

Table	Concentration*	Duration	Species	Results	Reference
12-9	100 μg/m^3 (0.3-0.6 μm) H_2SO_4	1 hr/day, 5 day wk, several mo	Donkey	Within the first few wk all four animals developed erratic bronchial mucociliary clearance rates, either slower than or faster than those before exposure. Those animals never pre-exposed before 100 μg/m^3 H_2SO_4 had slowed clearance during the second 3 mo of exposure.	Schlesinger et al., 1978
12-5 12-8	80 μg/m^3 (0.84 μm), 100 μg/m^3 (2.78 μm) H_2SO_4	52 wks cont.	Guinea pig	No significant blood effect; no lung alterations; no effect on pulmonary function.	Alarie et al., 1973a, 1975
12-5 12-8	380 μg/m^3 (1.15 μm); 480 μg/m^3 (0.54 μm) H_2SO_4	78 wks cont.	Monkey	No significant blood effect; no lung changes 380 μg/m^3 increased respiratory rate; 480 μg/m^3 altered distribution of ventilation early in exposure period but not later.	Alarie et al., 1973a
12-13	900 μg/m^3 (2.78 μm) H_2SO_4	12 mo cont.	Guinea pig	No significant effects on hematology, pulmonary function, or morphology.	Alarie, 1975

*All particle sizes in MMD

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TABLE 1-8. RESPONSES TO VARIOUS PARTICULATE MATTER MIXTURES

Table	Concentration	Duration	Species	Results	Reference
12-6	100 μg/m^3 open hearth dust	1 hr	Guinea pig	Pulmonary resistance +9% pulmonary compliance 0%.	Amdur and Underhill, 1968, 1970
12-6	500 μg/m^3 $(NH_4)_2SO_4$	1 hr	Guinea pig	Pulmonary resistance +23% pulmonary compliance -27%.	Amdur et al., 1978a
12-6	750 μg/m^3 Na_3VO_4	1 hr	Guinea pig	Pulmonary resistance +7%.	Amdur and Underhill, 1968
12-6	1000 μg/m^3 $FeSO_4$	1 hr	Guinea pig	Pulmonary resistance 2%.	Amdur and Underhill, 1968
	1000 μg/m^3 $MnCl_2$	1 hr	Guinea pig	Pulmonary resistance +4%.	Amdur and Underhill, 1968
12-10	500-5000 μg/m^3 Mn_3O_4	2 hr	Mouse	The aerosols increased the mortality from the subsequent standard airborne streptococcal infection: with Mn_3O_4 occurrence at 1550 μg/m^3 Mn.	Gardner et al., 1977b Adkins et al., 1979, 1980c
12-13	1400 μg/m^3 H_2SO_4 + 1500 μg/m^3 carbon or 1500 μg/m^3 carbon only	3 hr/day 5 day/wk, 20 wks	Mouse	Altered the immune system. Morphological changes observed; more severe with carbon only exposure.	Fenters et al., 1979
12-13	1100 μg/m^3 H_2SO_4, or 1500 μg/m^3 carbon or in combination	3 hr	Hamster	Carbon caused no change in ciliary beat frequency. Ciliary beat frequency was depressed after H_2SO_4 exposure. The combination produced similar effects, but recovery had occurred by 48 hr. post-exposure. Up to 48 hr. after exposure H_2SO_4 + carbon resulted in more tissue destruction than either pollutant alone.	Schiff et al., 1979

tions, durations and chemical composition. The following discussion highlights some of the variability in response that has been observed.

Oxides of sulfur that are of air pollution significance or have been used in inhalation studies as aerosols include: sulfuric acid (H_2SO_4), ammonium bisulfate and sulfate, and sulfate salts of zinc, iron, copper, manganese and others.

Alterations of pulmonary function, particularly the increase in pulmonary flow resistance, give the measure of response to acute exposure to sulfur oxide aerosols (see Section 12.3.3.1). Reports are variable regarding the irritation potency of various sulfate salts. However, according to many investigators, sulfuric acid appears to be most irritating. Table 1-6 shows that, for short-term exposures, the lowest concentration of sulfuric acid found to increase airway resistance was 100 μg/m^3 (one-hour exposure of guinea pigs). Experiments with various exposure protocols showed particle size to be an important factor; around 2 μm or smaller sizes were generally more effective in producing the observed effects. Perhaps due to variation in animal species and strains, and different particle sizes used in the experiments, the effects noted with sulfuric acid and sulfate salts are often contradictory. Guinea pigs are the most sensitive and show severe bronchoconstriction in response to sulfuric acid aerosols. Based on short-term (one-hour exposure) effects, a ranking of irritation potency (in terms of increased airway reisitance) has been made for various sulfur oxides as listed below:

Relative Irritant Potency of Sulfates in Guinea Pigs Exposed for One Hour[a] (Amdur et al., 1978a)

Sulfuric acid	100
Zinc ammonium sulfate	33
Ferric sulfate	26
Zinc sulfate	19
Ammonium sulfate	10
Ammonium bisulfate	3
Cupric sulfate	2
Ferrous sulfate	0.7
Sodium sulfate (at 0.1 μm)	0.7
Manganous sulfate	-0.9

[a]Data are for 0.3 μm (MMD) particles. Increases in airway resistance were related to sulfuric acid (0.41% increase in resistance per μg of sulfate as sulfuric acid) which was assigned a value of 100.

The irritation potency of sulfuric acid aerosols is complicated by its partial neutralization by ammonia present in the breath or in the air of animal exposure chambers. The resulting $(NH_4)_2SO_4$ and NH_4HSO_4 lessen the expected effects of H_2SO_4, but the extent to which this affects the results of available animal studies cannot be quantified.

As summarized in Tables 1-7 and 1-8, chronic effects of sulfuric acid and sulfate salts are less certain than acute exposure effects (see Section 12.3.3.2). Exposure to a concentration of 0.38 mg/m^3 sulfuric acid for 78 weeks produces no pulmonary function changes in monkeys, but measurable changes occurred at 0.48 to 4.79 mg/m^3 concentrations. Concentration,

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particle size, and chemical composition all appear to be important for pulmonary function changes, as suggested by information in Tables 1-7 and 1-8 (as well as Table 12-8).

Exposure to sulfuric acid aerosol causes an alteration of mucociliary clearance of viable and nonviable particles from the lung (see Section 12.3.4.1). The effects observed are variable; e.g., tracheal mucociliary transport in dogs was increased after exposure to H_2SO_4 aerosol (0.5 mg/m^3 for one hour), but was decreased in rats and hamsters after one to three hour exposure to 1 mg/m^3 H_2SO_4. Prolonged exposure of donkeys to similar concentration of H_2SO_4 caused a persistent slowing of mucociliary transport (see Table 12-9).

Resistance to bacterial infection was not affected by this sort of exposure to H_2SO_4 aerosol. However, various metal sulfates adversely affected this defense mechanism (see Table 12-10). The potency of these metal sulfates, based on a three-hour exposure causing an increased susceptibility to bacterial infection, may be ranked as: $CdSO_4$ > $CuSO_4$ > $ZnSO_4$ > $Al_2(SO_4)_3$ > $Al\ NH_4(SO_4)_2$. Sulfuric acid and the following sulfates at concentrations greater than 2.5 mg/m^3 were ineffective in this bacterial infection model: $(NH_4)_2SO_4$, NH_4HSO_4, Na_2SO_4, $Fe_2(SO_4)_3$ and $Fe(NH_4)_2(SO_4)_2$. It should be noted, however, that various non-sulfate metallic aerosols, especially Ni- or Cd-containing compounds, have substantial inhibitory effects on host defense mechanisms in general. A thorough discussion of this may be found in Sections 12.3.4.2, 12.3.4.3, and 12.3.4.4 of Chapter 12 of this report.

Morphological changes in the lung have been studied mostly after chronic exposure to sulfuric acid (see Section 12.3.2). Morphological changes were evident, such as in monkey lung, after a long-term (78 wk) exposure to relatively high levels of sulfuric acid (2.43 mg/m^3, 3.6 μm, aerodynamic diameter to 4.79 mg/m^3, 0.73 μm aerodynamic diameter). The major findings included thickening of the bronchial wall and bronchiolar epithelium, which may contribute to the changes in lung function. In other studies involving guinea pigs (0.1 mg/m^3 H_2SO_4 for one year) and dogs (0.89 mg/m^3 H_2SO_4 for about two years), neither morphologic nor physiologic changes were noted (see Table 12-5).

The lethal effects of sulfate aerosols are dependent on animal age (see Section 12.3.1). For example, 18 mg/m^3 was lethal to 1-2 month old guinea pigs as opposed to 50 mg/m^3 for 18 month old animals. Particle size is also important; LC_{50} for guinea pigs was 30 mg/m^3 with an aerosol size of 0.8 μm (aerodynamic equivalent diameter) as opposed to 109 mg/m^3 with an aerosol size of 0.4 μm (aerodynamic equivalent diameter). Bronchial spasm may be the major cause of animal death.

Suspended particles not related to sulfur oxides are also of considerable concern. However, because of the wide variety of such substances, it is difficult to summarize pertinent toxicological results. Information on the inhalation toxicology of several individual substances found in ambient air particulate matter is summarized in Table 1-8. Other relevant information can also be derived from non-inhalation toxicological studies. For example, numerous trace metals have been found as components of airborne particulate matter (see Section 12.5.4). In addition to being generally toxic, certain compounds of some of these

metals, including beryllium, cadmium, cobalt, chromium, iron, lead, nickel, titanium, and zinc, have been identified as carcinogenic under specific, non-respiratory laboratory exposure conditions.

Silicon is ubiquitous in the earth's crust and in coarse mode particles. Silicon dioxide (SiO_2), which is responsible for the disease silicosis, is found in 3 crystalline forms (quartz, cristobalite, and tridymite). As a generalization, the ranking of toxicity is tridymite > cristobalite > quartz. These uncombined forms of SiO_2 are generally called "free silica." SiO_2 is also found combined with cations, in which case the term silicates is applied. Very few animal toxicological studies of silicates exist. Several hypotheses of the etiology of silicosis have been developed, but no single one has been proven definitively.

Although many animal toxicological studies of SiO_2 exist, comparisons are difficult because of the species and strain of animal used, accidental infections, the size of SiO_2 particle used, and the crystalline form of SiO_2 used. Silicosis, similar to that observed in man, has been produced in animals exposed to high concentrations of quartz and other SiO_2 dusts via intratracheal instillation (30-50 mg) or chronic inhalation. Chronic exposures (2.5 yr) of dogs to earth containing 61 percent cristobalite produced fibrotic nodules in hilar lymph nodes, but not the lungs.

1.12.4 Effects of Complex Mixtures

It is difficult to assess with accuracy the toxicity of complex sulfur-containing aerosols in urban atmosphere based simply upon the sulfuric acid or sulfate content. The chemical composition of sulfate aerosols, particularly the metallic or cationic counterparts, are important in determining their relative toxicity. Since atmospheric aerosols may contain varying proportions of sulfuric acid and ammonium- and metal sulfates, it is not possible to extrapolate from animal toxicological data obtained with single compounds to human environmental situations.

Exposure to SO_2 together with liquid or solid aerosols, which may act as a carrier for the gas, seems to enhance the toxic effects of SO_2 in some cases (see Section 12.4). Table 1-9 shows some examples of this, where the aerosols are solutions of a salt such as NaCl, $MnCl_2$, or $FeSO_4$. Although the evidence is not clear, additive as well as synergistic effects have been observed by some investigators using H_2SO_4 and ozone (see Table 1-10), or SO_2 to H_2SO_4 may have increased the toxic potency. On the other hand, it may be seen from Table 1-11 that the addition of fly ash to mixtures of SO_2 and H_2SO_4 had no significant effect.

1.13 CONTROLLED HUMAN STUDIES

Human experimental studies of the health effects of exposure to specific pollutants in the ambient environment are of significance in scientific assessments of air pollution risks since they can demonstrate relationships between pollutant exposure and short-term health effects. Such studies utilizing man require strict controls so that their findings are relevant to larger populations. To date no human study of the health effects of exposure to

TABLE 1-9. RESPONSES TO ACUTE EXPOSURE COMBINATIONS OF SO_2 AND SOME PARTICULATE MATTER

Table	Concentration	Duration	Species	Results	References
12-11	1.0 ppm SO_2 + NaCl Aerosol (<40% RH end >80% RH)	1 hr	Guinea pig	No increase in pulmonary flow resistance at low RH; at high RH, potentiation was marked and evident during both early and late parts of exposure.	McJilton et al, 1973
12-11	1.0 ppm SO_2 + Aerosols of salts	1 hr	Guinea pig	Presence of soluble salt increased pulmonary flow resistance about three fold. The potentiation was evident early in the exposure.	Amdur and Underhill, 1968
12-11	2.0 ppm SO_2 + NaCl Aerosol	1 hr	Guinea pig	SO_2 alone produced an increase of 20% in pulmonary flow resistance; with 10 mg/m^3 NaCl the increase was 55% and the potentiation occurred later in exposure; with 4 mg/m^3 potentiation was reduced.	Amdur, 1961

TABLE 1-10. RESPONSES TO ACUTE EXPOSURE COMBINATIONS OF SULFURIC ACID AND OZONE

Table	Concentration	Duration	Species	Results	Reference
12-14	880 μg/m^3 H_2SO_4 + 0.1 ppm O_3	3 hr O_3 2 hr H_2SO_4	Hamster	H_2SO_4 depressed ciliary beat frequency. By 75 hr after exposure, recovery had occurred O_3 exposure had no effect. Sequential O_3 then H_2SO_4 exposure decreased ciliary beat frequency significantly but to a lesser extent than that caused by H_2SO_4 alone.	Grose, 1980
12-14	900 μg/m^3 H_2SO_4 + 0.1 ppm O_3	3 hr O_3 2 hr H_2SO_4	Mouse	In response to air-borne infections a significant increase in mortality only when O_3 was given immediately before exposure to H_2SO_4, and the response was additive.	Gardner et al., 1977a
12-14	1000 μg/m^3 H_2SO_4 0.4-0.5 ppm O_3	3 days cont.	Rat	Synergistic effects. Glycoprotein synthesis was stimulated in tracheal ring explants; lung DNA, RNA and protein content increased.	Last and Cross, 1978

TABLE 1-11. PATHOLOGICAL RESPONSES FOLLOWING CHRONIC EXPOSURE TO SO_2 ALONE AND IN COMBINATION WITH PARTICULATE MATTER

Table	Concentration	Duration	Species	Results	Reference
12-2	10 ppm SO_2	72 hr cont.	Mouse	Pathological changes in the nasal mucosa appeared after 24 hours and increased in severity after 72 hours. Mice free of upper respiratory pathogens were significantly less affected than the conventionally raised animal. Morphological alterations were qualitatively identical in both groups.	Gliddens and Fairchild, 1972
12-2	0.14, 0.64, 1.28 ppm SO_2	78 wk cont.	Cynomolgus monkey	No remarkable morphologic changes in the lung.	Alarie et al., 1972, 1973c
12-13	0.11, 1, 5 ppm SO_2 + 560 μg/m³ fly ash	78 wk cont.	Monkey	No effects on morphology.	Alarie et al., 1973b
12-13	1.0 ppm SO_2 + H_2SO_4 + fly ash	18 mo	Monkey	No significant effects on hematology or pulmonary function tests during exposure. At end of exposure to 0.99 ppm SO_2 + 930 μg/m³ H_2SO_4 (0.5 μm, MMD) lungs had morphological alterations in the bronchial mucosa. Exposure to 1.01 ppm SO_2 + 880 μg/m³ H_2SO_4 (0.54 μm, MMD) + 410 μg/m³ fly ash (4.1 μm, MMD) had similar alterations; thus fly ash did not enhance effect. Exposure to 990 μg/m³ H_2SO_4 ().64 μm, MMD) + 550 μg/m³ fly ash (5.34 μm, MMD) had slight alterations.	Alarie et al., 1975
12-13	0.11, 1, 5 ppm SO_2 + 560 μg/m³ fly ash	52 wk cont.	Guinea pig	No effects on morphology.	Alarie et al., 1973b
12-13	5.1 ppm SO_2 + 890 μg/m³ H_2SO_4	21 hr/day 620 days	Dog	After 225 days, dogs receiving H_2SO_4 had a lower diffusing capacity for CO than those that did not receive H_2SO_4. After 60 days, no morphological changes occurred. H_2SO_4 decreased net lung volume and total weight.	Lewis et al., 1969, 1973

sulfur oxides and particulate matter meet all the requirements of strict controls. Some basic information, however, can be garnered from many studies that have been published.

1.13.1 Effects of Sulfur Dioxide

SO_2 has been found to have effects on several physiologic functions. Through subjective reports, the reliability of which has been questioned, a level of 5 ppm has been established for detecting SO_2, with considerable variation below that level. Several sensory processes are affected by generally agreed-upon levels of concentration of SO_2. The odor threshold averages 0.8 to 1 ppm, with 0.47 ppm set in one study performed under ideal conditions. The sensitivity of the eye to light increases at 0.34 to 0.63 ppm, is maximal at 1.3 to 1.7 ppm, and decreases to normal by 19.2 mg/m^3 during dark adaptation. During light adaptation, the figures increase and decrease similarly but at slightly higher levels of exposure. The alpha-wave has been found to be attenuated by 0.9 to 3 mg/m^3 SO_2 during 20 seconds of exposure.

Studies of the effects of SO_2 on the respiratory system of the body have arrived at conflicting conclusions (see Table 1-12). Although two studies found respiratory effects after exposure to as little as 0.75-1 ppm SO_2 (Bates and Hazucha, 1973; Amdur et al., 1953), others could find no effect below 5 ppm for normal healthy subjects at rest. At the latter level, pulmonary flow resistance increased 39 percent in one study. Respiratory effects have been found to be proportional to the concentration of SO_2 to which study subjects are exposed. Although the bronchoconstrictive effects of exposure to SO_2 have been found to be fairly consistent, subjects vary considerably in response to exposures, and there are some especially sensitive subjects, which may represent as much as 10 percent of the population. Recent studies have suggested that asthmatics may be particularly sensitive.

In asthmatic subjects, mid maximum expiratory flow rate (MMFR) was significantly reduced after oral exposure to 1.31 mg/m^3 (0.5 ppm) SO_2 for 3 hours (Jaeger et al., 1979). As noted in Table 1-12, three of the subjects (2 asthmatics, 1 normal) incurred delayed effects (wheezing attacks at night) that may have been related to the exposure. Recent studies by Sheppard et al. (1980, 1981) and Koenig et al. (1980, 1981) have demonstrated pulmonary function changes observed in asthmatic subjects both at rest and during exercise. In the Sheppard et al. studies, at rest SR_{aw} increased significantly at SO_2 concentrations of 1, 3, 5 ppm for asthmatics and only at 5 ppm for normal and atopic (viral rhinitis) subjects. During exercise specific airway resistance (SR_{aw}) significantly increased in the asthmatic group at 0.5 and 0.25 ppm SO_2 and even at 0.1 ppm in the two most responsive subjects. At 0.5 ppm, three of the subjects experienced wheezing and shortness of breath and at 1.0 ppm, all six subjects experienced such symptoms. Sheppard et al. concluded that with resting subjects, the exaggerated bronchoconstriction produced by SO_2 in persons with asthma and the lesser bronchoconstriction produced in normal persons both appear to be mediated by parasympathetic neural pathways. Under SO_2 exposure concentrations more likely to be encountered in polluted cities (0.1 0.5 ppm SO_2) they also demonstrated that exercise modifies the bronchoconstriction

TABLE 1-12. CONTROLLED HUMAN EXPOSURE STUDIES - MAJOR STUDIES CITED IN CHAPTER 13

Concentration (ppm)	Duration of exposure (mins)	Number of subjects	Oral or nasal exposure	Rest (R) or exercise (E)*	Effects	Reference
SO_2 (5 - 30 ppm)	10	10	CO_2 stimulus (O)	R	Deep breathing significantly increased SR_{aw}.	Lawther, 1975
1	50	13	Chamber (N)	R		
3	-	17	O	R		
SO_2 (2.5, 5.0, 10.0 ppm)	10	15	O, N	R	SG_{aw} decreased less with nasal breathing.	Melville, 1970
SO_2 (5 ppm)	10	5	O, N	R	$MEF_{50\%}$ decreased less with nasal inhalation.	Snell and Luchsinger, 1969
SO_2 (1.1 - 3.6 ppm)	30	10	O	R	Deep breathing produced no effects.	Burton et al., 1969
SO_2 (1 - 8 ppm)	10	14	Face Mask	R	Pulse rate, respiratory rate increased; tidal volume decreased.	Amdur et al., 1953
SO_2 (0.75 ppm)	120	4 - 8	Chamber	E	Decrease in MEFR, FVC, $FEV_{1.0}$ MMFR also decreased.	Bates and Hazucha, 1973
SO_2 (1, 3, 5 ppm)	10	7, 7, 7 asthmatics	O	R	SR_{aw} increased significantly at all conc for asthmatics; only at 5 ppm for normals and atopic subjects.	Sheppard, et al., 1980
SO_2 (1 ppm)	60	9 asthmatics	Oral	R	Significant decreases in $\dot{V}_{max\ 50\%}$.	Koenig et al., 1980
SO_2 (0.50 ppm)	180	40 asthmatics	Oral	R	MMFR decreased 2.7%; recovery within 30 minutes; 3 subjects incurred delayed effects and required medication.	Jaeger et al., 1979
SO_2 (1 ppm) NaCl 1 mg/m^3 MMD 0.9 μ σg = 2.0 μm	30	8 asthmatics	Mask	E 10 minutes	$\dot{V}_{max\ 50\%}$, $\dot{V}_{max\ 75\%}$, $FEV_{1.0}$ and R_T decrease significantly in aerosol condition.	Koenig et al., 1981

TABLE 1-12. (continued)

Concentration (ppm)	Duration of exposure (mins)	Number of subjects	Oral or nasal exposure	Rest (R) or exercise (E)*	Effects	Reference
SO_2 (0.1, 0.25, 0.5, 1 ppm)	10	7, 6 asthmatics	0	E	SR_{aw} significantly increased in the asthmatic group at 0.5 and 0.25 ppm SO_2 and even at 0.1 in the two most responsive subjects. At 0.5 ppm, 3 subjects experienced wheezing and shortness of breath. At 1 ppm all six subjects experiences these symptoms.	Sheppard, et al., 1981
SO_2 (0.15 ppm) and O_3 (0.15 ppm)	120	6	E*	-	Significant enhanced decrease in SG_{aw} after exposure to SO_2 - O_3 in comparison to O_3 alone	Kagawa et al., 1979
0.35 - 5.0 mg/m^3 H_2SO_4 MMD 1 μm	15	15	Mask (rest)	-	Respiratory rates increased, max. insp. and expiratory flow rates and tidal decreased volumes	Amdur et al., 1952
H_2SO_4 (0, 100, 300, or 1,000 μg/m^3 MMAD 0.5 μm (σg = 1.9)	60	10	Nasal	-	No pulmonary function effects Broncial mucociliary clearance ↑ following 100 μg/m^3 but ↓ following 1000 μg/m^3. Mucociliary clearance distal to trachea more affected	Lippmann et al., 1980
SO_2 (1-60 ppm) plus H_2O_2 to form H_2SO_4 aerosol CMD 1.8 and 4.6 μm	Variable	24	(Rest)	-	Airway resistance increased especially with larger particles	Toyama and Nakamura, 1964

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produced by SO_2 in subjects with mild asthma. However, extrapolation of these observed quantitative exposure/effect relationships to what might be expected under ambient conditions could be questionable because of the use of forced mouth breathing with noseclips and rapid step-function changes in SO_2 exposure concentrations.

Because SO_2 is readily water soluble and the nasal and mouth passages differ in available moist surface area, the route of exposure will affect the response of individuals. Subjects report less throat and chest irritation when breathing through the nose, and pulmonary flow resistance increases are less in subjects who are nose breathing. Regardless of the route of exposure, 5 ppm SO_2 had limited effects on specific airway conductance (airway bronchoconstriction), although higher levels had a dose-dependent effect; that is, higher concentrations decreased SG_{aw} more than lesser concentrations. The average decrease was greater after oral exposure than after nasal administration.

The level of activity of the subjects tested affects the results because the actual dose delivered to lungs and airways is greater when subjects breathe through their mouth, as during exercise. Just having subjects breathe deeply through the mouth significantly affected specific airway resistance during exposure to 1 ppm SO_2 in one study, although another study found no such effect. Respiratory effects of exposure either by nose or by mouth are greatest after 5 to 10 minutes of exposure. Recovery takes about 5 minutes in normal subjects, but much longer (10 to 60 minutes) in sensitive subjects and those who are asthmatic. Studies of nasal mucus flow rates and airway resistance following about 6 hours of exposure to 1 and 5 ppm SO_2 per day for 3 days found some effects maximal after 1 to 6 hours.

An early study found mucus clearance increasingly reduced as length and concentration of exposure to SO_2 increased. Long exposures to 5 ppm SO_2 increased mucociliary clearance in one study; a decrease had been found in nasal clearance rates in another study. Available studies have not found a significant interaction of smoking with SO_2.

1.13.2 Effects of SO_2 in Combination with Particulate Matter

Particulate matter has been shown to be potentially important in enhancing the effects of SO_2 exposure. Airway resistance increased more after combined exposure to SO_2 and sodium chloride in several studies, although others have failed to reach the same conclusions. $MEF_{50\%}$ (maximal expiratory flow rate at 50% vital capacity) was found to be significantly reduced after exposure to a combination of saline aerosol and 13.1 mg/m^3 (5 ppm) SO_2 (Snell and Luchsinger, 1969). Most recently (Koenig et al., 1980, 1981), studies have been reported on pulmonary function changes observed in extrinsic asthmatics both at rest (1980) and during exercise (1981) with exposure to 2.62 mg/m^3 (1 ppm) SO_2 and 1 mg/m^3 NaCl (See Section 13.4). Significant decreases in $Vmax_{50\%}$ and $Vmax_{75\%}$ were observed under aerosol conditions both at rest and during exercise for asthmatics but not for all normals. However, NaCl alone did not produce such effects, suggesting that either the exercise or the combination of SO_2 and NaCl was important.

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1.13.3 Effects of Combined Sulfur Dioxide-Ozone Exposure

Previous studies involving sulfur dioxide and ozone together support the view that ozone is more toxic at a given concentration. Whether sulfur dioxide or its reaction products ever exacerbate the irritant response to ozone is still unresolved. For most studies involving SO_2 (0.37 ppm) and ozone (0.37 ppm) there are conflicting reports with respect to lung function decrements and synergistic effects of the combined pollutants. Recently, however, Japanese studies (Kagawa and Tsuru, 1979) involving a combination of SO_2 exposure at 0.15 ppm (393 $\mu g/m^3$) and O_3 at 290 $\mu g/m^3$ (0.15 ppm) have observed a significantly enhanced decrease in specific airway conductance (SG_{aw}) compared to the decrease in SG_{aw} observed in these subjects when exposed to O_3 alone. They suggest that the effect observed during exercise was synergistic and not just additive and refute the idea that sulfuric acid formation was responsible for the marked effects of O_3 in the presence of SO_2 (Section 13.4).

1.13.4 Effects of Sulfate Aerosols

Sulfuric acid and sulfates have been found to affect both sensory and pulmonary function in study subjects. The odor threshold for sulfuric acid aerosol has been set at 750 $\mu g/m^3$ in one study and 3000 $\mu g/m^3$ in another. Light sensitivity has been found to be consistently increased by 25 percent at 700 to 960 $\mu g/m^3$ concentration of sulfuric acid mist (300 $\mu g/m^3$). Optical chronaxie has also been found to be increased after exposure of subjects to 750 $\mu g/m^3$ sulfuric acid mist.

Respiratory effects from exposure to sulfuric acid mist (350 to 500 $\mu g/m^3$) include increased respiratory rate and decreased maximal inspiratory and expiratory flow rates and tidal volume. Several studies of pulmonary function in normal subjects indicated that pulmonary function was not affected when subjects were exposed to 100-1000 $\mu g/m^3$ sulfuric acid for 10 to 60 minutes, although in one study the bronchoconstrictor action of carbachol was potentiated by the sulfuric acid and sulfate aerosols more or less in relation to their acidity. In studies with asthmatic subjects, generally no changes in airway function have been demonstrated after exposure to sulfuric acid and sulfate salts at concentrations less than 100 $\mu g/m^3$. However, at higher concentrations (1000 $\mu g/m^3$) reduction in specific airway conductance and FEV_1 have been observed after H_2SO_4 and NH_4HSO_4 exposures. Mucociliary clearance was affected by exposure to sulfuric acid, being significantly increased after exposure to 100 $\mu m/m^3$ and significantly decreased after exposure to 1000 $\mu g/m^3$. Another study found no pulmonary effect of exposure of normal and asthmatic subjects to sulfuric acid, ammonium bisulfate, and ammonium sulfate.

In summary, the available evidence generally suggests that thresholds of detectable effects are somewhat above maximum likely ambient exposure concentrations for sulfate compounds. Also, in studies with asthmatic subjects, generally, no changes in airway function have been demonstrated after exposure to sulfuric acid and sulfate salts at concentrations less than 100 $\mu g/m^3$. However, reduction in specific airway conductance (SG_{aw}) and $FEV_{1.0}$ have been observed after H_2SO_4 and NH_4HSO_4 exposures at higher concentrations (1000 $\mu g/m^3$).

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1.14 EPIDEMIOLOGICAL STUDIES

Chapter 14 of this document discusses epidemiological studies on the effects of sulfur oxides and particulate matter. Some of the epidemiological studies reviewed appear to provide meaningful quantitative information on health effects associated with ambient air exposures to PM and SO_2. Others, however, do not meet as fully various objectives regarding study design and analysis to allow for quantification of exposure/effect relationships, or ambiguity exists regarding clear interpretation of their reported results. Only relatively few of the study results can, therefore, be accepted with a relatively high degree of certainty or confidence, whereas others may be seen as providing, at best, only suggestive evidence for reported associations between air pollutant parameters and health effects. The main focus of the present section will be on summarizing results and conclusions derived from selected key studies having a relatively high degree of certainty associated with their findings.

In general, the epidemiological studies reviewed provide evidence for severe health effects, such as mortality and respiratory disease, being associated with marked elevations of atmospheric levels of sulfur dioxide and particulate matter for certain populations at special risk. Those populations at special risk for such effects appear to include, mainly, the elderly and adults with chronic pre-existing cardiac or respiratory diseases (e.g., bronchitics). Increased lower respiratory tract illnesses and more transient (likely indicator) effects, e.g., decrements in pulmonary function, also appear to be associated for children with lower chronic exposures to sulfur dioxide and PM. Also, some qualitative epidemiological evidence suggests that asthmatics may be a susceptible population at special risk for experiencing pulmonary function decrements in response to elevations in SO_2 and PM.

1.14.2 Health Effects Associated with Acute Exposures to Sulfur Oxides and Particulate Matter

As discussed in Chapter 14, it is widely accepted that increases in mortality occur when either sulfur dioxide (SO_2) or particulate matter (PM) levels increase beyond 24-hr levels of 1000 $\mu g/m^3$. Such increased mortality, mainly in the elderly or chronically ill, may logically also be most directly attributed to very high short-term peak levels in the pollutants, which at times increased to several thousand $\mu g/m^3$ during certain major pollution episodes.

Much more difficult to establish is to what extent significant increases in mortality and morbidity are associated with exposures to SO_2 and/or particulate matter levels below 1000 $\mu g/m^3$. Concisely summarized in Table 1-13 are several key studies that appear to demonstrate with a reasonably high degree of certainty, mortality and morbidity effects associated with acute exposures (24 hrs) to these pollutants. The first two studies cited, by Martin and Bradley (1960) and Martin (1964), deal with a relatively small body of data from London in the late 1950s. No clear "threshold" levels were revealed by their analyses regarding SO_2 or BS levels at which significantly increased mortality began to occur. Based on their findings, there appears to be little question that mortality in the elderly and chronically ill was elevated in association with exposure to ambient air containing simultaneous SO_2 and BS levels

TABLE 1-13. SUMMARY OF QUANTITATIVE CONCLUSIONS FROM EPIDEMIOLOGICAL STUDIES RELATING HEALTH EFFECTS OF ACUTE EXPOSURE TO SO_2 AND PARTICULATE MATTER TO AMBIENT AIR LEVELS

Type of study	Effects studied	24-hr average pollutant level ($\mu g/m^3$)				Reference
		particulate matter				
		CoH	BS	TSP	SO_2	
Mortality	Likely increases in daily total mortality above a 15-day moving average during winter 1958-59 among persons with existing respiratory or cardiac disease in London.	-	≥1000	-	≥1000	Martin and Bradley (1960)
	Slight indication of likely increases in daily total mortality above a 15-day moving average during winters of 1958-59 and 1959-60 among persons with existing respiratory or cardiac disease in London.	-	750-1000	-	710-1000	Martin (1964)
Morbidity	Likely worsening of health status among a group of chronic bronchitis patients	-	250-500	-	500-600	Lawther et al. (1958, 1970)
	No apparent response or worsening of health status among a group of chronic bronchitis patients	-	<250	-	<500	Lawther et al. (1970, 1975)

somewhere in the range of 500-1000 μg/m^3. Greatest certainty applies for levels in excess of 700-750 μg/m^3. Much less certainty is attached to lower estimates possibly derived from a reanalysis of the same data set by Ware et al. (1981), which applies to mortality data from very brief periods during the two London winters. It seems more likely that levels well in excess of 500 μg/m^3 BS and SO_2 are typically necessary in order to induce mortality among highly susceptible elderly or chronically ill individuals.

Only very limited data exist by which to attempt to delineate any specific physical and chemical properties of PM associated with the observed increases in mortality. Based on information summarized in Section 1.3, it would seem that marked increases in small particles to levels above 500-1000 μg/m^3 appear to be most clearly associated with increased mortality, based on the BS aerometric measurements reported, although contributions from larger coarse-mode particles cannot be completely ruled out. It is not possible to state with certainty specific PM chemical species associated with the increases in mortality. We do know that large amounts of pollutants (e.g., elemental carbon, tarry organic matter, etc.) from incomplete combustion of coal were present in the air, but no single component or combinations of particulate pollutants can clearly be implicated. The relative contributions of SO_2 or particulate matter cannot be clearly separated based on these study results, and neither can possible interactive effects with increases in humidity (fog) be completely ruled out. However, temperature changes do not appear to be important in explaining the mortality effects observed in Martin's studies.

A study by Glasser and Greenberg (1971), not listed in the table, appears to suggest with less confidence that slight mortality increases were associated with increases in SO_2 above 786-1048 μg/m^3 and in CoHs levels of 5.0-7.0 in New York City. These latter levels likely correspond to concentrations in excess of 570-720 μg/m^3 BS equivalent units based on calibration studies by Ingram alluded to in Section 14.2 of Chapter 14. Again specific particulate chemical species cannot be clearly implicated nor the relative contributions of SO_2 and particulate matter separated. It should be noted that, whatever the causal agents, only very small increases in mortality may have been detected at the above pollutant levels in New York City.

Similar analysis of Lawther's morbidity studies listed in Table 1-13 suggests that acute exposure to elevated 24 hr PM levels in the range of 250-500 μg/m^3 (BS) in association with 24-hr SO_2 levels of 500-600 μg/m^3 were likely associated with the worsening of respiratory disease symptoms in chronically ill London bronchitis patients. Again, little can be said, however, in terms of specifying physical or chemical properties of PM associated with the observed effects beyond the comments noted above in relation to Martin's studies on mortality.

In regard to chronic exposure effects of SO_2 and particulate matter, the best pertinent epidemiological health studies are summarized in Table 1-14. No epidemiological studies are presently well-accepted as demonstrating associations between mortality and chronic (annual average) exposures to sulfur oxides or particulate matter. The Lambert and Reid (1970) study

does suggest, however, that respiratory disease symptoms (cough and phlegm) are associated with long-term (annual-average) exposures of adults to PM levels in the range of 100-200 $\mu g/m^3$ (BS) or above in association with SO_2 levels in the range of 150-200 $\mu g/m^3$ or above. The studies by Ferris et al. (1973, 1976) also suggest that lung function decrements may occur in adults at TSP levels in excess of 180 $\mu g/m^3$ in the presence of relatively low estimated SO_2 level, whereas no effects were observed by the same investigators at TSP levels below 130 $\mu g/m^3$ or by other investigators (Holland and Stone, 1965; Deane et al., 1965; Comstock et al., 1973) at TSP levels in the range of 70-163 $\mu g/m^3$, based on surveys of chest illness and symptoms prevalence. Other studies by Lunn et al. (1967, 1970) listed in Table 1-14 suggest that significant respiratory effects (increased respiratory disease; decreased lung function) occur in children in association with long-term (annual average) PM levels in the range of 230-301 $\mu g/m^3$ (BS) in association with SO_2 levels of 181-275 $\mu g/m^3$. No effects were seen for children, however, at PM levels in the range of 48-169 $\mu g/m^3$ (BS) or at SO_2 levels of 94-253 $\mu g/m^3$.

Again, no specific particulate matter chemical species can clearly be implicated as causal agents associated with the effects observed in those studies listed in Table 1-14. Nor can potential contributions of relatively large inhalable coarse mode particles be ruled out based on these study results; and, it should be noted that various occupational studies listed in Appendix C of Chapter 14 at least qualitatively suggest that coarse-mode size particles of many different types of chemical composition can be associated with significant pulmonary decrements, respiratory tract pathology, and morphological damage.

TABLE 1-14. SUMMARY OF QUANTITATIVE CONCLUSIONS FROM EPIDEMIOLOGICAL STUDIES RELATING HEALTH EFFECTS OF CHRONIC EXPOSURE TO SO_2 AND PARTICULATE MATTER TO AMBIENT AIR LEVELS

Type of study	Effects studied	Annual average pollutant levels ($\mu g/m^3$)				Reference
		particulate matter				
		CoH	BS	TSP	SO_2	
Cross-sectional (4 areas)	Greater prevalence of cough and phlegm in areas of elevated BS and SO_2 pollution, observed in survey of 10,000 British postal workers.	-	100-200+	-	150-200+	Lambert and Reid (1970)
Cross-sectional (4 areas)	Likely increased frequency of lower respiratory symptoms and decreased lung function in children	-	230-301	-	181-275	Lunn et al. (1967)
Cross-sectional (4 areas)	No observed effect on respiratory symptoms and lung function in children	-	48-169	-	94-253	Lunn et al. (1970)
Longitudinal and cross-sectional	Apparent improvement in lung function of adults in association with decreased PM pollution in Berlin, N.H.	-	-	180	-	Ferris et al. (1973, 1976)
Longitudinal and cross-sectional	Apparent lack of effects and symptoms, and no apparent decrease in lung function in adults	-	-	80-131	-	Ferris et al. (1973, 1976)
Cross-sectional (5 cities)	No apparent evidence of increased symptom prevalence or chest illness among telephone plant workers	-	-	70-163	-	Holland and Stone (1965) Deane et al. (1965) Comstock et al. (1973)